EUROPEAN SYMPOSIUM ON APPLIED THERMODYNAMICS

LISBON
10-13 MAY 2026

34th ESAT
BOOK OF ABSTRACTS

E-MAIL: esat2026@fct.unl.pt
WEBSITE: esat-2026.sci-meet.net/

NOVA SCHOOL OF SCIENCE & TECHNOLOGY
LAQV requimte LABORATÓRIO ASSOCIADO PARA A QUÍMICA VERDE
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34th EUROPEAN SYMPOSIUM ON APPLIED THERMODYNAMICS

BOOK OF
ABSTRACTS

Lisbon, Portugal

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Preface

Dear Participants,

We welcome you to the **34th European Symposium on Applied Thermodynamics** (ESAT 2026), in Lisbon, Portugal.

Established in 1974 in Berlin (West Germany) through the initiative of Professor Helmut Knapp, ESAT is the oldest and most respected conference of its kind in Europe. Since its inception, it has been hosted all over Europe, highlighting both the scientific excellence and cultural richness of the continent.

From the beginning, one of the core objectives of ESAT has been to strengthen university-industry collaboration, fostering joint research from fundamental studies to industrial applications, especially in separation processes and phase equilibria. Over the years, the scope has been broadened to include eco-friendly processes and components and other topics aligned with today's societal and environmental challenges.

ESAT has grown into a truly global conference, attracting, in 2026, more than 200 participants from 38 different countries, from Europe, North and South America, Asia, and Africa. Many of the most innovative works presented at ESAT are the basis of groundbreaking publications in high-impact international journals.

In this edition, the EFCE Michael L. Michelsen Award 2026 will be presented to Professor Ioannis G. Economou, who will deliver a lecture on "Multi-scale simulation of complex chemical systems: Structure and physical properties for novel material and process design". As usual, the Helmut Knapp award will be given to the best PhD Student poster.

Besides this, ESAT 2026 will include three special moments.

Monday afternoon will be reserved to honour Professor John Prausnitz, who has been the dominant figure of Applied Thermodynamics for many years. His prolific publications and prominent texts pioneering the breadth and depth of the area have been cited innumerable times, and his inspiring lectures are models of communication effectiveness. He attended many ESAT meetings and his friendship with Helmut Knapp, founder of the ESAT series, is legendary. The organizers of ESAT 2026 have chosen to show gratitude of the European Applied Thermodynamics Community for Professor Prausnitz's contributions to our vibrant community by dedicating sessions of invited lectures celebrating his significance in our work and his leadership in guiding our advancements. The first session has presentations by two of his closest colleagues, Edmundo Gomes de Azevedo of Instituto Superior Técnico (PT) and John P. O'Connell of University of Viginia (US) recounting Professor Prausnitz' accomplishments and impacts, as well as insights into his scholarly and personal values. Following these, are talks by prominent researchers connecting their work to the foundations and applications of Professor Prausnitz and the positive impacts he has had on their lives.

The Industrial Use of Thermodynamics round table also joins in acknowledging Professor John Prausnitz's accomplishments. We are happy to host this recognition in Portugal, since Professor Prausnitz is a very dear friend. We are deeply grateful to Professor John O'Connell for his valued advice and support during the preparation of these sessions.

The other two special moments constitute our most sincere tributes to Professor Karel Aim and Professor Maurizio Fermeglia, who sadly are missing. Professor Karel Aim, an outstanding colleague of the thermodynamic community, who was an esteemed member of the International Steering Committee of ESAT since 2000, a role in which he served with distinction for over two decades. Professor Maurizio Fermeglia was a distinguished researcher, former Rector of the University of Trieste, and a cherished participant of the ESAT conferences. It is a mark of our respect and appreciation to dedicate two plenary sessions to their memories.

We are happy to offer our grateful thanks to the invited speakers, to the members of the International Steering Committee for their valuable input, all communication contributors and all participants who bring and share their knowledge and expertise.

We would like to express our gratitude to our sponsors, whose valued support has been essential to the preparation of this conference.

We look forward to an outstanding programme filled with engaging scientific discussions, as well as the opportunity for you to experience the unique history, vibrant culture, and natural beauty of our country.

And now, it is our hope that when you return to your own homes with the happiest of memories and you remember the great Portuguese discoveries of another age, you will have made, in this age, some meaningful discoveries of your own in the field of Applied Thermodynamics.

On behalf of the Local Organising Committee,

Maria Eugénia Rebello de A. Macedo (Chair)

Ana B. Pereiro (Co-Chair)

João M. Mendes de Araújo (Co-Chair)

History of ESAT

The **European Symposium on Applied Thermodynamics (ESAT)** started in Berlin (West Germany), in 1974, under the initiative of Professor Helmut Knapp. Since then, ESAT has been hosted by Northern, Southern, Eastern and Western European countries, representing the diversity and richness of cultures in the continent.

Below is the list of organisers for the previous editions of ESAT.

Year	Edition	Host	City	Country
2026	34th	University of Porto + NOVA University Lisbon	Lisbon	Portugal
2024	33rd	University of Edinburgh	Edinburgh	United Kingdom
2022	32nd	Technical University of Graz	Graz	Austria
2021	31st	IFP Energies Nouvelles	Paris (online)	France
2018	30th	The Czech Academy of Sciences	Prague	Czech Republic
2017	29th	University Politehnica of Bucharest	Bucharest	Romania
2015	28th	National Technical University of Athens	Athens	Greece
2014	27th	Eindhoven University of Technology	Eindhoven	The Netherlands
2012	26th	Technical University of Berlin and DECHEMA	Potsdam	Germany
2011	25th	Saint Petersburg State University + Russian Academy of Sciences + The Mendeleev Russian Chemical Society	Saint Petersburg	Russia
2009	24th	University of Santiago de Compostela	Santiago de Compostela	Spain
2008	23th	ENSIC-INPL, Nancy	Cannes	France
2006	22th	Technical University of Denmark	Elsinore	Denmark
2005	21st	Warsaw University of Technology	Jurata	Poland
2003	20th	VDI-GVC + Bayer AG + Technische Universität Kaiserslautern	Lahnstein	Germany
2002	19th	National Technical University of Athens	Santorini	Greece

Year	Edition	Host	City	Country
2000	18th	Institute of Chemical Technology in Prague + Institute of Chemical Process Fundamentals	Kutna Hora	Czech Republic
1999	17th	University of Porto + University of Aveiro	Vilamoura	Portugal
1997	16th	Univ. Metz + ENSIC-INPL	Pont-à-Mousson	France
1996	15th	ICI, Runcorn	Runcorn	United Kingdom
1994	14th	National Technical University of Athens	Marathon	Greece
1993	13th	University of Marseille	Marseille	France
1991	12th	Technical University of Berlin	Berlin	Germany
1990	11th	Technical University of Denmark	Rungsted	Denmark
1988	10th	University of Porto	Ofir	Portugal
1987	9th	Norsk Hydro, Posgrunn	Bergen	Norway
1985	8th	University of Trieste	Trieste	Italy
1983	7th	University of Dortmund	Dortmund	Germany
1982	6th	Institut Français du Pétrole	Rueil Malmaison	France
1980	5th	Linde AG	Sachrang	Germany
1979	4th	Shell	Amsterdam	The Netherlands
1978	3rd	Technical University of Denmark	Lyngby	Denmark
1976	2nd	Technical University of Berlin	Berlin (West)	Germany
1974	1st	Technical University of Berlin	Berlin (West)	Germany

Committees

ORGANISING COMMITTEE

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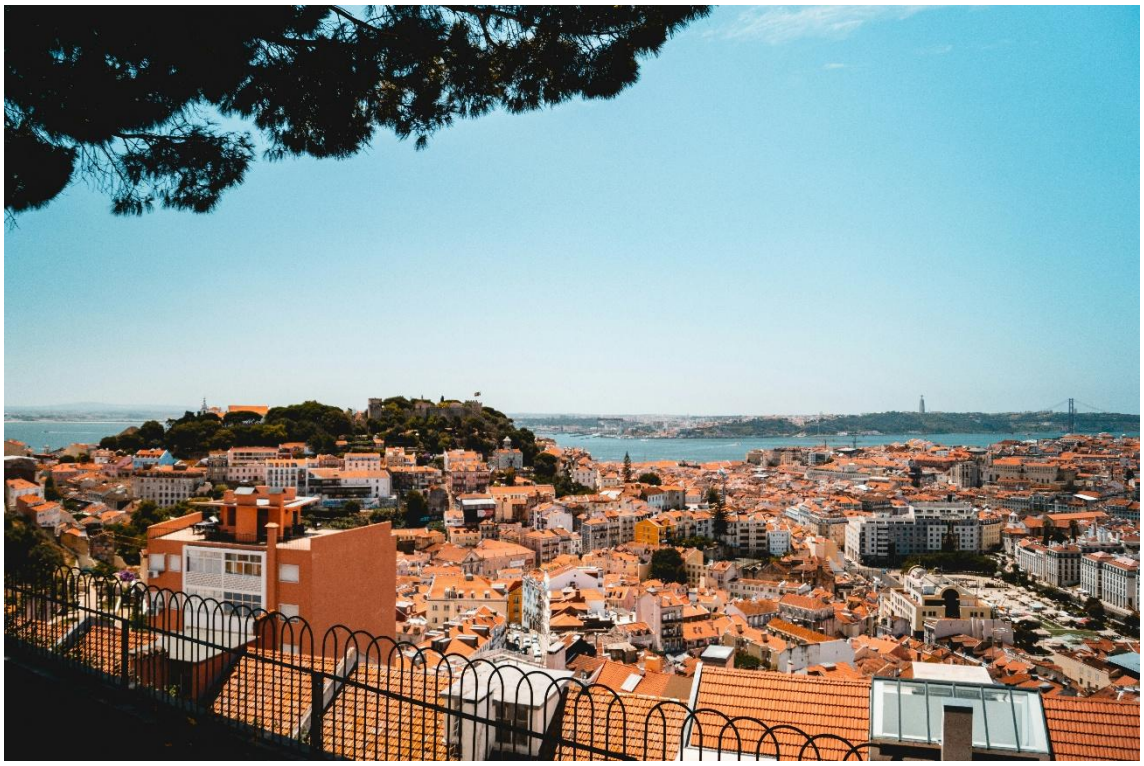
Tim **Zeiner**, Austria

General information: Lisbon



Lisbon, awarded Europe's Leading City Destination 2024 by the World Travel Awards, stands out as a vibrant and welcoming capital. Renowned for its safety, visitors can explore its streets comfortably at any hour, discovering a city where tradition and modernity coexist seamlessly. Its rich culinary heritage is exemplified by the countless ways to prepare its iconic "bacalhau", while a diverse range of hotels and restaurants ensures options for every preference and budget. With its unique blend of authenticity, historic charm, cultural vitality, and forward-looking innovation, Lisbon offers an inspiring setting for both visitors and events alike.

Find further information about Lisbon's top attractions, events, restaurants and more on this official website: https://www.visitlisboa.com/.

Time zone: The time zone in Lisbon is WEST (summer) and GMT (winter).

Water: Tap water in Portugal is considered safe.

Electricity: Standard voltage is 220V AC. Plugs are European style with two round pins.

Currency, banks and post offices: The national currency in Portugal is the Euro. Banks are open from Monday to Friday between 8h30 and 15h. Post offices are usually open between 8h30 and 18h. Exchange houses operate every day between 9h and 13h and from 14h to 19h.

Sponsors

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Programme summary

Sunday, May 10th			Room
15h30	20h30	Registration	South foyer
17h30	18h30	Opening session	Arrábida I-II
18h30	19h30	Plenary session - Michael L. Michelsen Award	Arrábida I-II
19h30	20h30	Plenary session - Agílio Pádua	Arrábida I-II
20h30	22h30	Welcome reception	Near outdoor swimming pool

Monday, May 11th			Room
8h15	19h30	Registration	South foyer
8h30	9h30	Plenary session - Ellen Steimers	Arrábida I-II
9h30	10h30	Parallel sessions I	*(see programme)*
10h30	10h50	Coffee break	South foyer
10h50	12h30	Parallel sessions II	*(see programme)*
12h30	13h30	Lunch break	-
13h30	14h30	Parallel sessions III	*(see programme)*
14h30	15h20	Special session - John Prausnitz	Arrábida I-II
15h20	16h10	Parallel sessions John Prausnitz I	*(see programme)*
16h10	16h20	Group photo	-
16h20	16h40	Coffee break	South foyer
16h40	19h10	Parallel sessions John Prausnitz II & Round Table Discussion IUT	*(see programme)*
19h10	19h55	Poster session I	-
19h55	20h30	-	-
20h30	21h30	Dinner	-

Tuesday, May 12th			Room
8h15	19h30	Registration	South foyer
8h30	9h30	Plenary session - Hans Hasse	Arrábida I-II
9h30	10h30	Parallel sessions IV	*(see programme)*
10h30	10h50	Coffee break	South foyer
10h50	12h30	Parallel sessions V	*(see programme)*
12h30	13h30	Lunch break	-
13h30	14h30	Parallel sessions VI	*(see programme)*
14h30	16h10	Parallel sessions VII	*(see programme)*
16h10	16h30	Coffee break	South foyer
16h30	18h45	Special session - Maurizio Fermeglia	Arrábida I-II
18h45	19h30	Poster session II	-
19h30	20h00	-	-
20h00	23h00	Gala dinner	-

Wednesday, May 13th			Room
8h30	13h30	Registration	South foyer
8h30	10h45	Special session - Karel Aim	Arrábida I-II
10h45	11h05	Coffee break	South foyer
11h05	12h45	Parallel sessions VIII	*(see programme)*
12h45	13h15	Closing session	Arrábida I-II
13h15	14h15	Lunch break	-

Venue and maps

The event will take place at the **Design Tróia Hotel**, a five-star contemporary resort located in Tróia, a unique peninsula south of Lisbon and integrated within a protected Natural Reserve.

The Design Tróia Hotel offers excellent views of the Atlantic Ocean, extensive beaches, the Sado river, and the distinctive Arrábida mountain range, providing a calm and inspiring environment. The hotel combines a sophisticated and comfortable atmosphere, with thoughtful design in every detail, and offers high-quality facilities.

We are confident that this venue will provide an excellent setting for the conference and contribute positively to the overall experience of all participants.

For more information, please visit: https://www.troiadesignhotel.com/pt/

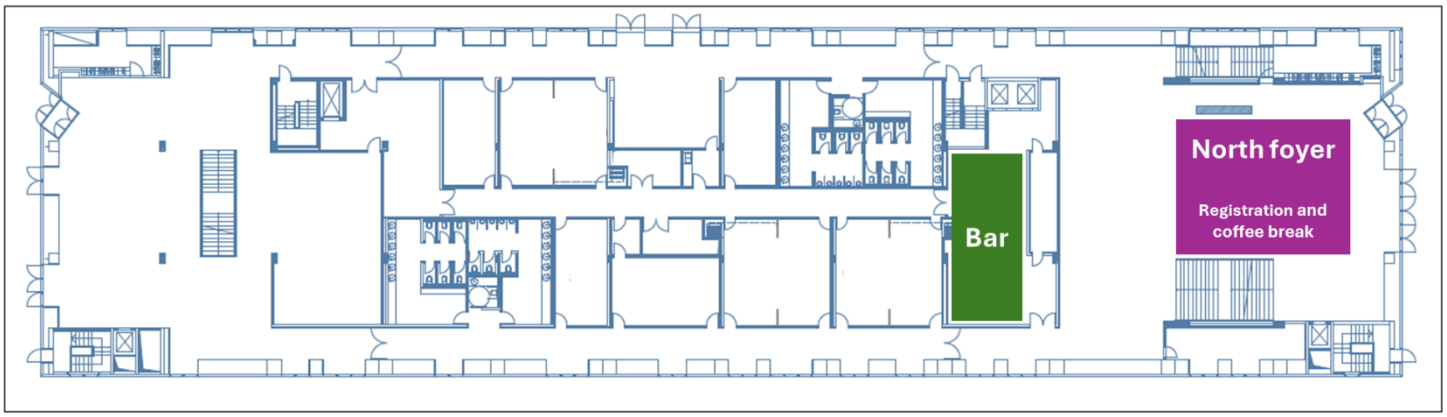
Address:

Tróia Design Hotel, Marina de Tróia - Península de Tróia

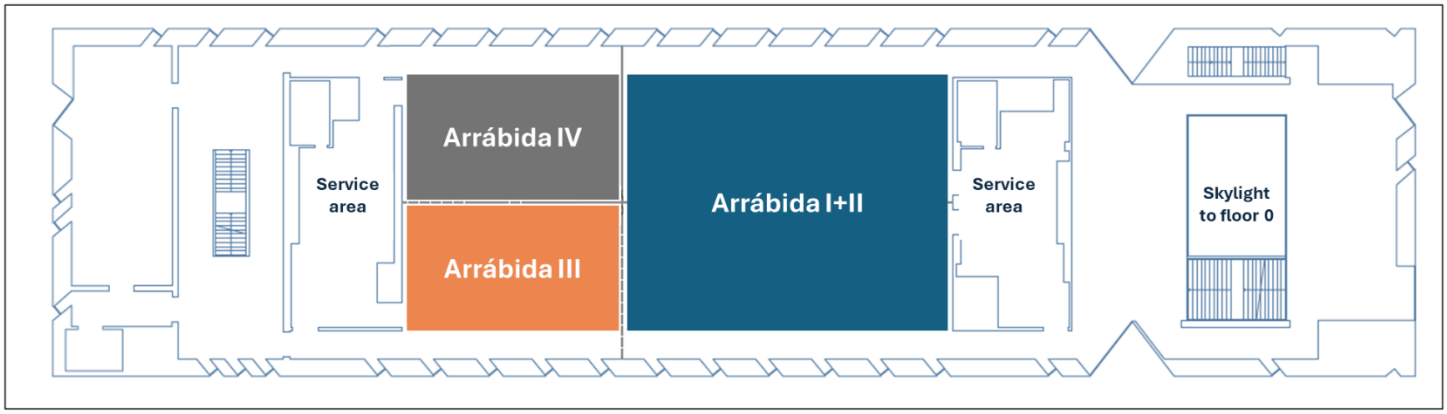
7570-789 Carvalhal, Grândola

Portugal

GROUND FLOOR | Conference centre



FIRST FLOOR | Conference centre



OPEN WIFI

Conference Centre: Troia Eventos

Troia Design Hotel: Troia Design Hotel

Technical information

LECTURES

Plenary Lectures | **PL**

50 (talk) + 10 (Q&A) min

Invited Lectures – John M. Prausnitz | **IL**

20 (talk) + 5 (Q&A) min

Oral Lectures | **OL**

15 (talk) + 5 (Q&A) min

Flash Lectures | **FL**

5 (talk) + 5 (Q&A) min

Please help keep our conference programme on schedule by adhering to these time limits.

Please prepare your PowerPoint presentations in 16:9 format and send them to esat2026@fct.unl.pt before the start of the conference. Alternatively, you may deliver them in person in the designated presentation room, no later than the session preceding your own.

POSTER SESSION

Monday, May 11th | 19h10 – 19h55

Tuesday, May 12th | 18h45 – 19h30

Room: Conference centre

Posters can be mounted from the morning of May 10th. **The posters will be exhibited from May 10th to 13th.**

Each poster has been assigned a number, which will also be displayed on the movable wall. Our staff will be on hand to assist you in finding your designated poster spot and will provide mounting material as well as assistance. Please remember to remove your posters at the end of the conference.

SOCIAL PROGRAMME

Welcome reception | Sunday, May 10th | 20h30 – 22h30

After gathering in the Arrábida I–II room for the opening session and for the first two plenary sessions, we will proceed to the welcome reception, which will take place near the outdoor swimming pools at the Troia Design Hotel.

Gala dinner | Tuesday, May 12th | 20h00 – 23:00

The Conference dinner will be held at the Restaurant of the Show Centre in the Troia Design Hotel and will include a surprise cultural moment during the evening.

Group photo

Monday, May 11th | 16h10 – 16h20

The official group photo will be taken on the staircase between the ground and first floors of the Conference Centre.

Scientific programme: Talks

Sunday, May 10th

OPENING SESSION

Room: Arrábida I-II

17h30 – 18h30	**OPENING SESSION**

PLENARY SESSION - Michael L. Michelsen Award

Room: Arrábida I-II
Chairs: A. Gonçalves da Silva and Grazia de Angelis

18h30 – 19h30	**MULTI-SCALE SIMULATION OF FISCHER-TROPSCH SYNTHESIS FOR THE GAS-TO-LIQUID PROCESS: FROM DENSITY FUNCTIONAL THEORY CALCULATIONS TO PHYSICAL PROPERTYPREDICTIONS**
PS	**Ioannis G. Economou**, Texas A&M University, Qatar

PLENARY SESSION – Agílio Pádua

Room: Arrábida I-II
Chairs: A. Gonçalves da Silva and Grazia de Angelis

19h30 – 20h30	**POROUS IONIC LIQUIDS FOR SEPARATIONS, CONVERSIONS AND DELIVERY**
PS	**Agílio Pádua**, ENS de Lyon, France

WELCOME RECEPTION

Room: near the outdoor swimming pools (Troia Design Hotel)

20h30 – 22h30	**WELCOME RECEPTION**

Scientific programme: Talks

Monday, May 11th

PLENARY SESSION - Ellen Steimers

Room: Arrábida I-II
Chair: Georgios M. Kontogeorgis

8h30 – 9h30	**FROM PREDICTION TO PRACTICE: PHYSICAL PROPERTY DATA FOR INDUSTRIAL PROCESS SOLUTIONS**
PS	**Ellen Steimers**, BASF, Germany

PARALLEL SESSIONS I – Equations of state

Room: Arrábida I-II
Chair: Fèlix Llovell

09h30 – 09h50	**APPLICATION OF CP-PC-SAFT WITH UNIVERSAL K_{12} VALUE FOR SIMULTANEOUS PREDICTION OF VLE, LLE AND CRITICAL LOCI IN SYSTEMS OF GASES AND ALIPHATIC HYDROCARBONS WITH SUBSTITUTED AROMATIC AND HETEROCYCLIC COMPOUNDS**
Oral	**Ilya Polishuk**, Ariel University, Israel
09h50 – 10h10	**USING THE HELMHOLTZ FREE-ENERGY EQUATION OF STATE FOR MIXTURES**
Oral	**Jan Froeke Kikstra**, Cargill, the Netherlands
10h10 – 10h30	**DEVELOPMENT AND COMMERCIAL IMPLEMENTATION OF A COMPUTATIONALLY EFFICIENT POLAR PC-SAFT EQUATION OF STATE FOR LARGE SCALE INDUSTRIAL APPLICATIONS**
Oral	**Bennett D. Marshall**, Exxon Mobil Technology and Engineering Company, USA

PARALLEL SESSIONS I – Absorption & Adsorption

Room: Arrábida III
Chair: Nicolas von Solms

09h30 – 09h50	**FROM POULTRY WASTE TO CRITICAL RAW MATERIAL RECOVERY: THERMODYNAMIC INSIGHTS INTO PLATINUM GROUP METAL ADSORPTION**
Oral	**Helena Passos**, FEUP, Portugal
09h50 – 10h10	**THERMODYNAMIC VS KINETIC CONTROL OF BRUSH COMPOSITION IN GRAFTING TO REACTIONS: A COMBINED EXPERIMENTAL AND GRAND CANONICAL MONTE CARLO STUDY**
Oral	**Cosimo Brondi**, Universitas Mercatorum, Italy
10h10 – 10h30	**HYDROGEN ADSORPTION WITH 3D CLASSICAL DENSITY FUNCTIONAL THEORY**
Oral	**Nadine Thiele**, University of Stuttgart, Germany

PARALLEL SESSIONS I – General

Room: Arrábida IV
Chair: Hiroyuki Matsuda

09h30 – 09h50	**PREDICTIVE COSMO-SAC CARBON-BASED MAGNETIC KINETIC PROMOTERS FOR ACCELERATED AND EFFICIENT CO_2 HYDRATE FORMATION**
Oral	**Mawadda A. A. Adam**, King Fahd University of Petroleum and Minerals, Saudi Arabia
09h50 – 10h10	**MULTISCALE MODELING FROM PREDICTIVE THERMODYNAMICS TO PROCESS SUSTAINABILITY: THE SCIENTIFIC LEGACY OF MAURIZIO FERMEGLIA**
Oral	**Andrea Mio**, University of Trieste, Italy

PARALLEL SESSIONS II – General

Room: Arrábida I-II
Chair: António Queimada

10h50 – 11h10	**A CLASSIFICATION FOR ELECTROLYTES BASED ON INTERMOLECULAR INTERACTIONS**
Oral	**Gabriel M. Silva**, Technical University of Denmark
11h10 – 11h30	**MEASUREMENTS OF CARBON DIOXIDE SOLUBILITY IN CYRENE FOR CO_2 REMOVAL APPLICATIONS**
Oral	**Valentina Schiattarella**, Politecnico di Milano, Italy
11h30 – 11h50	**PHASE BEHAVIOUR OF HARD CLOVER-SHAPED PARTICLES FROM MONTE CARLO SIMULATIONS**
Oral	**Nathan B. de Souza**, Universidade Estadual de Campinas, Brazil
11h50 – 12h10	**STATISTICAL THERMODYNAMICS OF SUPERCOOLED WATER**
Oral	**Claudio Cerdeiriña**, University of Vigo, Spain

PARALLEL SESSIONS II – Novel solvents and supercritical fluids

Room: Arrábida III
Chair: Ilya Polishuk

10h50 – 11h10	**PHASE EQUILIBRIUM AND THERMOPHYSICAL PROPERTIES OF THE DEEP EUTECTIC SOLVENT CHOLINIUM CHLORIDE & ETHYLENE GLYCOL WITH HYDROFLUOROCARBON GASES**
Oral	**Aaron M. Scurto**, University of Kansas, USA
11h10 – 11h30	**ENHANCING LOW-CONCENTRATION CO_2 CAPTURE ABILITIES OF AMINIUM IONIC LIQUIDS THROUGH BLENDING WITH ACETATE IONIC LIQUIDS**
Oral	**Takashi Makino**, Nat. Inst. of Adv. Industrial Science and Technology, Japan
11h30 – 11h50	**THE STRUCTURE AND ORIGIN OF THE SUPERCRITICAL (WIDOM) ANOMALIES**
Oral	**Attila R. Imre**, Budapest University of Technology and Economics, Hungary
11h50 – 12h10	**SORPTION THERMODYNAMICS OF WATER AND METHANOL IN GLASSY POLYIMIDES: A MULTISCALE APPROACH COMBINING GRAVIMETRIC, FT-IR IN SITU EXPERIMENTS WITH A NON-EQUILIBRIUM STATISTICAL THERMODYNAMICS THEORY**
Oral	**Giuseppe Scherillo**, University of Naples Federico II, Italy

PARALLEL SESSIONS II – Molecular Modelling and Simulation

Room: Arrábida IV
Chair: Alberto Striolo

10h50 – 11h10	**ACCURATE THERMODYNAMIC MODELLING AND 3E CYCLE ANALYSIS FOR APPLICATIONS IN THE SEARCH FOR SUSTAINABLE ABSORPTION REFRIGERATION WORKING PAIRS**
Oral	**Fèlix Llovell**, Universitat Rovira i Virgili, Spain
11h10 – 11h30	**EXPLORING THE INTERACTION BETWEEN PLASMA PROTEINS AND POLYMERIC MATERIALS IN MEDICAL DEVICES: INSIGHTS FROM MOLECULAR SIMULATIONS**
Oral	**Amr Saleh**, Université Clermont Auvergne, France
11h30 – 11h50	**ELECTRO COALESCENCE OF IONIC LIQUID/ALKANOL LADEN WATER DROPLET: A MOLECULAR DYNAMICS STUDY**
Oral	**Sandip Khan**, Indian Institute of Technology Patna, India
11h50 – 12h10	**REVISION OF THE eSAFT-VR MIE EQUATION OF STATE FOR ELECTROLYTE SOLUTIONS**
Oral	**Ziyi Zhou**, Technical University of Denmark, Denmark
12h10 – 12h30	**FLASH LECTURES SESSION**
Flash	

PARALLEL SESSIONS III – Phase equilibria & Equations of state

Room: Arrábida I-II
Chair: William Smith

13h30 – 13h50	**COMMENTS ON THE CORRELATION OF AQUEOUS TWO-PHASE SYSTEMS (ATPS) INVOLVING POLYMERS**
Oral	**Antonio Marcilla**, University of Alicante, Spain
13h50 – 14h10	**IMPROVEMENT OF LIQUID PHASE SPLITTING OF WATER + ETHANOL + ISOBUTANOL MIXTURES IN THE PRESENCE OF ELECTROLYTE AT ATMOSPHERIC PRESSURE**
Oral	**Salal H. Khudaida**, Technische Universität Dortmund, Germany
14h10 – 14h30	**OPTIMAL STRATEGY FOR THE PARAMETRISATION OF THE ASSOCIATION TERM OF SAFT MODELS**
Oral	**Haziq Asmuni**, University of Lorraine, France

PARALLEL SESSIONS III – Multiscale models

Room: Arrábida III
Chair: Romain Privat

13h30 – 13h50	**MODELLING AMORPHOUS CHAIN TOPOLOGY IN SEMICRYSTALLINE POLYMERS AND ITS IMPACT ON POLYMER DEGRADATION**
Oral	**Michele Valsecchi**, Columbia University, USA
13h50 – 14h10	**AN INTEGRATED PHYSICS-BASED AND DATA-DRIVEN STRATEGY FOR MIXED-GAS SOLUBILITY IN POLYMER MEMBRANES**
Oral	**Eleonora Ricci**, University of Edinburgh, Scotland

14h10 – 14h30	**CONECTING MICROSCOPIC WITH MESOSCOPIC TRANSPORT IN MODEL NANOPOROUS MATERIALS**
Oral	**Marcelle Spera**, University Grenoble Alpes, France

PARALLEL SESSIONS III – Polymers and complex materials

Room: Arrábida IV
Chair: Aaron Scurto

13h30 – 13h50	**PREDICTION OF MASS TRANSPORT IN A GLASSY POLYETHERIMIDE IN PRESENCE OF SPECIFIC INTERACTIONS BASED UPON SELF-CONSISTENT NETGP-PC-SAFT DIFFUSION MODEL**
Oral	**Antonio Baldanza**, Scuola Superiore Meridionale, Italy
13h50 – 14h10	**MOLECULAR MODELLING OF GAS TRANSPORT AT A POLYMER/MOF INTERFACE**
Oral	**Tiziano Cavalieri**, University of Edinburgh, Scotland

SPECIAL SESSION – John M. Prausnitz

Room: Arrábida I-II
Chair: Doros Theodorou and Ralf Dohrn

14h30 – 14h55	**I FIRST MET JMP ON… AUGUST 1981**
Oral	**Edmundo G. de Azevedo**, Instituto Superior Técnico, Portugal
14h55 – 15h20	**HONORING JOHN M. PRAUSNITZ: GUIDING SPIRIT OF APPLIED THERMODYNAMICS**
Oral	**John O'Connell**, University of Virginia, USA

PARALLEL SESSIONS JOHN M. PRAUSNITZ I – Phase equilibria & Simulation

Room: Arrábida I-II
Chair: Ilja Siepmann and Mark Shiflett

15h20 – 15h45	**REVIEW SERIES ON HIGH-PRESSURE PHASE EQUILIBRIA: TRENDS, EXPERIMENTAL METHODS, AND SYSTEMS INVESTIGATED**
Oral	**Ralf Dohrn**, TU Hamburg, Bayer AG, Germany
15h45 – 16h10	**MORPHOLOGY DEVELOPMENT IN SEMICRYSTALLINE POLYETHYLENE: A MOLECULAR SIMULATION STUDY**
Oral	**Doros Theodorou**, Nat. Tech. University of Athens and Academy of Athens, Greece

PARALLEL SESSIONS JOHN M. PRAUSNITZ I – Sustainable processes

Room: Arrábida III
Chair: José Nuno C. Lopes and Phillip Choi

15h20 – 15h45	**EXTRACTION OF NATURAL COMPOUNDS USING SUSTAINABLE SOLVENTS – WHAT CAN THERMODYNAMICS BRING US?**
Oral	**Nicolas Papaiconomou**, Université Côte d'Azur, France

15h45 – 16h10	**DEVELOPMENT OF THERMO-CATALYTIC DECOMPOSITION PROCESS OF METHANE INTO HYDROGEN AND GRAPHITE AND OTHER MATTERS**
Oral	**Justin Salminen**, Hycamite TCD Technologies, Finland

PARALLEL SESSIONS JOHN M. PRAUSNITZ I – Phase equilibria & Interfaces

Room: Arrábida IV
Chair: David Kofke and Leo Lue

15h20 – 15h45	**ADSORPTION OF CHAINLIKE AMPHIPHILES ON SOLID NANOPARTICLES FROM AQUEOUS MIXTURES: PREDICTION FROM A MOLECULAR MODEL**
Oral	**Alexey Victorov**, St. Petersburg State University, Russia
15h45 – 16h10	**PEG/CITRATE AQUEOUS TWO-PHASE EXTRACTION OF FISH PROTEINS**
Oral	**Oscar Rodríguez**, Universidade de Santiago de Compostela, Spain

PARALLEL SESSIONS JOHN M. PRAUSNITZ II – Phase equilibria & Interfaces

Room: Arrábida I-II
Chair: Alexey Victorov and Nicolas Papaiconomou

16h40 – 17h05	**SEPARATION OF AZEOTROPIC REFRIGERANT MIXTURES USING IONIC LIQUIDS**
Oral	**Mark B. Shiflett**, University of Kansas, USA
17h05 – 17h30	**TRANSPORT PROPERTIES AND GLASS TRANSITION TEMPERATURES OF POLYMERS AS DETERMINED BY MACROMOLECULAR THEORY AND SIMULATIONS**
Oral	**Phillip Choi**, University of Regina, Canada
17h30 – 17h55	**MOLECULAR THERMODYNAMICS OF PHASE EQUILIBRIA FOR COMPLEX SYSTEMS WITH APPLICATIONS**
Oral	**Nicolas von Solms**, Technical University of Denmark, Denmark
17h55 – 18h20	**LIQUID-LIQUID EQUILIBRIUM ISLANDS IN TERNARY SYSTEMS COMPRISING AN IONIC LIQUID**
Oral	**Héctor Rodriguez**, Universidade de Santiago de Compostela, Spain

PARALLEL SESSIONS JOHN M. PRAUSNITZ II – Modelling & General

Room: Arrábida III
Chair: Justin Salminen and Oscar Rodríguez

16h40 – 17h05	**THERMODYNAMIC CONTRIBUTIONS OF MOBILE AND STATIONARY PHASES TO RETENTION IN DIFFERENT MODES OF CHROMATOGRAPHY**
Oral	**J. Ilja Siepmann**, University of Minnesota, USA
17h05 – 17h30	**INFERENCE OF VIRIAL COEFFICIENTS FROM EXPERIMENTAL DATA**
Oral	**David Kofke**, University at Buffalo, USA
17h30 – 17h55	**MODELLING THE STRUCTURE AND DYNAMICS OF IONIC LIQUID MEDIA**
Oral	**José Nuno Canongia Lopes**, Universidade de Lisboa, Portugal
17h55 – 18h20	**A DENSITY GRADIENT THEORY OF SURFACTANT SOLUTIONS**
Oral	**Leo Lue**, University of Strathclyde, Scotland

18h20 – 18h45	**RECENT ADVANCEMENTS IN THE FUNDAMENTAL UNDERSTANDING IN THE ROLE OF ADDITIVES IN MODULATING CLATHRATE HYDRATES**
Oral	**Alberto Striolo**, University of Oklahoma, USA

ROUND TABLE DISCUSSION – IUT

Room: Arrábida IV
Chair: Jean-Charles de Hemptinne and Antoon ten Kate

16h35 – 16h40	**PRESENT OBJECTIVE AND TOOLS**
	Jean-Charles de Hemptinne, IFPEN, France
16h40 – 16h55	**INTRODUCTION AND THERMOCHEMICAL PERSPECTIVE ON A TRANSIENT WORLD**
Oral	**Antoon ten Kate**, Chemspiration, Netherlands
16h55 – 17h10	**EXPERIMENTAL AND MODELLING INSIGHTS INTO ANION EXCHANGE MEMBRANES FOR MOISTURE-DRIVEN DIRECT AIR CAPTURE**
Oral	**Maria Grazia de Angelis**, University of Edinburgh, Scotland
17h10 – 17h25	**THERMODYNAMICS AND PROCESS MODELLING FOR A (MORE) SUSTAINABLE CHEMICAL INDUSTRY**
Oral	**José M. S. Fonseca**, AVEVA, England
17h25 – 17h40	**THERSAURUS: TOWARDS A THERMODYNAMICS OF SUSTAINABILITY**
Oral	**Alicia Valero**, Universidad de Zaragoza, Spain
17h40 – 17h55	**ENERGY IS CONSERVED – ENERGY IS DESTROYED: RETHINKING EFFICIENCY FOR CIRCULAR INDUSTRIAL PROCESSES**
Oral	**Jean-Noël Jaubert**, Université de Lorraine, France
17h55 – 18h10	**PROCESS ENGINEERING AND THERMODYNAMICS CHALLENGES IN PLASTICS CIRCULARITY: CLOSING THE LOOP WITH INDUSTRIAL RECYCLING TECHNOLOGIES**
Oral	**Bernhard von Vacano**, BASF SE, Germany
18h10 – 18h25	**ROLE OF THERMODYNAMICS IN BATTERY RECYCLING AND CRITICAL RAW MATERIAL RECOVERY**
Oral	**Daniele Marchisio**, Politecnico di Torino, Italy
18h25 – 18h30	**HOW IS THERMODYNAMICS USED TODAY IN SHAPING THE DEVELOPMENT OF SUSTAINABLE TECHNOLOGIES?**
	The Current Role
18h30 – 18h45	**HOW IS THERMODYNAMICS USED TODAY IN SHAPING THE DEVELOPMENT OF SUSTAINABLE TECHNOLOGIES?**
	Discussion
18h45 – 18h50	**WHAT PRINCIPLES ARE NOT SUFFICIENTLY UNDERSTOOD OR KNOWN FOR SUPPORTING CIRCULARITY?**
	Expanding the Role
18h50 – 19h05	**WHAT PRINCIPLES ARE NOT SUFFICIENTLY UNDERSTOOD OR KNOWN FOR SUPPORTING CIRCULARITY?**
	Discussion
19h05 – 19h10	**FINAL COMMENTS**
	Jean-Charles de Hemptinne, IFPEN, France

Scientific programme: Talks

Tuesday, May 12th

PLENARY SESSION – Hans Hasse

Room: Arrábida I-II
Chair: Jean-Noël Jaubert

08h30 – 09h30	**REALIZING THE DREAM OF THERMODYNAMIC MODELING**
PS	**Hans Hasse**, RPTU Kaiserslautern, Germany

PARALLEL SESSIONS IV – Equations of state

Room: Arrábida I-II
Chair: Epaminondas Voutsas

09h30 – 09h50	**SOME RECENT DEVELOPMENTS IN ELECTROLYTE THERMODYNAMICS**
Oral	**Georgios M. Kontogeorgis**, Technical University of Denmark, Denmark
09h50 – 10h10	**MIXING RULES FOR CUBIC EQUATIONS OF STATE: WHAT WORKS, WHAT FAILS, AND WHAT REMAINS TO BE INVESTIGATED**
Oral	**Romain Privat**, University of Lorraine, France
10h10 – 10h30	**SPECIATION IN SAFT-γ MIE: FORMULATION AND APPLICATION FOR LOADED AQUEOUS MONOAMINE SOLUTIONS**
Oral	**Evangelos Tsochantaris**, Technical University of Denmark, Denmark

PARALLEL SESSIONS IV – Absorption and adsorption

Room: Arrábida III
Chair: Antonio Marcilla

09h30 – 09h50	**ADSORPTION OF PARACETAMOL ON GRAPHITE: A THERMODYNAMIC STUDY COMBINING ISOTHERMAL TITRATION CALORIMETRY AND SPECTROSCOPY**
Oral	**Jean Duprat**, Institut de Chimie de Clermont-Ferrand, France
09h50 – 10h10	**MOLECULAR INVESTIGATION OF CO_2 EFFECTS ON FKM ELASTOMERS FOR CO_2 TRANSPORT APPLICATIONS**
Oral	**Matteo Minelli**, University of Bologna, Italy
10h10 – 10h30	**SOLUBILITY, DISSOLUTION AND MIXING ENTHALPIES OF METALLIC SALTS IN IONIC LIQUIDS**
Oral	**Margarida Costa Gomes**, CNRS, France

PARALLEL SESSIONS IV – Sustainable processes

Room: Arrábida IV
Chair: Christoph Held

09h30 – 09h50	**ELECTROCHEMICALLY DRIVEN RECOVERY OF CADMIUM AND TELLURIUM FROM CDTE SOLAR CELLS: A THERMODYNAMIC MODELING AND SIMULATION STUDY**
Oral	**Gaurav Das**, OLI Systems Inc, USA
09h50 – 10h10	**GREEN SOLVENT MIXTURES FOR BIOMASS VALORIZATION: A SYNERGISTIC APPROACH COMBINING EXPERIMENTS AND MOLECULAR DYNAMICS SIMULATIONS**
Oral	**Vojtěch Jeřábek**, Univ. of Chemistry and Technology Prague, Czech Republic
10h10 – 10h30	**EXTENDING THE SAFT-γ MIE APPROACH: FROM POLYCYCLIC AROMATIC COMPOUNDS TO ASPIRIN**
Oral	**Amparo Galindo**, Imperial College London, United Kingdom

PARALLEL SESSIONS V – Phase equilibria

Room: Arrábida I-II
Chair: Joachim Groß

10h50 – 11h10	**THERMODYNAMIC CONSISTENCY OF DATA FORELECTROLYTE MODEL PARAMETERIZATION: A CASE STUDY PROPOSED BY ELETHER JIP**
Oral	**Jean-Charles de Hemptinne**, IFP Energies Nouvelles, France
11h10 – 11h30	**THERMODYNAMIC EXPERIMENTS AND MODELLING OF CYCLOPENTANE HYDRATES IN PRESENCE OF PURE AND MIXED SALTS FROM NABR, KBR, NaCl, KCl, Na_2SO_4, K_2SO_4 AND $CaCl_2$**
Oral	**Baptiste Bouillot**, Ecole des Mines Saint-Etienne, France
11h30 – 11h50	**A NEW METHOD FOR MULTIPHASE ISENTHALPIC FLASH CALCULATIONS BY DIRECT MAXIMIZATION OF ENTROPY**
Oral	**Dan V. Nichita**, Université de Pau et des Pays de l'Adour, France
11h50 – 12h10	**INVESTIGATION OF THE HSA SOLVATION IN DIVERSE SOLVENTS AT HIGH CONCENTRATIONS**
Oral	**Abtin R. Shirazi**, Ecole des Mines de Saint-Etienne, France

PARALLEL SESSIONS V – Carbon capture, utilisation and storage

Room: Arrábida III
Chair: Clare McCabe

10h50 – 11h10	**A UNIVERSAL ACTIVITY COEFFICIENT MODEL WITH FIRST-PRINCIPLES/ATOMISTIC-SIMULATION-DRIVEN GIBBS ENERGY MINIMIZATION FOR PREDICTING CO_2 REACTIVE ABSORPTION**
Oral	**William R. Smith**, University of Guelph, Canada
11h10 – 11h30	**PREDICTIVE THERMODYNAMIC MODELLING OF GAS SORPTION AND PERMEATION IN POLYMERS FOR HIGH-PRESSURE GAS HANDLING APPLICATIONS**
Oral	**Gaia Lazzari**, Alma Mater Studiorum - University of Bologna, Italy

11h30 – 11h50	**THERMOPHYSICAL PROPERTIES OF BINARY MIXTURES AMINE + CARBON DIOXIDE FOR THE DEPLOYMENT OF CARBON CAPTURE**
Oral	**Xavier Paredes**, University of Valladolid, Spain
11h50 – 12h10	**EXTENSION OF RAND-BASED CHEMICAL EQUILIBRIUM CALCULATION TO MULTIPLE ELECTROLYTE-CONTAINING PHASES IN CO_2 CAPTURE MODELING**
Oral	**Antonio C. L. Neto**, Technical University of Denmark, Denmark

PARALLEL SESSIONS V – Mesoscale methods and COSMO-RS

Room: Arrábida IV
Chair: Sabrina Reartes

10h50 – 11h10	**COSMOTHERM PREDICTION OF CARBON DIOXIDE SOLUBILITY IN BIO-BASED SOLVENTS**
Oral	**Filippo Marchelli**, University of Genova, Italy
11h10 – 11h30	**CALCULATION METHODS FOR COSMO-BASED ACTIVITY COEFFICIENT MODELS**
Oral	**Wei Yan**, Technical University of Denmark, Denmark
11h30 – 11h50	**THERMODYNAMIC MODELING OF PFAS PHYSICOCHEMICAL PROPERTIES WITH COSMO-RS**
Oral	**Daria Grigorash**, Technical University of Denmark, Denmark
11h50 – 12h10	**BOOSTING THERMOPHYSICAL PROPERTY PREDICTIONS WITH GRAPH NEURAL NETWORKS**
Oral	**Martin Richter**, Dassault Systèmes, Germany

PARALLEL SESSIONS VI – Equations of state & Distillation

Room: Arrábida I-II
Chair: Eleonora Ricci

13h30 – 13h50	**ENHANCING THE PR EQUATION OF STATE FOR THE HYDROGEN ECONOMY WITH A NOVEL HYBRID NEURAL NETWORK FRAMEWORK**
Oral	**Elahe Rostaminikoo**, University of Lancashire, United Kingdom
13h50 – 14h10	**PROCESS INTENSIFICATION AND OPTIMIZATION OF AROMA COMPOUNDS PRESERVATION IN THERMAL DEALCOHOLISATION OF BEER**
Oral	**Mariangela Falconieri**, Technical University of Munich, Germany
14h10 – 14h30	**ONE EOS TO RULE THEM ALL? SYSTEMATIC REVIEW OF EQUATIONS OF STATE FOR PURE COMPONENT PREDICTION**
Oral	**Simon Müller**, Hamburg University of Tehcnology, Germany

PARALLEL SESSIONS VI – New fuels and refrigerants & Interfaces

Room: Arrábida III
Chair: Helena Passos

13h30 – 13h50	**COMPARATIVE 3D VISUALIZATION OF PROCESSES IN POWER-TO-HEAT AND HEAT-TO-POWER CYCLES USING VARIOUS TYPES OF WORKING FLUIDS**
Oral	**Réka Kustán**, Budapest University of Technology and Economics, Hungary
13h50 – 14h10	**A HYBRID COMPUTATIONAL FRAMEWORK FOR THE DISCOVERY AND THERMODYNAMIC CHARACTERISATION OF NEW WORKING FLUIDS**
Oral	**Tiago Mendonça Eusébio**, Universitat Ramon Llull, Spain
14h10 – 14h30	**ROLE OF ACIDS IN STABILIZING REVERSE MICELLES: CASE OF DODECY SULFATE**
Oral	**Qixuan Li**, Ruhr-University Bochum, Germany

PARALLEL SESSIONS VI – Separation processes & General

Room: Arrábida IV
Chair: Hector Rodríguez

13h30 – 13h50	**FIRST APPLICATION OF MEMBRANE-ABSORPTION INTEGRATION FOR THE SEPARATION OFAZEOTROPIC REFRIGERANT BLENDS**
Oral	**Miguel Viar Fernández**, Universidad de Cantabria, Spain
13h50 – 14h10	**LIQUID-LIQUID EQUILIBRIA FOR THE BINARY SYSTEMS Γ-VALEROLACTONE + HYDROCARBON: EXPERIMENTAL DATA AND MODELLING**
Oral	**Hiroyuki Matsuda**, Nihon University, Japan
14h10 – 14h30	**ADVANCING THERMODYNAMIC APPROACHES TO MODEL THE PHASE BEHAVIOUR OF PEPTIDES IN AQUEOUS AND MIXED SOLVENTS**
Oral	**Shubhani Paliwal**, Imperial College London, UK

PARALLEL SESSIONS VII – Molecular modelling and simulation

Room: Arrábida I-II
Chair: Matteo Minelli

14h30 – 14h50	**INSIGHTS INTO THE MOLECULAR MECHANISMS UNDERLYING DIFFERENCES IN PROPERTIES OF STRUCTURALLY SIMILAR COMPOUNDS**
Oral	**Maria Fontenele**, Roquette Frères, Carbohydrate & Advanced Process Tech., France
14h50 – 15h10	**PREDICTIVE METHODS FOR ESTIMATING THE THERMAL CONDUCTIVITY OF PURE SUBSTANCES AND MIXTURES USING ENTROPY SCALING**
Oral	**Julia Burkhardt**, University of Stuttgart, Germany
15h10 – 15h30	**SURFACTANT-BASED REMEDIATION OF CONTAMINANTS ON SOLID SURFACES AND IN AQUEOUS ENVIRONMENTS: A MOLECULAR DYNAMICS STUDY**
Oral	**Hector Dominguez**, Universidad Nacional Autónoma de México, México

15h30 – 15h50	**THERMODYNAMICS AND STRUCTURES IN SELF-ASSEMBLY PROCESSES OF SOFT MATTER**
Oral	**Giuseppe Milano**, Università di Napoli Federico II, Italy
15h50 – 16h10	**REVISITING THE CLASSIFICATION OF PHYSISORPTION ISOTHERMS WITH CLASSICAL DENSITY FUNCTIONAL THEORY**
Oral	**Thomas Bernet**, Imperial College London, UK

PARALLEL SESSIONS VII – Novel solvents and equations of state

Room: Arrábida III
Chair: Catinca Secuianu

14h30 – 14h50	**FROM AI TO THERMODYNAMICS: PREDICTING PURE-COMPONENT EOS INPUTS WITH ENSEMBLE LEARNING**
Oral	**Jean-Noël Jaubert**, University of Lorraine, France
14h50 – 15h10	**COSMO-NET: EFFICIENT GRAPH NEURAL NETWORK SURROGATES FOR COSMO-BASED MOLECULARDESCRIPTORS**
Oral	**Saman N. Boroujeni**, Imperial College London, United Kingdom
15h10 – 15h30	**PREDICTION OF THE SURFACE TENSION OF AMINE-BASED SOLVENTS WITH A NEW GROUP-CONTRIBUTION MACHINE-LEARNING MODEL: GUSTO**
Oral	**Thomas Bernet**, Imperial College London, United Kingdom

PARALLEL SESSIONS VII – Machine learning and data-driven methods

Room: Arrábida IV
Chair: Wei Yang

14h30 – 14h50	**CONFIDENTIALITY-PRESERVING TRAINING OF THERMODYNAMIC MODELS WITH FEDERATED LEARNING**
Oral	**Pascal Zittlau**, RPTU Kaiserslautern, Germany
14h50 – 15h10	**TERPENE-BASED EUTECTIC MIXTURES AS GREENSOLVENTS FOR CO_2 CAPTURE: EXPERIMENTALCHARACTERIZATION AND MOLECULAR INSIGHTS**
Oral	**Esteban Cea-Klapp**, Pontificia Universidad Católica de Chile, Chile
15h10 – 15h30	**TWENTY YEARS OF DEEP EUTECTIC SOLVENTS: ARE THERMODYNAMIC MODELS READY FOR INDUSTRY?**
Oral	**Reza Haghbakhsh**, Universidade Nova de Lisboa, Portugal
15h30 – 15h50	**A THERMODYNAMIC FRAMEWORK TO DESIGN GREENHOUSE GAS CAPTURE UNITS USING PHOSPHONIUM-BASED IONIC LIQUIDS**
Oral	**Sabrina B. R. Reartes**, Universitat Rovira i Virgili, Spain

SPECIAL SESSION – Maurizio Fermeglia

Room: Arrábida I-II

Chair: Eugénia A. Macedo and Andrea Mio

16h30 – 16h45	**PRESENTATION IN HONOUR OF MAURIZIO FERMEGLIA** **Andrea Mio**, University of Trieste, Italy
16h45 – 17h45	**DEVELOPMENT OF MACHINE LEARNING MODELS FOR THERMOPHYSICAL PROPERTIES REQUIRED FOR PROCESS MODELING AND OPTIMIZATION OF CARBON CAPTURE PROCESSES** PS **Peter T. Cummings**, Heriot-Watt University, Scotland
17h45 – 18h45	**USING MOLECULAR SIMULATION TO PROVIDE INSIGHTS INTO SKIN BARRIER FUNCTION** PS **Clare McCabe**, Heriot-Watt University, Scotland

Scientific programme: Talks

Wednesday, May 13th

SPECIAL SESSION – Karel Aim

Room: Arrábida I-II
Chair: Ana Soto and Martin Lisal

08h30 – 08h45	**PRESENTATION IN HONOUR OF KAREL AIM**
	Martin Lisal, Institute of Chemical Process Fundamentals, Czech Republic
08h45 – 09h45	**EXPERIMENTS AND MODELLING AT MODERATE AND HIGH PRESSURES: CHALLENGES AND PERSPECTIVES**
PS	**Catinca Secuianu,** Nat. Univ. of Sci. and Tech. Politehnica Bucharest, Romania
09h45 – 10h45	**NEW EQUATIONS OF STATE: FROM NON-SPHERICAL TO CONFINED PARTICLES**
PS	**Luís F. M. Franco**, Universidade Estadual de Campinas, Brazil

PARALLEL SESSIONS VIII – Molecular modelling and simulation

Room: Arrábida I-II
Chair: Margarida Costa Gomes

11h05 – 11h25	**INCLUSION COMPLEXATION OF NATIVEAND FUNCTIONALIZED α-, β-, AND γ-CYCLODEXTRINS WITH PFAS**
Oral	**Bowen Sha**, Delft University of Technology, the Netherlands
11h25 – 11h45	**SUSTAINABLE EPOXY NETWORK DESIGN BY MULTISCALE SIMULATION: TOWARDS HIGH PERFORMANCE MEMBRANES FOR GAS SEPARATION**
Oral	**Amro Mohamed**, Heriot-Watt University, Scotland
11h45 – 12h05	**FROM SMALL MOLECULES TO COLLOIDAL ASSEMBLIES - TOWARDS A UNIFYING THEORY OF NANOSCALE MATTER**
Oral	**Thi Vo**, Johns Hopkins University, USA
12h05 – 12h25	**MECHANICAL BEHAVIOR OF POLYMERS UNDER SHOCK LOADING: A MOLECULAR DYNAMICS STUDY**
Oral	**Claire Lemarchand**, Université Paris-Saclay, France
12h25 – 12h45	**READY-TO-USE DURVILLAEA INCURVATE EXTRACT USING EDIBLE DEEP EUTECTIC SOLVENTS**
Oral	**Nicolás F. Gajardo Parra**, Pontificia Universidad Católica de Chile, Chile

PARALLEL SESSIONS VIII – Phase equilibria & LOHC

Room: Arrábida III
Chair: Eva Rodil

11h05 – 11h25	**FROM MOLECULAR SIMULATION TO EQUATION OF STATE: CO2 ADSORPTION ENTHALPIES ON CALF-20**
Oral	**Ana Paula de Barros Barreto Mazó**, Univ. Estadual de Campinas, Brazil

11h25 – 11h45	**THERMODYNAMIC AND DYNAMIC ASPECTS OF GLASS TRANSITION OF WATER AND AQUEOUS SYSTEMS**
Oral	**Vitaly Kocherbitov**, Malmö University, Sweden
11h45 – 12h05	**HOW RENEWABLE CAN GREEN AMMONIA BE? HOW EXERGY COSTS AFFECT NATURAL RESOURCES AVAILABILITY AND IMPACT PLANETARY BOUNDARIES**
Oral	**Alessandro J. T. B. de Lima**, Universidad de Zaragoza, Spain
12h05 – 12h25	**THIRD VIRIAL COEFFICIENT OF HYDROGEN FROM FIRST PRINCIPLES**
Oral	**Philipp Marienhagen**, Universität der Bundeswehr Hamburg, Germany

PARALLEL SESSIONS VIII – Molecular modelling and simulation

Room: Arrábida IV
Chair: Begoña Gonzalez

11h05 – 11h25	**NOVEL COMPUTATION OF THE CO_2 HYDRATE PHASE DIAGRAM: IDENTIFYING THE HYDRATE-LIQUID-VAPOR COEXISTENCE AND QUADRUPLE POINT Q_2**
Oral	**Jesús A. Fernández**, Universidad de Huelva, Spain
11h25 – 11h45	**MONTE-CARLO SIMULATIONS OF VAPOR-LIQUID PHASE EQUILIBRIA OF THE ARGON-XENON BINARY SYSTEM IN THE CONTEXT OF NOBLE GASES DETECTORS**
Oral	**Quentin Berger**, Laboratoire Interdisciplinaire Carnot de Bourgogne, France
11h45 – 12h05	**CONFINED ACTIVE COLLOIDS: WALL ACCUMULATION AND MOTILITY-INDUCED PHASE SEPARATION**
Oral	**Martin Lisal**, Institute of Chemical Process Fundamentals, Czech Republic
12h05 – 12h25	**PREDICTING EQUILIBRIUM AND KINETICS OF ESTERIFICATION REACTIONS USING ELECTROLYTE THERMODYNAMICS AND THE IMPORTANCE OF H_3O^+ ACTIVITY**
Oral	**Paul Figiel**, TU Dortmund, Germany

CLOSING SESSION

Room: Arrábida I-II

12h45 – 13h15	**CLOSING SESSION**

Scientific programme: Posters

Monday, May 11th: 19h10-19h55

Tuesday, May 12th: 18h45-19h30

Room: Conference centre

PHASE EQUILIBRIA

P01	**BUBBLE POINT PRESSURE MEASUREMENTS AND PREDICTIONS FOR DIMETHYL ETHER-CHLOROFORM-ETHANOL AND PROPANE-CHLOROFORM-ETHANOL AT 313.15 K** **Tomoya Tsuji**, Universiti Teknologi Malaysia, Malaysia
P02	**SURFACE TENSION OF n-ALKANE MIXTURES: MODEL COMPARISION AND PERFORMANCE ANALYSIS** **Virginia Vadillo-Rodríguez**, Universidad de Extremadura, Spain
P03	**Fives ProSim, A RANGE OF PROCESS ENGINEERING SOFTWARE DEDICATED TO INDUSTRIALS AND MODEL DEVELOPERS** **Edouard Moine**, Fives ProSim, France
P04	**IMPACT OF NANOSTRUCTURING ON THE CHEMICAL AND PHASE EQUILIBRIA OF SWITCHABLE HYDROPHOBICITY SOLVENTS** **Tanja Traini**, Technical University of Munich, Germany
P05	**A NOVEL METHOD FOR MULTIPHASE EQUILIBRIUM CALCULATIONS FOR CO_2-WATER-HYDROCARBON MIXTURES** **Juan Heringer**, University of Pau, France
P06	**THERMODYNAMIC MODELLING OF CARBON DIOXIDE, WATER AND SODIUM CHLORIDE SYSTEMS AT MODERATE PRESSURES** **Renato M. M. Barcellos**, Federal University of Rio de Janeiro, Brazil
P07	**CHARACTERISATION AND MODELLING OF LIQUID-LIQUID EQUILIBRIA FOR NOVEL TERNARY SYSTEMS CONTAINING WATER AND ETHYL ACETATE** **Pedro Velho**, University of Porto, Portugal
P08	**POLYMER-BASED AQUEOUS TWO-PHASE SYSTEMS AS A SUSTAINABLE SEPARATION STRATEGY FOR THE TEXTILE INDUSTRY: DYE PARTITIONING** **Afonso M. Madaleno**, University of Porto, Portugal
P09	**AQUEOUS TWO-PHASE SYSTEMS BASED ON GREENER SOLVENTS: PHASE EQUILIBRIA, THERMODYNAMIC MODELLING AND AMOXICILLIN REMOVAL** **Eduardo Sousa**, Faculdade de Engenharia da Universidade do Porto, Portugal
P10	**SOLUBILITY OF BIOACTIVE COMPOUNDS CONTAINED IN SPENT COFFEE GROUND: COMPUTATIONAL SCREENING AND EXPERIMENTAL DATA** **Emilio J. González**, Universidad Politécnica de Madrid, Spain
P11	**DENSITY GRADIENT THEORY FOR INTERFACIAL TENSION: CUBIC EoS AND FLORY-HUGGINS APPROACHES** **Anna Šmídová**, University of Chemistry and Technology, Prague, Czech Republic

P12	**PHASE EQUILIBRIA, eNRTL MODELLING AND QUANTUM-INFORMED FORCE-FIELDS: AQUEOUS BIPHASIC SYSTEMS BASED ON SODIUM FORMATE** **Eugénia A. Macedo**, University of Porto, Portugal
P13	**DETERMINATION OF HENRY'S LAW COEFFICIENTS OF CO_2 IN CYRENE** **Valentina Schiattarella**, Politecnico di Milano, Italy
P14	**MODELING THE COMPLETE PEG/CITRATE AQUEOUS TWO-PHASE SYSTEM PHASE DIAGRAM** **René Gómez-Pineda**, Universidade de Santiago de Compostela, Spain
P15	**DETERMINATION AND PREDICTION OF EXCESS MOLAR ENTHALPIES AT HIGH PRESSURE OF THE BINARY SYSTEMS CARBON DIOXIDE + BIO-BASED SOLVENT** **Taichi Izawa**, Nihon University, Japan
P16	**SURFACE TENSION FOR 27 ALKENES. SELECTION OF DATA AND CORRELATION WITH THE TEMPERATURE** **Ángel A. Mulero.**, Universidad de Extremadura, Spain
P17	**SCREENING OF AQUEOUS TWO-PHASE SYSTEMS FOR FISH PROTEIN RECOVERY** **Eva Rodil**, Universidade de Santiago de Compostela, Spain
P18	**PHASE TRANSITIONS OF POLYMER NETWORKS UNDER TENSION** **Michele Valsecchi**, Columbia University, USA
P19	**MOFs AS POTENT ICE RECRYSTALLIZATION INHIBITORS: MECHANISTIC INSIGHTS FROM MACHINE LEARNING AND MOLECULAR SIMULATIONS** **Jayant K. Singh**, Indian Institute of Technology, India

MOLECULAR MODELLING AND SIMULATION

P20	**EVALUATION OF EXCESS SURFACE TENSIONS AT NORMAL AND HIGH PRESSURE FOR BINARY AND TERNARY SYSTEMS USING WILSON- AND ASOG-SURTENSION MODELS** **Katsumi Tochigi**, Nihon University, Japan
P21	**MOLECULAR DYNAMICS SIMULATIONS OF THE DIELECTRIC CONSTANT OF R410A** **Estefânia P. Canzian**, Universidade Estadual de Campinas, Brazil
P22	**THERMODYNAMIC BEHAVIOUR OF 2-(2-ETHOXYETHOXY)ETHANOL + 1-ALKANOL MIXTURES: EXCESS MOLAR ENTHALPIES AND MOLECULAR INTERACTIONS** **Fernando Aguilar Romero**, University of Burgos, Spain
P23	**SIMULATION OF THE N_2 HYDRATE-WATER INTERFACIAL FREE ENERGY FROM COMPUTER SIMULATION ALONG THE DISSOCIATION LINE OF THE N_2 HYDRATE** **Miguel J. T. Ríos**, Universidad de Huelva, Spain
P24	**MOLECULAR DYNAMICS INSIGHTS INTO SOLVENT-BIOMASS INTERACTIONS IN GREEN SOLVENT MIXTURES** **Vojtěch Jeřábek**, University of Chemistry and Technology, Prague, Czech Republic
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Short bios & Abstracts

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Agílio Pádua is a professor of physical chemistry at the Ecole Normale Supérieure (ENS) de Lyon, a research-intensive institution on fundamental sciences delivering diplomas at masters and doctoral levels. He studies the molecular interactions, microscopic structure, and thermodynamic and transport properties of ionic liquids and related systems. The main scientific questions are related to solvation and interfaces, leading to the design of solvents and electrolytes. A. Padua has used molecular simulation and developed molecular interaction models to study ionic liquids for more than 20 years. He is the author of 200 publications.

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Clare McCabe received her bachelors and Ph.D. degrees in Chemistry from Sheffield University. After postdoctoral and research faculty appointments at the University of Tennessee, she joined the Colorado School of Mines faculty as an Assistant Professor of Chemical Engineering in January 2002. In 2004, she moved to Vanderbilt University, where she rose through the ranks and was appointed the Cornelius Vanderbilt Chair of Engineering and Professor of Chemical and Biomolecular engineering in 2017. In 2022 she moved to Heriot-Watt University as Bicentennial Professor. Her research interests focus on the use of molecular modeling techniques to understand and predict the thermodynamic and transport properties of complex fluids and materials. She is a fellow of the Royal Society of Chemistry, the American Association for the Advancement of Science, the American Institute of Chemical Engineers, and the American Institute of Biomedical Engineers.

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Prof. Peter T. **Cummings**
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Peter T. Cummings holds the position of Bicentennial Professor at Heriot-Watt University in Edinburgh, Scotland. Prior to this, he was the John R. Hall Professor of Chemical Engineering at Vanderbilt University for just over 20 years, from 2002 to 2022. For 9 years (2013-2022), he held the position of Associate Dean for Research in the Vanderbilt University School of Engineering. For 20 years (1994-2013), he was associated with Oak Ridge National Laboratory (ORNL) at levels of effort ranging from 40 to 50%, most recently (2007-2013) serving as the chief scientist of ORNL's Center for Nanophase Materials Sciences (CNMS). His research interests include statistical mechanics, molecular simulation, computational materials science, computational and theoretical nanoscience, and computational biology. He is the author of over 470 refereed journal publications. He was elected to the US National Academy of Engineers in 2023. In the US, he was the PI on over $45M in awarded grants, primarily from the National Science Foundation (NSF) Department of Energy (DOE), and National Institutes of Health, and was co-PI on over $240M in awarded grants. He has served on advisory boards to the DOE (the Basic Energy Sciences Committee) and the NSF (the Engineering Directorate Advisory Committee and the Advanced Cyber-Infrastructure Committee). He has been elected fellow of the American Physical Society, of the American Association for the Advancement of Science (AAAS), of the American Institute of Chemical Engineers, of the American Society of Mechanical Engineers (ASME), and of the Royal Society of Chemistry in the UK. He is the recipient of many awards, perhaps the most relevant being the 2013 John Prausnitz award, the most prestigious international research award in chemical engineering thermodynamics, presented every three years at the Properties and Phase Equilibria for Process and Product Design (PPEPPD) Conference.

Michael L. Michelsen Award

Prof. Ioannis G. **Economou**
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Ioannis G. Economou is Professor of Chemical Engineering and Executive Director of Research and Graduate Studies in Texas A&M University at Qatar. He holds a Diploma in Chemical Engineering from the National Technical University of Athens, Greece (1987) and a PhD also in Chemical Engineering from The Johns Hopkins University in Baltimore, Maryland, USA (1992). He was a post-doctoral researcher in Delft University of Technology in the Netherlands (1993 – 94) and in Exxon Research and Engineering Company, in New Jersey, USA (1994 – 95). From 1995 to 2009, he worked at the National Center for Scientific Research "Demokritos" in Athens, Greece where he held the position of Director of Molecular Thermodynamics and Modeling of Materials Laboratory. From 2009 until 2012, he was the Associate Provost for Graduate Studies and Professor of Chemical Engineering at the Petroleum Institute, Abu Dhabi. In 2013, he was appointed Professor of Chemical Engineering in Texas A&M University at Qatar (TAMUQ), where he served in various senior administrative positions. He is a Fellow of the American Institute of Chemical Engineers (2021).

He held various visiting / research positions including research fellow in University College London and Princeton University, and visiting Professor in the Technical University of Denmark, the American College of Greece, and the Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany. Starting December 2026, he will be Professor of Chemical Engineering in the Technical University of Denmark.

Prof. Economou's research interests are related to the development and validation of molecular and macroscopic physical property models for the design of novel materials and sustainable industrial processes for the oil & gas, chemical and pharmaceutical industry. He has supervised 20 MSc students, 15 PhD students and 23 post-docs, and has published 250 peer-reviewed research papers in leading journals in Chemical Engineering, Physical Chemistry and Polymer Science. In addition, he co-authored 10 book chapters and co-edited 1 book entitled "Natural Gas Processing from Midstream to Downstream" (Wiley, 2019). His H-index is 64 according to Scholar Google. He is Editor of *Fluid Phase Equilibria* (Elsevier).

Multi-scale Simulation of Fischer-Tropsch Synthesis for the Gas-To-Liquid Process: From Density Functional Theory Calculations to Physical Property Predictions

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Syngas conversion into liquid hydrocarbons, known also as Gas-To-Liquid (GTL) process, is a catalytic Fischer-Tropsch Synthesis (FTS) that has attracted growing interest by industry in the last two decades. The performance of FTS catalysts is highly dependent on the nature of the metal active sites and their interactions with support materials. A fundamental understanding of the interactions between the catalyst (in most cases, cobalt) and the catalyst support (usually titania, alumina or silica) remains crucial for understanding the catalytic process, which will permit further improvements and optimization. In this work, a systematic hierarchical multi-scale study is performed starting from Density Functional Theory (DFT) calculations in order to elucidate the structure and predict the electronic properties of TiO_2[1] followed by investigation of the cobalt adsorption on the TiO_2 anatase surface (101) through a computational approach combining DFT, *ab initio* molecular dynamics (AIMD) simulation, and genetic algorithm-based force field parameterization.[2] Our findings highlight how metal-support interactions (MSI) influence cobalt cluster stability, electron transfer, and surface restructuring, directly impacting catalytic performance and resistance to sintering. Finally, molecular dynamics (MD) simulations are performed for the full GTL system that consists of wax, water, and cobalt nanoparticles confined in TiO_2 using accurate detailed atomistic and mesoscopic models to predict important physical properties, such as diffusion coefficients of the various components.[3]

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Porous ionic liquids for separations, conversions and delivery

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Porous liquids combine the permanent porosity and high sorption capacity of solids with the fluidity and processability of liquids. Here we present recent work on porous ionic liquids, which consist of suspensions of nanoparticles of metal-organic frameworks (MOFs) in bulky ionic liquids. These heterogeneous systems have emerged as candidates for separations, as catalytic reaction media, or as vehicles for the delivery of small molecules. We combine experimental characterization of thermodynamic and transport properties with molecular dynamics simulations, aiming to improve our molecular-level understanding of the structure, stability and performance of the porous ionic liquids. We start by addressing some fundamental aspects related to suspension stability in ionic liquids by studying their rheological behavior, focusing on how the liquid-phase ordering of the ionic liquid and its organization at the solid interface can influence the flow behaviour and interparticle interactions [1]. Next, to explore the applicability of porous liquids in green chemistry, we investigate solute partitioning in porous ionic liquids to evaluate their potential as electrolytes for the electrochemical reduction of nitrogen to ammonia, a key target reaction in the development of sustainable chemical processes. Finally, to expand the applicability of porous ionic liquids into bio-medical systems, we develop and validate a polarizable and flexible force field for the simulation of CD-MOF-1, a biocompatible MOF based on cyclodextrins, and evaluate its potential for the encapsulation of active pharmaceutical ingredients.

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From Prediction to Practice: Physical Property Data for Industrial Process Solutions

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Physical property data and thermodynamic models are fundamental for development, design, and optimization of chemical processes. Increased availability and accuracy of physical properties such as vapor pressures and activity coefficients enable more reliable process simulations, leading to safer, more efficient, and more sustainable scale-up and process development. However, experimental data are still often incomplete or unavailable, especially for novel compounds and complex mixtures, or in the early stages of process development. In such cases, predictions of physical properties play a crucial role in supporting decision-making and guiding process concepts.

Recent advances in machine learning techniques have accelerated the development of predictive methods for physical properties, making them widely accessible and usable. This democratization of predictive methods has increased the demand for standardized evaluation procedures and uncertainty assessments. Well-designed test datasets, reference systems, and transparent comparison frameworks are key to validating predictive methods and enabling their integration into industrial workflows.

This contribution focuses on the interplay between experimental data, databases, and modeling strategies, illustrating how predictions and measurements complement each other throughout process development. It emphasizes the need for careful evaluation of predictive methods, not only to support democratization but also to support sustainable and innovative solutions in the chemical industry.

Realizing the Dream of Thermodynamic Modeling

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The ultimate dream of thermodynamic modeling is within reach: predicting thermodynamic properties directly from the substance's structural formulae - for any property, any pure substance and any mixture, even when no experimental data are available. This is becoming achievable through hybrid thermodynamic models that combine physical modeling with machine learning (ML) - a new class of models that has emerged only recently.

Two hybridization strategies are currently used: In the first, an existing physical thermodynamic model provides the framework, and a data-driven ML algorithm is trained to predict its parameters. This straightforward approach yields hybrid models that are essentially new parameterizations of established models, preserving the strengths of the physical model, but also inheriting its limitations.

The second strategy replaces the traditional physical model entirely with an ML model, enabling model structures that are not fixed a priori but instead learned from data during training. To ensure physical consistency and robust extrapolation into uncharted regions, such models must incorporate explicit physical knowledge into their architecture.

We will discuss the application of both strategies to modeling phase equilibria of fluid mixtures, with particular emphasis on the second. The field is currently undergoing a rapid transformation, driven by hybrid models that can predict phase equilibria solely from the structural formulae of the components and deliver unprecedented scope and accuracy.

Development of Machine Learning Models for Thermophysical Properties Required for Process Modeling and Optimization of Carbon Capture Processes

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Over 40% of energy-related carbon dioxide (CO_2) emissions are due to the burning of fossil fuels for electricity generation. Carbon capture and sequestration (CC&S) remains the one of the most promising techniques for significantly reducing CO_2 emissions from fossil-fuel-fired power plants. CC consists of removing CO_2 from the plant's flue gas, using an industrial chemical process (known as amine scrubbing) first patented over 90 years ago (US patent US1783901, assigned to Robert R. Bottoms) as a method for producing high-purity CO_2 for sale as an industrial gas. The process uses an aqueous amine solution as a liquid solvent to selectively adsorb CO_2 from flue gas in an adsorber column; the CO_2 is released from the solvent in the solvent recovery column. Many improvements have been made to the process, particularly to increase heat integration, and some consideration of other amines and/or mixed amines as solvents (in aqueous solution). Among the key criticisms of CC&S is that the CC process is energy-intensive, requiring ~30% of the energy produced to run the chemical process that produces CO_2 primarily for desorbing CO_2 from the solvent; This is frequently referred to as parasitic energy cost of current CC methods.
As part of a broader project aimed at optimising CC&S using artificial intelligence (AI) methods, we focused on the optimizing the CC component. Specifically, we investigated the use of alternative aqueous amine solvents in order to reduce the parasitic energy requirement. In order to model the process, Process-level simulation requires thermodynamic properties (phase equilibria and surface tension properties between CO_2 and solvent in the adsorber and the solvent recovery columns (at very different state conditions) and transport (viscosity of both the neat and CO_2-laden solvent) properties. Published experimental data for such properties is limited. Therefore, to develop machine learning (ML) models for all of these properties, we used molecular simulation to add data for training the ML models. In this talk, we describe the simulation methodologies used, and the ML model development, and the application of these models to process-level simulation of novel, as yet unsynthesized, amines [1] generated by a novel molecule-generating utility MolGrouper developed within our group.

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Using Molecular Simulation to Provide Insights into Skin Barrier Function

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Skin's function as a barrier to infection, dehydration and chemical assault is critical to health and survival. Its barrier effectiveness rests almost entirely in the thin, outer membrane, called the stratum corneum (SC), which consists of dead skin cells embedded in a highly organized dense lipid-rich environment [1]. This organization of the SC lipids into ordered gel or crystalline phases can be ascribed to its unique composition: mostly ceramides, free fatty acids and cholesterol. An impaired skin barrier, which is coincidental with abnormalities in composition, organization and structure of the SC lipids, is the primary event in the pathogenesis of skin disease and even some systemic diseases (e.g., the occurrence of asthma and allergic rhinitis in patients with atopic dermatitis). An improved understanding of the relationship between SC lipid composition, structure, and organization and barrier function is needed to understand the relationship between skin disease, reduced barrier function, and effective treatment. While experimental lipid systems that mimic the SC can be designed and studied, any understanding of the relationship between barrier function and lipid composition and organization can only be inferred; accurate computational studies on well-characterized systems allow the mechanistic basis of these relationships to be clearly probed. Using a multi-scale modeling approach that combines simulations at the atomistic and coarse-grained (CG) levels, insight into the molecular level organization of, and interactions between, SC lipid molecules in equilibrated assemblies of SC lipids modeling normal and diseased skin can be obtained. In contrast to experimental studies, the computational models allow for variations in the composition of the SC models to be easily investigated.

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Experiments and Modelling at Moderate and High Pressures: Challenges and Perspectives

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Understanding the behaviour of matter at moderate and high pressures is essential to many areas of science and engineering, from energy systems and materials processing to environmental and planetary studies. Despite decades of progress, the accurate determination and prediction of phase equilibria and thermophysical properties under such conditions remain among the most demanding tasks in experimental and theoretical thermodynamics. Experimental investigations at elevated pressures face persistent challenges related to precise temperature and pressure control, fluid purity, and reliable detection of phase transitions and equilibria. The design of measurement systems must reconcile mechanical robustness with analytical sensitivity, particularly when dealing with asymmetric mixtures.

Over the past two decades, our research has been dedicated to the combined experimental and modelling study of systems containing carbon dioxide, with a particular focus on high-pressure phase equilibria, density measurements, and the development of predictive cubic equations of state. Our laboratory has designed and refined experimental apparatuses capable of providing high-precision phase equilibrium data under various pressure and temperature conditions. These measurements have enabled the systematic characterisation of CO_2 containing mixtures relevant to energy conversion, carbon capture, and transport processes. The reliability and consistency of these data have provided a solid basis for testing and improving thermodynamic models. On the modelling side, we have advanced the use of cubic equations of state to describe complex phase behaviour, emphasising temperature-dependent parameters, cross-interaction rules, and the physical interpretation of model constants. Our recent developments demonstrate that, when appropriately parameterised, these models can achieve predictive accuracy comparable to more complex multiparameter formulations while retaining computational simplicity.

In this plenary lecture, we will present key results from our experimental and modelling work, discuss the challenges encountered in both measurement and interpretation, and outline the methodological advances that have emerged from this integrated approach. Particular attention will be given to the interplay between data quality and model performance, and to the lessons learned from over two decades of work on CO_2-containing systems. The talk concludes with perspectives on future directions for high-pressure thermodynamics, towards more consistent, physically grounded, and transferable predictive models.

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New equations of state: from non-spherical to confined particles

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In this plenary lecture, I will present two new equations of state: one for non-spherical particles and another for confined fluids. In the first one, by applying perturbation theory considering a non-spherical geometry for the reference fluid, I will show how we can obtain excellent results for the coexistence curve of simple molecules (up to *n*-octane) [1,2,3,4], and how we can extend it to mixtures. This approach avoids the consideration of the chain contribution from Wertheim's first-order thermodynamic perturbation theory, and as a consequence avoids the fitting of non-integer number of spherical segments, as commonly done in SAFT equations of state. For confined fluids, I will present an extension of SAFT-VR Mie equation of state for confined fluids, by applying the generalized van der Waals theory to describe solid-fluid interactions. The final model is able to correlate quite accurately the adsorption isotherms of pure components [5], and to predict the adsorption isotherms of binary and ternary mixtures [6]. Recently, we have extended this model for confined associating molecules, and applied particularly to carbon capture considering the coadsorption of water and carbon dioxide in new materials such as CALF-20.

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ORAL LECTURES

Abstracts

Application of CP-PC-SAFT with universal k_{12} value for simultaneous prediction of VLE, LLE and critical loci in systems of gases and aliphatic hydrocarbons with substituted aromatic and heterocyclic compounds

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One of the major factors determining the extent of phase separations in fluid systems are the interrelations between the pure compound T_c and P_c. The differences between them are expressed in degrees of asymmetry and extends of phase splits. For example, the molar solubilities of gases are clearly dependent on their critical temperatures. As the T_{c1} get lower, the systems become more asymmetric, increasing thus the extends of phase separations and decreasing the solubilities. However, in the cases of more symmetric systems the P_{c1} become particularly important. Typically, higher P_{c1} of solvents results in their higher solubilities. For example, although benzene and *n*-octane have relatively similar T_{c1} values, benzene is much more solvable in various solvents, which could be attributed to its higher P_{c1}. Such considerations may also explain a behaviour characteristic for the homologues series of *n*-alkanes. Unsurprisingly, the largest extends of phase separation occur in the systems of CH_4 and they decrease moving to C_2H_6, C_3H_8, and *n*-C_4H_{10}. Usually, the smallest LLE phase splits and the lowest UCSTs take place in the systems of around *n*-C_4 – *n*-C_6. However, further increasing the chain length of n-alkanes results in gradual growth of LLE and rise of UCSTs. On one hand the heavier *n*-alkanes have higher T_{c1} and, therefore, their systems are supposed to be more symmetric, which should reduce the LLE. However, on the other hand, their P_{c1} decrease, which supposed to have quite the opposite effect. Apparently, in the cases of most *n*-alkane's homologies series, influence of the decreasing P_{c1} after *n*-C_6 becomes stronger and the LLE actually increase. The critical constants of solvents also influence the extents of phase splits. In particular, the increase of T_{c2} results in growing immiscibility. Obviously, quantitative portrayal of the systems asymmetry created by interrelations between the pure compound T_c and P_c is a non-trivial task. However, strict adherence to these critical constants is supposed to improve the over-all robustness and reliability of EoS models. The Critical Point-based Revision of PC-SAFT (CP-PC-SAFT)[1] satisfies this criterion. Thus far [2,3], the capabilities of its simplest polarity- and association-neglecting version to simultaneously predict VLE and LLE in systems of Ionic Liquids with universal k_{12} values was considered. The current presentation summarizes its application with the universal k_{12} = 0.023 adjusted to the VLE data of the randomly selected system propane – phenol for predicting the VLE, LLE and binary critical data available for a large variety of systems containing non-associative gases and aliphatic hydrocarbons as solutes and various solvents, including substituted aromatic compounds (phenol, *m*-cresol, 2-methoxyphenol, 2-phenylethanol, 2-ethylphenol, pyridine, aniline, benzylamine, *o*-toluidine, acetophenone, and benzaldehyde) along with heterocyclic compounds (*N*-methyl-2-pyrrolidone, pyrrole, furan, tetrahydrofuran, thiophene, 1,4-dioxane, tetrahydrothiophene, *γ*-valerolactone, 2,3-benzofuran, and sulfolane). It is demonstrated that CP-PC-SAFT reliably predicts both the available high pressure VLE and the UCST data in diverse homologies series. Besides that, this approach accurately estimates the compositions of the solvent-rich LLE phases, but overpredicts the content of solvents in the *n*-alkane-rich ones. Predictions of ternary LLE in industrially important systems containing sulfolane are also presented. Impacts of the pure compound T_c and P_c data on the considered phase equilibria are also discussed.

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Using the Helmholtz Free-energy Equation of State for Mixtures

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For high-precision thermo-dynamic modelling of pure components, the Helmholtz free-energy equation of state is the standard. For describing mixtures of components it is hardly used, only for specific (quasi-)binary mixtures, like sea-water and NH_3/H_20 mixtures. The drawbacks of using this method are complexity, a high calculational load, and poor extrapolation outside the pure component phase envelopes. This paper addresses the poor extrapolation with a structured approach to extrapolation from the phase-boundary, and it addresses the high calculational load with A) a solution strategy that takes pressure and temperature as input, and by using analytical derivatives and smart convergence strategy minimizes the number of iterations, and B) calculates phase equilibrium using the auxiliary equation for the saturation line (like an Antoine-based vapor pressure curve) and (NRTL-based) activity coefficients instead of solving for Gibbs equilibrium.
In mixtures with, for example sugars, the boiling point elevation ensures that water stays in the liquid phase at elevated temperatures, so one can have liquid water at a pressure of 1 bara and temperature of 110 °C. Likewise, one can have water vapor at a temperature of 50 °C and pressure of 1 bara with sufficient dilution with a non-condensable gas. Calculations of these systems are vital for (food) processing. Process simulation tools typically use high precision water/steam tables for places where only pure water exists, like in a steam heating system, while they use much simpler thermodynamic models for the mixtures. This is problematic when the two meet, for example in multi-effect evaporators. Water evaporates from a mixture, like a sugar-solution, in one effect on the cold side and condenses as pure water vapor in a next effect on the hot side. Switching thermo-dynamic models between those places is a source of errors which may well lead to incorrect results. If one was to use simplified thermodynamic models this yields an inaccurate model, as a cross-check with the water/steam tables would immediately reveal. The inaccuracy of the simplified models means that they cannot be used at all for processes that go close to or into the supercritical zone.
In this paper we present an extension of the IAPWS-95 water/steam tables and all similar Helmholtz based thermodynamic models by extrapolation and interpolation as depicted in figure 1, such that they can be used for mixtures. The mixture model typically used is one of ideal mixing, in which the mass-based enthalpy, specific volume, entropy etc. are the mass-based weighted averages of the pure component properties. The extensions outside the pure component phase envelopes have been written such that the functions are all continuous, including their first derivatives, for consistency as well as for calculational efficiency. This approach has been used throughout the process simulation work at Cargill, examples show its superior performance over traditional approaches.

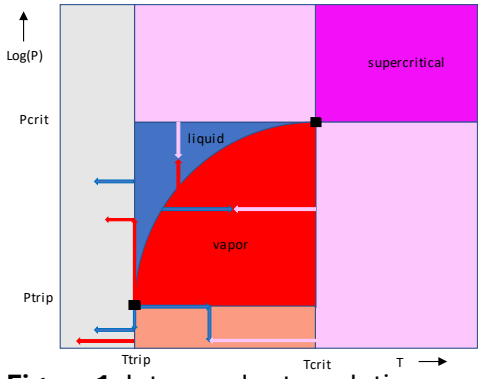

Figure 1. Inter- and extrapolation outside pure comp. phase envelope.

Development and Commercial Implementation of a Computationally Efficient Polar PC-SAFT Equation of State for Large Scale Industrial Applications

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In this work we describe the implementation of a SAFT EoS in a custom thermodynamics package which is then linked to PRO/II, Aspen as well as proprietary equipment design and reservoir simulation software packages. The vision being a single equation of state for use across the petrochemical industry from reservoir simulation, petroleum refining, chemicals production and carbon capture. The starting point was the polar[1] PC-SAFT[2] EoS using the simplified[3] PC-SAFT hard sphere approach. Due to the possibility of large numbers of associating and polar species in any given calculation, the polar[4] and hydrogen bonding contributions of the free energy were modified such that the computational load of these contributions only increase linearly as the number of polar species are increased, not exponentially as in the standard representation. These simplified hydrogen bonding and polar free energies give nearly identical results to the un-simplified versions, hence new parameterization is not required. The exponential decrease in computational penalty for including large list of hydrogen bonding and polar molecules allows for the optimal parameterization of the component library to account for the classes of intermolecular actions and their asymmetries in mixtures. Hydrogen bonding stoichiometry is enforced for self-associating molecules such as water and alcohols, as well as non-self-associating hydrogen bonding acceptors such as ketones, aldehydes, ethers, esters, alkenes, alkynes and aromatics. Long range polarity is included for ketones, aldehydes, esters, ethers, sulfides, mercaptans, aromatics and water. New physics is included to account for polarization of unsaturated hydrocarbons by polar molecules through the inclusion of phantom dipoles[5], as well as a second order perturbation theory contribution for the formation of cyclic dimers[6] with carboxylic acids. We conclude with several illustrative examples of commercial applications being accelerated by use of this advanced EoS.

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From Poultry Waste to Critical Raw Material Recovery: Thermodynamic Insights into Platinum Group Metal Adsorption

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The recovery of Platinum Group Metals (PGMs), classified by the EU Commission as critical raw materials, has become increasingly relevant due to their scarcity and high demand across various industrial sectors. PGMs are crucial for green technologies, and as these industries expand, particularly in the hydrogen-based energy sector, their shortage has become an urgent concern. At the same time, conventional mining processes are highly energy-intensive and generate toxic byproducts, which, together with the depletion of primary ores, make the development of more sustainable recovery routes essential.
Bio-based materials have emerged as promising alternatives for metal recovery, combining high selectivity, sustainability, and environmental benefits. In this study, we developed protein-based adsorbents derived from poultry industry residues - chicken feathers (rich in keratin) and egg white (rich in ovalbumin) - and applied them for the selective recovery of PGMs from both synthetic multimetallic solutions and real HCl–based leachates obtained from spent autocatalytic converters. Key parameters, including pH, temperature, metal concentration, and contact time, were systematically evaluated to optimize the adsorption performance.
Thermodynamic analyses were crucial to elucidate the mechanisms behind the preferential adsorption of PGMs, particularly Pd. The results demonstrate that poultry industry waste can be upcycled into efficient and selective adsorbents, while providing fundamental thermodynamic insights to guide the design of sustainable strategies for critical raw material recovery.

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Thermodynamic vs Kinetic Control of Brush Composition in Grafting to Reactions: a Combined Experimental and Grand Canonical Monte Carlo Study

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Grafting to reactions represent the most widespread approach used to produce polymer brushes with tuned thickness and grafting density[1,2]. Nonetheless, some key aspects of this process remain not fully understood and need to be shed light on.
The main novelty of this work consists in exploiting the timescales that are typical of grafting process when preferential grafting occurs due to competing grafting of short vs long chains[1]. To this aim, polystyrene blends containing equimolar amounts of two telechelic polystyrenes with different molecular weights have been experimentally studied by grafting on silicon oxide substrates. In this way, it was also possible to tune the modeling of disperse polymer systems provided by combined statistical thermodynamics and reactive Grand Canonical Monte Carlo.
The feature of this work is related to the study, for each blend, of different end groups such as hydroxy or phosphate groups. Main findings can be attributed at observations conducted at (i) short and (ii) long timescales[2].
(i) At short times, in case of hydroxy-terminated polystyrene blends, the shortest chains prevail in the preferential grafting due to their lower entropy loss when the reactive group approaches the substrate, with the brush composition (short/long chains ratio) being independent on the grafting time and the temperature. In contrast, in case of phosphate-terminated polystyrene blends, the grafting of short chains occurs at the beginning and the brush composition continuously increases.
(ii) At long times, their brush composition converges at the same final value of the hydroxy-terminated chains. This unexpected occurrence indicates that, a short times, the brush composition is dictated by a fast absorption of the short chains at the expense of the longer chains due to the strong polarity of the phosphate group, taking place even before the grafting process. In turn, as the grafting proceeds, the brush composition evolves towards its thermodynamic composition.

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Hydrogen Adsorption with 3D Classical Density Functional Theory

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Hydrogen purification and storage through adsorption in porous materials is a key challenge in enabling a transition to a hydrogen-based economy. At low temperatures, where adsorption is most effective, quantum effects play a crucial role and must be properly accounted for in thermodynamic modeling, requiring a thermodynamic approach that captures both classical and quantum effects.
In this work, we employ classical density functional theory (DFT) in combination with Helmholtz energy functionals based on the Statistical Associating Fluid Theory of Quantum Corrected Mie Potentials (SAFT-VRQ Mie) equation of state [1] to model hydrogen adsorption. Quantum effects are accounted for by a first-order Feynman-Hibbs correction [2], which allows a temperature- and mass-dependent treatment of intermolecular interactions without additional fitting parameters.
The implementation takes advantage of GPU parallelization [3] to improve the computational performance and to enable efficient three-dimensional DFT calculations in metal-organic frameworks (MOFs). The predicted adsorption isotherms are validated against experimental data and grand canonical Monte Carlo (GCMC) simulations, demonstrating the accuracy and predictive power of the SAFT-VRQ Mie-based DFT approach. It enables high-throughput screening of porous materials, which we will use to accelerate the discovery of promising hydrogen storage and separation candidates.

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Multiscale Modeling from Predictive Thermodynamics to Process Sustainability: The Scientific Legacy of Maurizio Fermeglia

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From predictive thermodynamics to decision metrics, this work traces Maurizio Fermeglia's scientific trajectory in multiscale modeling (Figure 1). The arc begins with molecular physics, advances through predictive property models, propagates parameters into process simulators, and culminates in sustainability assessment. Early studies on complex mixtures enabled a pivotal advance: extension of UNIFAC-based vapor-liquid equilibrium prediction to solvent-salt systems via group contribution ion-solvent interactions, achieving transferable and data efficient predictions beyond concentration dependent approaches. Building on this, a molecular-to-process methodology was formalized: equation-of-state parameters derived from Quantum Mechanics (QM) and Molecular Dynamics (MD) data were directly implemented in process simulators, reducing regression and enhancing extrapolative reliability for small molecules and polymers. This foundation established statistical mechanics simulations as a bridge to unit operations. Grand Canonical Monte Carlo (GCMC) and MD generated adsorption isotherms, selectivity, and transport pathways for H_2S capture in zeolites. Validated against experiments, these results were incorporated into fixed-bed models, accelerating material screening and process design under thermodynamic consistency. The same hierarchical strategy was extended to soft matter. In fact, atomistic simulations of interfacial energetics informed mesoscale morphologies and finite-element predictions of thermo-mechanical response in polymer/clay nanocomposites, providing a priori guidance on compatibility, exfoliation, and mechanical performance. Similarly, MD/GCMC-derived densities and solubilities were embedded in CFD simulations of polyurethane foam expansion to predict density evolution and thermal histories. This bottom-up logic generalized into integrated pipelines: atomistic and mesoscopic simulations populated validated property databases for thermoplastic polyurethanes, bridging molecular structure to macroscopic behavior. Finally, Maurizio Fermeglia extended the paradigm to sustainability, embedding life cycle thinking into the multiscale workflow. By coupling molecular and process simulations with consistent inventory generation, his group enabled prospective, decision-oriented assessments that benchmarked materials and process routes on a thermodynamic footing. Overall, Fermeglia's thermodynamics-first paradigm established a rigorous, transferable methodology for decision-oriented engineering across separations, foams, nanocomposites, and energy systems.

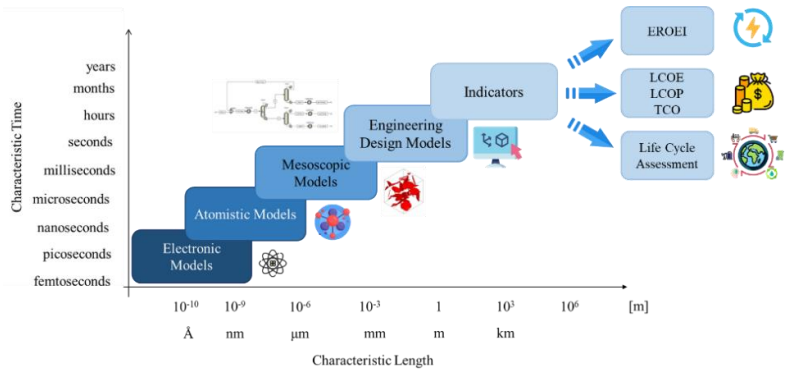

Figure 1. Multiscale Modeling scheme

A Classification for Electrolytes Based on Intermolecular Interactions

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Traditional electrolyte classifications, such as strong and weak which are based on the degree of association of a salt in a solvent, are insufficient for describing the complex thermodynamic behaviour observed across the full range of solubility [1]. Not only these classifications are not ideal, but they do also not allow a clear quantitative connection between the observed thermodynamic properties and the underlying intermolecular interactions. This work introduces the Interaction Balance Theory (IBT), a novel framework that classifies electrolytes based on the quantitative balance of their underlying intermolecular forces. By analysing experimental mean ionic activity coefficient (MIAC) data, we provide a physically meaningful system to understand why electrolytes with similar characteristics, like NaCl, NaBr, and NaF, exhibit vastly different thermodynamic signatures and properties.

The methodology links macroscopic experimental data to microscopic interactions by through integral equation theories to effectively connect them through structural. The result is a Potential of Mean Force which is decomposed into competing force contributions: (1) attractive vs. repulsive, (2) short-range vs. long-range, and (3) salt-salt vs. salt-solvent. By analysing each contribution, we establish quantitative ratios that define eight distinct electrolyte classes such as those dominated by long-range attractions, and those dominated by repulsive solvent-mediated forces. This classification provides crucial insights for the targeted development and validation of advanced thermodynamic models. With the electrolyte being classified, and its intermolecular forces being weighted relatively, it is possible to investigate which contributions are most important to model a given electrolyte solution, which can be used to develop electrolyte equations of state and activity coefficient models.

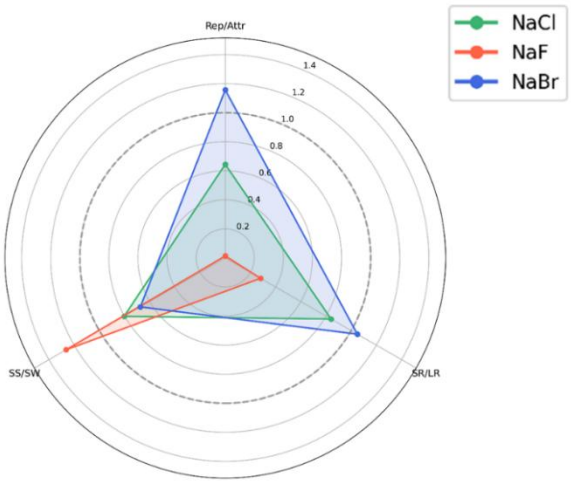

Figure 1. The balance of forces for NaCl, NaF, NaBr in water between Salt-Salt and Salt-Solvent (SS/SW), Short-Range and Long-range (SR/LR), and Repulsive and Attractive (Rep/Attr)

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Measurements of carbon dioxide solubility in Cyrene for CO_2 removal applications

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Physical absorption is a widely used and efficient method for CO_2 removal, particularly for separating CO_2 from industrial gases, such as natural gas and syngas. The search for sustainable alternatives to conventional solvents has gained increasing attention, aiming to reduce environmental impacts. Dihydrolevoglucosenone (Cyrene), a biodegradable, non-mutagenic and non-toxic solvent derived from biomass, has emerged as a promising bio-based candidate due to its properties comparable to N-Methyl-2-Pyrrolidone (NMP) [1,2], the solvent employed in the Purisol® CO_2 removal process.
Despite its promise, to the authors' knowledge, experimental data on CO_2 solubility in Cyrene remain limited, with measurements reported only as a series of eight data at 313.15 K [3] and as one point at 333.15 K [4]. Therefore, this work aims to expand the available dataset by providing new solubility measurements at 323.15 K, 333.15 K and 353.15 K by using the solubility unit installed at the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano. These temperatures have been selected as they lie within the typical range for physical absorption processes for CO_2 removal.
The reliability of the measurements is supported by the prior validation of the solubility unit with MonoEthanolAmine (MEA) [5], successfully reproducing several experimental data reported in the literature.
This work has been carried out in the context of the PRIN 2022 project "GREEN-based water-lean SOLvent for CO_2 capture" (GREENSOL), funded by the European Union – NextGenerationEU, CUP D53D23003100001 – and we acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component C2, Call for tender No. 104 published on 2.2.2022 by the Italian Ministry of University and Research (MUR).

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Phase behaviour of hard clover-shaped particles from Monte Carlo simulations

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Understanding how anisotropic and nonconvex particles spontaneously organize into ordered structures is a central challenge in colloidal materials design, particularly when geometry alone dictates assembly through excluded-volume interactions. Unlike simple convex particles, four-leaf-clover-shaped particles introduce pronounced rotational and positional degeneracy: their concave boundaries and multiple equivalent orientations generate complex local packing motifs, making the prediction of stable ordered phases less intuitive. Classical theoretical approaches, such as Onsager theory [1], scaled-particle theory, or DFT/FMT-based methods, become analytically intractable for such shapes. Alternatively, molecular simulations provide a rigorous and practical route to determine thermodynamically stable equilibrium structures. Here, we investigate the phase behavior of purely repulsive, four-leaf-clover-shaped particles using extensive Monte Carlo simulation methods. We employ floppy-box Monte Carlo [2] to explore a wide landscape of candidate crystalline structures without imposing symmetry constraints, followed by Frenkel–Ladd thermodynamic integration [3, 4] to compute absolute solid free energies and identify the most thermodynamically stable polymorphs. In addition, isothermal–isobaric Monte Carlo simulations are used to construct pressure–density curves, providing an independent characterization of phase behavior. To determine coexistence with the isotropic fluid phase, we also compute the free energy of the liquid-crystalline state via the thermodynamic integration method of de Miguel *et al*. [5]. Alongside these calculations, we evaluate a comprehensive set of positional and orientational order parameters, including nematic, smectic, cubatic, chiral, and bond-orientational order, as well as structure factors and radial distribution functions, to identify second-order transitions. This integrated approach allows us to detect subtle symmetry breakings and intermediate liquid-crystalline regimes emerging purely from geometric packing frustration. The resulting phase diagram reveals how fourfold symmetry and nonconvex geometry favour distinct ordering pathways compared to classical anisotropic shapes. In this dense colloidal system, the emergent void network illustrates how particle shape alone governs the arrangement of pathways for transport, a feature relevant for templated materials, photonic crystals, and catalyst supports, where packing morphology influences performance. By connecting the entropy associated with particle shape at the microscopic level to the collective order that emerges at the mesoscale, this work establishes a simulation-based route to designing functional materials whose behavior is encoded geometrically rather than chemically.

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Statistical thermodynamics of supercooled water

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Thermodynamics sharply distinguishes water from common simple substances such as argon or methane. One of water's crystalline phases, ice Ih, is less dense than its coexisting liquid, implying an unusual negative slope of the freezing line in the pressure-temperature p-T plane. Likewise unusual is the behavior of the liquid phase. In contrast to the general case, the density ρ of liquid water decreases as T is lowered below a temperature of maximum density TMD(p), with TMD ≈ 277 K at $p \simeq 1$ bar. The pattern of behavior gets even rarer as T is further lowered down below the freezing point while metastably maintaining the sample as a supercooled liquid, with thermodynamic response functions such as the isothermal compressibility k_T exhibiting sharp rises.

Molecular simulation has taught us [1] that a most plausible explanation of the intriguing behavior of liquid and supercooled water is the very existence of a second, liquid–liquid critical point, with coordinates $T_c \approx 200$ K and $p_c \approx 1200$ bar according to the latest estimates [2]. Nevertheless, a definitive experimental proof has hitherto been prevented by fast crystallization of liquid samples at the low temperatures of interest. This leaves alternative scenarios open [3]. One of them invokes a supercooled spinodal determining a low-T limit for the liquid to exist, so that the rises in response functions are the onset of a stability limit at which they diverge.

An approach to the overall physical picture on the grounds of statistical thermodynamics calls, in the first instance, for a description at the coarse-grained level of the one early provided by van der Waals for simple fluids. This is certainly a nontrivial issue since a proper characterization of supercooled water demands describing both liquid and cristal phases as well as the transitions between them and the associated metastable states. Altogether, these requirements raise a stringent test for theory and, as far as we are aware, a statistical-mechanical prototype meeting all of them does not exist yet.

Here we solve this water's theoretical puzzle with the aid of suitably-devised Ising-like models contemplating gas, liquid, and crystalline phases. On working them out at a mean-field level, we find that they exhibit a transition between two liquid phases that terminates at a critical point and is metastable with respect to the crystal. One variant further contemplates a supercooled liquid spinodal and supports the emerging view that the realization of water's stability-limit scenario most likely relies on the existence of two distinct liquid phases [3,4].

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Phase Equilibrium and Thermophysical Properties of the Deep Eutectic Solvent Cholinium Chloride & Ethylene Glycol with Hydrofluorocarbon Gases

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Increasing concerns about the global warming potential (GWP) of hydrofluorocarbons (HFCs) has resulted in laws and regulations to phaseout HFCs with the highest GWPs. Due to the near azeotropic nature of most HFC blends, traditional fractional distillation is not feasible. Recently, Deep Eutectic Solvents (DESs) have shown great potential to selectively separate HFC blends in an extractive distillation system. This would allow the HFCs with lower GWP to be recycled and provide the high GWP HFCs as a feedstock to other chemical and materials. One of the most common refrigerant blends for home air-conditioning is R-410A which is composed of HFC-32 (difluoromethane) and HFC-125 (pentafluoroethane). R-407C that is composed of HFC-32, HFC-125 and HFC-134a (tetrafluoroethene). In this study, a model DES composed of cholinium chloride ([Ch]Cl) and ethylene glycol (EG) with a molar ratio of 1:3 was investigated. The thermodynamic properties of binary vapor-liquid equilibrium (VLE, gas solubility) and liquid density was measured for the DES and HFCs (HFC-32, HFC-125, and HFC-134a) at temperatures from 25 to 75 °C and pressures up to 50 bar using our custom-built Phase Equilibrium Transport Properties Apparatus (PETPA). The full transport properties including viscosity, thermal conductivity, and Fickian diffusivity were also measured providing a complete data package that could be used for engineering an EDS system for separations. VLE data indicates that HFC-32 has higher solubility in [ChCl]:EG (1:3) than HFC-134a, and HFC-125. Ideal selectivity calculations based on the binary data from these single gas measurements indicate that [ChCl]:EG (1:3) has a high selectivity and could be used in EDS to break the azeotrope and separate blends of HFC-32, HFC-125, and/or HFC-134a. For all studied refrigerants, the viscosity of the liquid phase decreased with increasing refrigerant composition. On the other hand, increasing refrigerant composition led to increases in the density of the liquid phase. The PC-SAFT equation of state was used to correlate the VLE data, model the saturated liquid densities, and combined with entropy scaling to correlate the saturated liquid viscosities. Other DES systems were also investigated in the pursuit of higher capacity with high selectivity. This complete data and reliable model allow for future process development of extractive distillation systems involving DESs.

Enhancing Low-Concentration CO_2 Capture Abilities of Aminium Ionic Liquids through Blending with Acetate Ionic Liquids

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The efficient capture of low-concentration CO_2 is essential for achieving carbon neutrality and recycling. This study explored aminium and acetate ionic liquid (IL) mixtures for enhanced CO_2 capture. The physical properties, nuclear magnetic resonance spectra, and CO_2 solubilities of the mixtures of *N*-2-hydroxyethyl-aminoethylaminium bis(trifluoromethanesulfonyl)imide (**1**·[Tf_2N]) and 1-ethyl-3-methylimidazolium acetate ([C_2mim][AcO]) were compared with those of the corresponding [C_2mim][Tf_2N] mixtures. It was found that the mixtures were less dense and viscous than the pure aminium IL, enabling faster absorption/desorption kinetics and lowering energy consumption. In addition, mixtures containing 10 and 30 mol% **1**·[Tf_2N] absorbed greater amounts of CO_2 than the pure ILs at CO_2 partial pressures of up to 10 kPa, with a lower absorption heat than pure **1**·[Tf_2N]. This was attributed to the formation of nonionic components via proton recombination, along with the suppression of ammonium formation by proton sharing between the CO_2 adduct and the $[AcO]^-$ anions. Blending [C_2mim][AcO] with other aminium ILs further enhanced the CO_2 absorption capability at low partial pressures, offering a higher CO_2 solubility and a lower enthalpy compared to the **1**·[Tf_2N] mixture. Overall, the results indicated that mixing aminium ILs with [C_2mim][AcO] enhances low-concentration CO_2 capture and is applicable to various aminium ILs, providing an effective alternative to chemical modification for the development of CO_2 separation materials.

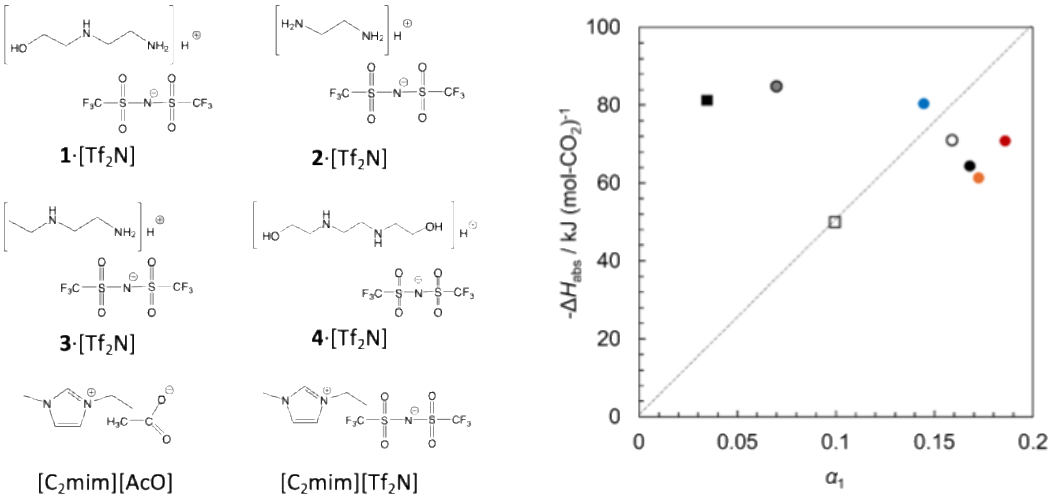

Figure 1. Enthalpies of the CO_2 solutions in [C_2mim][AcO] systems at 313.2 K and using a CO_2 pressure of 1.0 kPa. Open squares, [C_2mim][AcO]; closed squares, **1**·[Tf_2N]; closed circles, **1**·[Tf_2N] (10 mol%) + [C_2mim][AcO]; open circles, **1**·[Tf_2N] (30 mol%) + [C_2mim][AcO]; gray circles, **1**·[Tf_2N] (70 mol%) + [C_2mim][AcO]; red circles, **2**·[Tf_2N] (10 mol%) + [C_2mim][AcO]; orange circles, **3**·[Tf_2N] (10 mol%) + [C_2mim][AcO]; blue circles, **4**·[Tf_2N] (10 mol%) + [C_2mim][AcO].

The structure and origin of the supercritical (Widom) anomalies

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Widom anomalies (i.e. anomalous behaviour of several properties, including response functions) can be seen in a region above the critical point; in the temperature-pressure diagram, they are located in a triangular arrowhead-shaped region, pointed to the critical point and have the axis of symmetry approximately in the extension of the saturation curve [1].
Various properties show different types of anomalies; the differences are not only in extent (i.e. the influenced region in the *T-p* phase space) and in magnitude, but also in "shape". There are quantities where the liquid-like properties shift smoothly into vapour-like ones, and in the anomalous region, the values are between those characteristic of liquids and vapours. One of the classical examples is density; here, one can see a sigmoid-like dependence in the temperature-density diagram (at a fixed pressure value) [1]. It is like boiling, but spread over a finite temperature range, so this transition is often called pseudo-boiling [2]. In other cases, the anomaly can be seen as a peak, where, during the liquid-like to vapour-like transition, the given quantity (such as isobaric heat capacity or isothermal compressibility) can reach values exceeding those seen for normal fluids by even two orders of magnitude [1].
Recently, we have been attempting to demonstrate the common origin of the various anomalies. This approach enables one to separate the different layers, thereby differentiating between temperature- and pressure-dependent "normal" fluid properties and criticality-induced anomalies [3]. For several "visually" different anomalous quantities, mathematical and physical similarities can be shown, suggesting a common origin.
The reason for this study is partly theoretical; however, it can have several applied results because supercriticality and Widom anomalies are increasingly important in various fields, including energy engineering [4,5].

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Sorption Thermodynamics of Water and Methanol in Glassy Polyimides: a Multiscale Approach Combining Gravimetric, FT-IR in Situ Experiments with a Non-Equilibrium Statistical Thermodynamics Theory

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Sorption thermodynamics of respectively water and methanol in glassy polyimides is investigated by combining in situ FT-IR spectroscopy with a macroscopic non-equilibrium thermodynamic framework (NETGP-PC-SAFT) accounting for specific interactions as well for possible penetrant induced swelling. The latter is modelled on the basis of a self-consistent perturbative approach (DGRPT-NETGP-PC-SAFT) [1,2] In situ FT-IR spectroscopy properly combined with 2D correlation analysis [3] provides the interactional scenario within the glassy mixture allowing in particular the estimation of the number of the different kinds of specific interaction occuring within the glassy phase. The thermodynamic model is properly implemented on pure components equilibrium data to retrieve the self model parameters and on out-of-equilibrium binary sorption data to estimate the binary mean field and interactional parameters. Once all the model parameters are obtained the model outcomes are validated against the predictive estimation of the number of cross (polymer/penetrant) and self (penetrant/penetrant) specific interaction within the glassy phase.

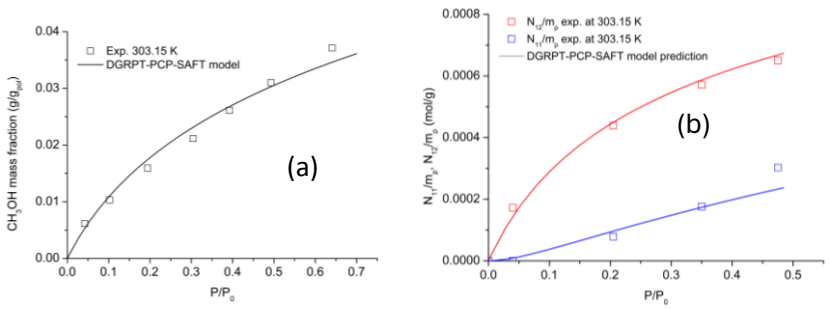

Figure 1. (a) Fitting of methanol sorption isotherm in Polyetherimide. (b) Comparison of the model prediction and FT-IR estimation of the number of self and cross specific interaction contacts for mass of polymer.

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Accurate Thermodynamic Modelling and 3E Cycle Analysis for Applications in the Search for Sustainable Absorption Refrigeration Working Pairs

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Enhancing the sustainability of thermal systems has stimulated increasing attention toward renewable, biodegradable, and environmentally benign compounds. In this context, biomass-derived solvents offer remarkable benefits compared to conventional petroleum-based options, supporting the principles of a circular economy. In this work, we present a comprehensive thermodynamic approach to evaluate the potential of novel refrigerant–solvent working pairs for absorption refrigeration systems (ARS). These pairs combine fluorinated refrigerants and CO_2 with Propylene Carbonate, Solketal, Terpinolene, γ–Valerolactone, and Rhodiasolv Polarclean, based on new available experimental data [1]. The solubility of refrigerants in these solvents is modeled using an extended version of the SAFT–VR Mie equation of state, incorporating descriptors for planar ring structures and polar contributions. Refrigerants are treated as non–associating but dipolar fluids, and their thermophysical properties are successfully reproduced. Mixture behavior is captured with a single, temperature–independent binary interaction parameter, enabling reliable extrapolation to process conditions. The validated model is employed to quantify the working capacity of each refrigerant–solvent pair, serving as a pre–screening tool to choose the most promising pairs for cycle simulation. Single–stage (SE) and compression-assisted (CA) ARSs are evaluated through a detailed parametric study. Then, a comprehensive 3E analysis (energetic, exergetic, and environmental) is conducted, incorporating Key Performance Indicators, including the energy and exergy coefficients of performance, circulation ratio, high-pressure levels, and the total equivalent warming impact (TEWI). Finally, the TOPSIS multi–criteria decision-making method is applied to rank the working pairs and identify the best options for each configuration [2].

Acknowledgements

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Exploring the interaction between plasma proteins and polymeric materials in medical devices: insights from molecular simulations

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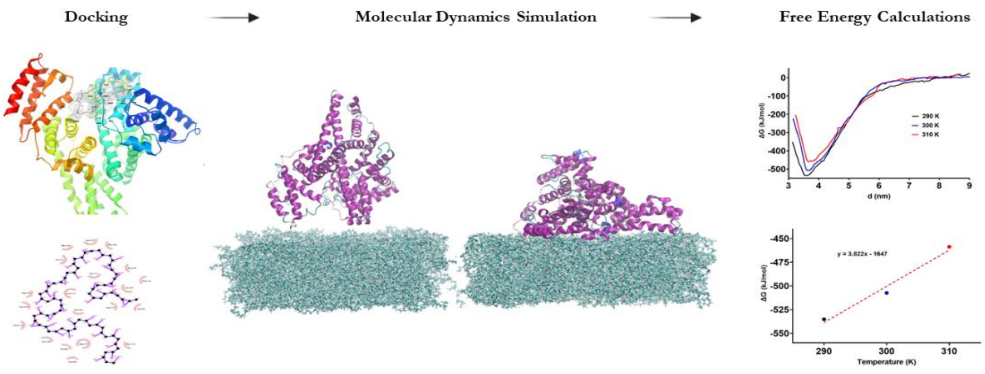
Understanding the physio-chemical factors underlying the process of biofouling is of crucial relevance for enhancing the design of new biomaterials. In this study, we initially evaluated the affinity of plasma proteins towards Polyvinyl chloride (PVC) using molecular docking. Human Serum Albumin (HSA) was found to be the most relevant plasma protein to study its adsorption on the PVC surface. From 0.5 µs long MD simulations, we quantitatively studied the interactions between HSA and PVC while carefully monitoring potential structural changes of the protein during the adsorption process. HSA was found to spontaneously adsorb on the PVC surface without enduring substantial damage to its secondary structure. Moreover, we evaluated the thermodynamics parameters governing the adsorption process by calculating the Potential of Mean Force (PMF). The Gibbs free energy of adsorption was found to be -507.38 kJ/mol at 300 K, indicating that the process is spontaneous and thermodynamically favored. We also studied the adsorption process at different temperatures (290 K and 310 K) and we have found that the results are consistent and that the process is enthalpy-driven. The findings of this molecular study provide an extensive evaluation of one of the most critical processes determining medical devices compatibility. More investigations involving other plasma proteins and more complicated biomaterials are being conducted to provide more insights to guide the design of new materials in the biomedical industry.



Scheme 1. Docking of HSA protein, followed by MD simulations and free energy calculations of the adsorption process at several temperatures (290 K, 300 K, and 310 K).

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Electro coalescence of Ionic Liquid/alkanol Laden Water Droplet: A Molecular Dynamics Study

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Coalescence of droplets or condensation of water droplet is very common phenomena in nature such as formation of rain drops from cloud, condensation of fog or dew on leaves. It has also immense importance in many industrial applications such as petrochemical, food, pharmaceutical, droplet-based micro/nano-fluidics devices, electric displays, water harvesting devices etc. This study employs molecular dynamics (MD) simulations to investigate the interfacial behaviour and coalescence dynamics of ionic liquid (IL)/alkanol-laden water droplets. The organization of IL and alkanol molecules are characterized through orientation and density profiles across the interface, highlighting the stabilizing effect of IL/alkanols molecules. The influence of IL/alkanols concentration and electric field strength on electro coalescence was examined, revealing significant rearrangement of interfacial molecules.

Surface area solvent-accessible (SASA) and free energy analyses is performed to explore the molecular mechanism of the droplet coalescence. Further, the droplet coalescence behaviour on surface is examined and found that the molecular arrangement at the three-phase contact line and liquid-vapor interface plays an important role. These insights advance the molecular understanding of field-induced droplet coalescence at the bulk and at the surface.

Keywords: Molecular dynamics simulations, Electro-coalescence, alkanols and Ionic liquids laden droplet, Interfacial phenomenon

Revision of the eSAFT-VR Mie equation of state for electrolyte solutions

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eSAFT-VR Mie [1-3] equation of state for electrolyte solutions has been proven to be a successful model for mean ionic activity coefficient (MIAC), density, gas solubility, vapor-liquid and liquid-liquid equilibrium calculations for mixed salts and solvents. Due to the success of the model, we have developed a software [4] performing these calculations which we plan to extend to other properties. In this work, we have extended the eSAFT-VR Mie (as presented in [2,3]) parameter matrix to more include more ions. Our previous published articles contained parameters for 1:1 salts only, more specifically for Li^+, Na^+, K^+, F^-, Cl^-, Br^-, I^-. In this work, we have determined additional parameters for several additional ions (Rb^+, Cs^+, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, SO_4^{-2}, NO_3^-, ClO_4^-), by simultaneously fitting MIAC and density data for 54 strong salts (1:1, 2:1, 1:2, 2:2). Furthermore, to ensure the applicability of the model to a wide temperature range, the model parameters have a built-in temperature dependency, and special care has been taken to cover high molality and approach the solubility limit of the salts, conditional to the availability of experimental data.
The results show that the eSAFT-VR Mie is able to capture MIAC and density for all 54 salts with a satisfactory accuracy. Average deviation for MIAC at 298.15 K is 6.3% and for density in the range 290-300 K is 1.7%. In the complete database spanning a wide temperature range, the corresponding deviations are 7.0% for MIAC and 1.6% for density respectively.

Acknowledgements

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Comments on the Correlation of Aqueous Two-Phase Systems (ATPS) Involving Polymers

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Aqueous Two-Phase Systems (ATPS) present, among other possible equilibrium regions, a liquid-liquid region where both phases in equilibrium are composed predominantly of water. Although different types of ATPS exist depending on the components mixed with water, the most common are: a) polymer/polymer ATPS, and b) polymer/salt ATPS.

The mole fraction of the polymer is always extremely low, due to its high molecular weight, what poses a great problem in the correlation of ATPS. Mass fractions are always used for graphical representations in these systems. The problem arises when addressing the LLE data correlation since the thermodynamic framework, using conventional models as NRTL, is based on mole fractions, an awkward unit of concentration for systems including polymers. In the present work, the strategy proposed by other authors for solving this problem [1-4] is analyzed. From the results presented we will show that, under the appearance of achieving optimal correlation results, this method hides thermodynamic inconsistencies while not solving the problem of working with extremely low values of the polymer compositions.

Papers that apply the methodology under discussion indicate the convenience of using mass fractions (w_i) for LLE correlation in ATPS's. The NRTL equation that they use is the result of a *transformation* from mole (x_i) to mass fractions (w_i), using the corresponding function x_i=f(w_i). After simplifications, the ratio (w_i/M_i) appears in the place of the mole fraction (x_i) in the original NRTL model. However, numerically the results are exactly the same as those obtained using the original NRTL equation, and so the same problems remain. These problems are mainly related to negligible activity coefficients for the polymer, and so negligible activities and difference of activities in both liquid phases that supposedly should be in equilibrium. From the Gibbs energy of mixing ($g^M=G^M/RT$) point of view, the g^M function (surface) is extremely flat what causes *uncertainty* in the equilibrium calculations. This is explained because LLE calculations require the fulfilment of the Gibbs common tangent equilibrium criterion and, for flat g^M functions, any combination of two liquid mixtures satisfy the common tangent criterion (multiple solutions). Consequently, the published parameters are not useful for LLE calculations.

An alternative methodology that solves the problem of LLE correlation in systems including polymers is presented in this work. The proposal is based on using *auxiliary* composition variables (z_i) as a function of mole fractions (x_i) and two new parameters. These compositions (z_i) are used in the equilibrium calculations replacing mole fractions (x_i). The additional optimization parameters allow the NRTL model to provide a reliable LLE solution free of uncertainty. When the equilibrium compositions have been calculated, the previous change is reversed to obtain mole (or mass) fractions to be compared with the experimental ones.

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Improvement of liquid phase splitting of water + ethanol + isobutanol mixtures in the presence of electrolyte at atmospheric pressure

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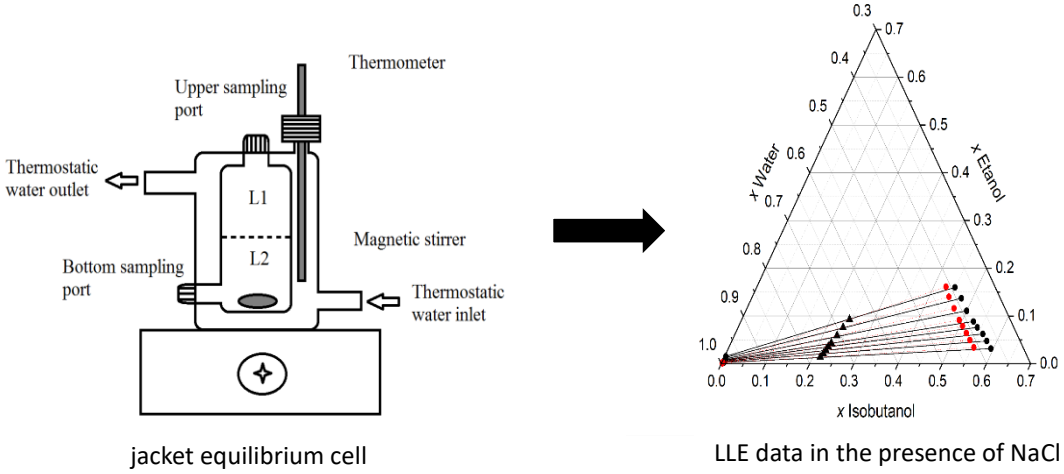
Salting-out extraction systems composed of alcohols and salts are widely used in industrial processes for the separating valuable chemicals and fuels from aqueous solutions. Therefore, in this study, phase splitting was investigated for the water + ethanol + isobutanol system in the presence of an electrolyte compound (NaCl). Liquid–liquid equilibrium (LLE) for the ternary system (water + ethanol + isobutanol) and the quaternary system (water + ethanol + isobutanol + NaCl) were measured at temperature ranges from 293.15 to 323.15 K and at atmospheric pressure using a jacket equilibrium cell, as shown in Figure 1. The effect of increasing NaCl concentration in the LLE of ethanol + water + isobutanol were varied the concentrations of 5 wt% and 10 wt%. Adding NaCl enhanced the heterogeneous region and enhanced the overall performance of isobutanol separation from an aqueous ethanol solution. Increasing the NaCl concentration from 5 wt% to 10 wt% further intensified the salting-out effect, thereby promoting liquid–liquid phase splitting. The eNRTL and ePC-SAFT models were employed to satisfactorily correlate the LLE data for the investigated mixtures.



jacket equilibrium cell — LLE data in the presence of NaCl

Figure 1. Schematic diagram of the LLE measurements

Optimal Strategy for the Parametrisation of the Association Term of SAFT Models

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Thermodynamic models are at the heart of modelling tools in process engineering. They provide, on the one hand, the description, both qualitative and quantitative, of phase equilibria of complex mixtures, and on the other hand, the measurement of different energetic properties such as enthalpies, entropies, heat capacities necessary for energy and exergy balances. This work addresses the equations of state from the statistical associating fluid theory (SAFT) applied onto pure compounds.

Our main objective is to analyse the parametrisation methods of the association term of SAFT models. These terms reflect essentially the impact of the hydrogen bonds on the thermodynamic properties of a fluid. Parametrisation, in this case, covers the determination of the optimal association scheme and the fitting of the corresponding association parameters. This work is motivated by the various practices by model developers observed throughout the thermodynamic community.

Our analysis relies on the PC-SAFT equation of state, considered as a good representative of the SAFT family, and a database of properties for 1800 pure components, divided into 1252 non-associated species and 548 self-associating species introduced in a previous article. (1,2)

The influence of the association scheme and the fitting of association parameters on the performance of the equation of state have been studied for different families of strongly associating molecules and in particular: the alcohols, amines and carboxylic acids. Different strategies have been considered: (i) the use of transferable parameters, i.e., the same association parameters are used for all the compounds of the same chemical series and (ii), the use of component-specific association parameters.

Association parameters are fitted to 2 to 4 pure component properties selected among the vapour pressure, the liquid density, the enthalpy of vaporisation and the liquid heat capacity.

Results are discussed by comparing the accuracy of SAFT EoS using the different parameterisation strategies. A comparison with what we consider to be the best cubic EoS, in terms of estimation of pure component properties, is also proposed.

As a major conclusion of this work, in the light of our observations, it will be possible to identify the best practice concerning the parameterisation of the association terms of SAFT EoS.

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Modelling amorphous chain topology in semicrystalline polymers and its impact on polymer degradation

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The thermophysical properties of semicrystalline polymers are believed to be strongly dependent on degree of the connectivity of the crystalline domains through amorphous chain segments (bridges and bridging entanglements, collectively "tie-chains"). We have observed that semicrystalline PET subject to accelerated aging embrittles and begins to spontaneously release micro-nanoplastics after a characteristic time which depends only on the total number of scission events on the polymer's backbone [1]. By means of a random scission model, we have argued that the critical fraction of scission events is inversely proportional to the mean length of the tie-chains and is thus typically of the order of a few % or less. In order to understand how polymer morphology controls this critical parameter, we have developed a pseudo-equilibrium model of semicrystalline polymers.
The conformational properties of the chains are predicted with self-consistent field theory (SCFT) by maximising the entropy in the kinetically-selected lamellar-stack morphology [2]. Our model can be considered an extension of the classic Gambler's Ruin approach [3] to enforce a finite chain molecular weight and a uniform amorphous phase density. Our main findings are as follows. 1) The surface density of bridges is given universally by $(3pl_a)^{-1}$, where p is the packing length of the amorphous polymer and l_a the inter-lamellar distance, for long chains and large l_a. 2) Chain ends are preferentially segregated at the crystal-amorphous interphase to relieve the excess of injected chains; however, a few long tails displace loops and bridges from the core of the amorphous domains, thereby reducing the number of tie-chains. 3) Chains are found to be slightly elongated perpendicular to the lamellae to maximize entropy, leading to a higher predicted fraction of bridges than the classic Huang-Brown estimate [4].

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An Integrated Physics-Based and Data-Driven Strategy for Mixed-Gas Solubility in Polymer Membranes

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This work aimed at combining physics-based and data-driven methods for the calculation of mixed-gas sorption in polymer membranes for gas separations. The proposed multi-method modelling framework leverages machine learning to bridge the atomistic and the macroscopic descriptions of the system, to overcome limitations inherent in the use of each technique in modelling gas-polymer phase equilibria, i.e. the high computational requirements of molecular simulations and the lack of experimental data for the parameterization of macroscopic models.

A computational dataset of pressure-volume-temperature (PVT) properties of polymers was generated through atomistic molecular dynamics (MD) simulations. Initial structures were generated at high temperature and subsequently cooled stepwise to room temperature at three different pressures. The results were validated against a subset of available experimental PVT measurements, finding close agreement.

The simulated PVT data were then fit to the Sanchez-Lacombe (SL) equation of state to obtain SL parameter sets for the pure polymers. These were utilized to train machine learning models for the prediction of the SL parameters, based on the polymer chemical structure, comparing two featurisation methods, i.e. Extended Connectivity Fingerprints (ECFP) and polyBERT fingerprints, obtained from the SMILES string of the polymers through a polymer chemical language model [1]. Such a choice improves the generalisability of the approach compared to conventional group contribution methods explored in past works for this task [2]. The results obtained using the polyBERT fingerprint were found to outperform ECFP.

The predicted SL parameters were then used to calculate the PVT properties of polymers that were not included in the dataset, and then to calculate sorption isotherms of pure-gas and mixed-gas CO_2/CH_4 solubility in polymers. The proposed framework has the potential to be widely applicable in the field of gas separations, as it enables the screening of large numbers of polymers, and it is directly transferable to different gas pairs without the need to repeat the more computationally costly PVT simulations, which can accelerate the discovery of suitable materials for new gas separations.

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Connecting Microscopic with Mesoscopic Transport in Model Nanoporous Materials

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Fluid transport in porous materials, including geological formations such as soils, rocks, and shales, is central to many industrial and environmental processes. Characterizing transport in these media is challenging because of their multiscale pore structure, which ranges from subnanometer confinement to macroscopic voids. This wide range of pore sizes gives rise to different, scale-dependent transport mechanisms. Moreover, the thermodynamic state of the confined fluid varies with pore size and must also be accounted for. To address these challenges, we build on a previously developed model [1] that upscales molecular simulations to describe adsorption and transport at the mesoscopic scale. In this framework, adsorption and transport behavior under varying temperature, pressure, and pore size are first captured through molecular simulations. The resulting local chemical potential and density profiles are then combined with the mass conservation law to predict mesoscale fluxes on a grid, effectively incorporating confinement effects induced by solid-fluid interactions. A key strength of this model is that it requires no assumptions about adsorption mechanisms or flow type. As a result, it provides a thermodynamically consistent way to address the main challenges of multiscale transport: capturing the interplay between adsorption and transport, accounting for the breakdown of hydrodynamics at nanometer scales, and enabling robust upscaling across pore-size regimes.

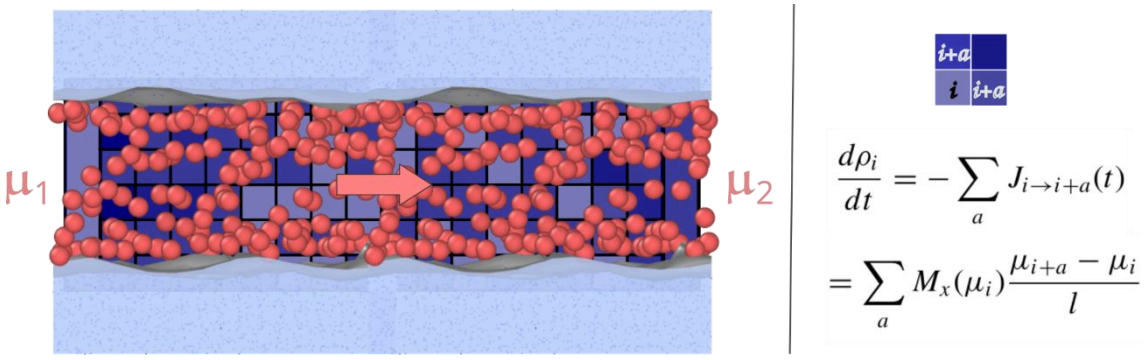

Figure 1. Slit pore under a chemical potential gradient. The confined space is split into grids of size *l*, and the corresponding flux *J* is calculated applying mass conservation, with local permeability $M_x(\mu_i)$ extrapolated from molecular simulations (see [1] for details).

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Prediction of Mass Transport in a Glassy Polyetherimide in Presence of Specific Interactions Based Upon Self-Consistent NETGP-PC-SAFT Diffusion Model

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Non-Equilibrium Thermodynamics for Glassy Polymers (NETGP) framework [1], implemented with equation of state model such as Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [2], is adopted to describe mass transport of pure CO_2, H_2O and their mixtures into an amorphous glassy polyetherimide (PEI). To this aim, a self-consistent constitutive equation of the penetrant diffusive fluxes is provided by combining NETGP-PC-SAFT chemical potential expressions with a phenomenological constitutive equation of mobility parameter inspired by the Free Volume Theory resulting in the NETGP-PC-SAFT diffusion model (NETGP-PC-SAFT-DM). Free volume parameters are obtained via non-linear regression of sorption kinetics or permeability data of the corresponding binary penetrant/polymer sub-system. Once all the binary parameters are obtained, the model has been applied in a full predictive manner to calculate the kinetic evolution of the self- and cross-specific interactions of PEI/H_2O system (Figure 1a) and CO_2 permeability coefficients at different temperatures and relative humidities (R.H.) (Figure 1b). The model predictions have been satisfactorily validated against experimental data collected by our group [3].

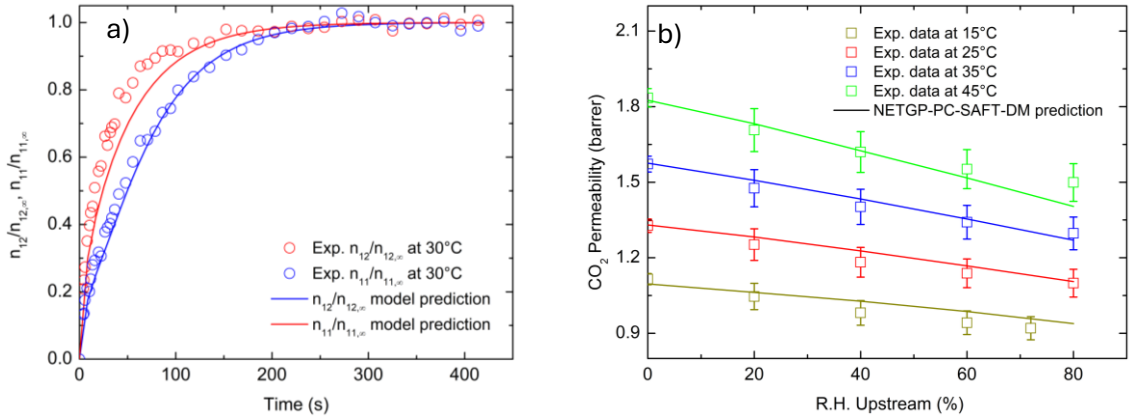

Figure 1. (a) Prediction of the normalized time evolution of the self- (n_{11}) and cross-specific (n_{12}) interactions during a sorption kinetics of H_2O in PEI at 30°C. (b) Prediction of CO_2 permeability coefficients data through PEI at different R.H. and temperatures. R.H. of downstream side is equal to 0%.

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Molecular Modelling of Gas Transport at a Polymer/MOF Interface

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Mixed matrix membranes (MMMs) are composite materials made of a polymeric matrix with nanoparticles dispersed within. MMMs saw significant interest in recent years for their application to gas separation processes, thanks to the possibility to achieve improved separation performance compared to dense polymeric membranes. However, predicting the properties of the composite and which polymer/filler combination results in improved performance is not straightforward, due to the non-idealities that arise from the interfacial interactions between the two phases, for which there are no comprehensive theoretical frameworks available.
In this work, we performed molecular simulations to study a MMM made of Matrimid® and ZIF-8 metal organic framework (MOF). We analysed the transport of CO_2, CH_4, and N_2 in the isolated phases as well as in a composite system consisting of a slab of ZIF-8 in between two polymer layers. All simulations were performed with LAMMPS. Two methods were implemented, which mimic the way experimental solubility and permeability tests are performed. In the first set of tests, the system was put in contact with two gas phases at the same concentration on both sides and Molecular Dynamics (MD) runs were performed, which resemble the conditions of a pressure decay sorption experiment (Figure 1a). In the second set of tests, two different concentrations were imposed at the opposite sides of the systems and Concentration Gradient Driven MD simulations [1] were performed, which resemble the conditions of a constant pressure permeation test (Figure 1b).
Comparison with experimental dry polymer density and pure gas sorption isotherms guided the force field selection and validation of the simulation protocol. The single-phase systems and the composite ones were systematically compared in terms of solubility, diffusivity, density profiles, local dynamics, and radial distribution functions. This allowed to highlight preferential interaction sites for the gas as well as interface effects on the polymer packing and chain dynamics, and in turn their effect on gas transport.

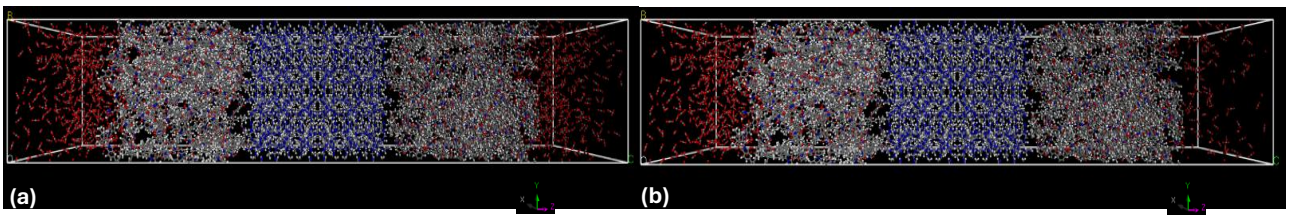

Figure 1. Two MMM molecular models, consisting of a ZIF-8 surface slab in between two slabs of Matrimid® polymer, in contact with CO_2 gas phases (a) at the same concentration or (b) different concentration on each side.

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I First Met JMP On….August 1981

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I had the privilege of working with John Prausnitz for the last decades. This talk reports my understanding of Prausnitz's most relevant contributions to the field of chemical engineering science and education. The former includes methods and techniques widely used in the chemical and biochemical industrial practices and forms the core of important methods and processes in use today. The latter spans decades of teaching at different universities around the world that shaped the careers of many young (and not so young) chemical engineers. I will also address my personal knowledge of John Prausnitz's personality and interests, his thinking in different areas and how a work relationship evolved into a personal and firm decades-long friendship I am very proud of.

Honoring John M. Prausnitz: Guiding Spirit of Applied Thermodynamics

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Contemporary chemical engineering research and application of fundamental and applied thermodynamics have their roots in the work and person of John M. Prausnitz. His approach of molecular thermodynamics dominated the field's great advancements for more than four decades. In addition, his personal qualities of grace, generosity, and mentorship have inspired countless members of our international properties community to strive for broader and greater personal and professional lives. To honor John at ESAT 2026, this presentation will give some elements of John's persona and his impacts, with references for further exploration

Review Series on high-pressure phase equilibria: Trends, experimental methods, and systems investigated

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The research and enormous impact of John Prausnitz covers the entire field of Applied thermodynamics, including theory, modeling and experiments. Though his own focus was on theory and modeling, he continuously encourages experimental work, particularly in areas where models need input from real world data, e.g., at higher pressures. Precise high-pressure phase equilibrium data are essential in many fields, from the scientific understanding of natural processes, e.g., in Earth and Planetary Sciences, to the optimization of industrial processes [1].
In a series of reviews [2-5], experimental methods for high-pressure phase equilibria have been described and classified and surveys on systems investigated have been given covering more than 7000 articles. In this work results of the continuation of the review series are given, including recent developments and trends.
The annually published number of articles on high-pressure phase equilibria is still increasing, from 68/year (1988-1993) to more than 400/year (2017-2020). The absolute number of articles with HP equilibrium data published in the top 3 journals (JCED, FPE, JSF) has doubled over time, but their relative percentage decreased significantly (Figure 1): from 75% (1988–1993) to 39% (2017–2020). Apart from 25 systematically searched journals, articles were found in more and more different other journals: 7 other journals (1988–1993), 26 other journals (2009–2012), 137 other journals (2017–2020). Concerning the experimental method used, there is a shift towards methods that do not require sampling. For reliable and precise measurements, the investment is not only in acquisition of equipment or the development of custom-made experimental setups, but also in developing qualified and experienced personnel.

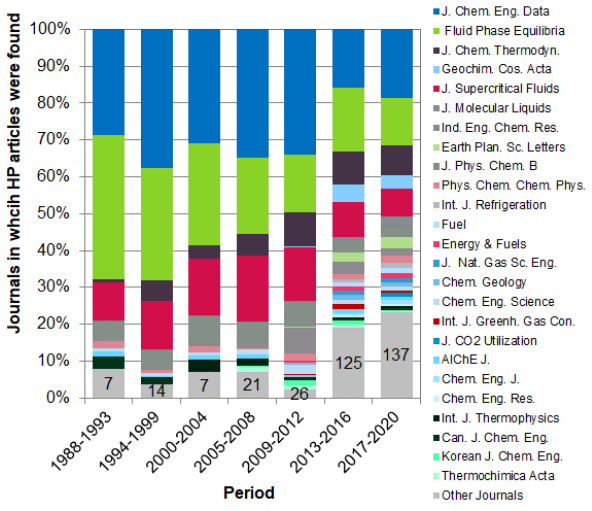

Figure 1. Journals with High-Pressure Phase Equilibrium Data

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Morphology Development in Semicrystalline Polyethylene: A Molecular Simulation Study

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John Prausnitz's seminal contributions to chemical engineering thermodynamics have enabled the prediction of properties and phase equilibria in pure substances and mixtures from molecular geometry and interactions. They have formed a basis for solving a wide variety of important design problems in the chemical, materials, and pharmaceutical industries.

In this talk we will focus on a very common polymeric material, polyethylene. The semicrystalline morphology of this material depends sensitively on molecular architecture, molar mass distribution, and processing conditions. This morphology, in turn, determines its permeability and mechanical properties. A quantitative understanding of these complex interdependences can facilitate the design of recyclable monomaterial packaging, which is urgently needed for a sustainable economy. We will discuss an atomistic simulation strategy aimed at gaining insight into the mechanisms that govern polyethylene crystallization, elucidating aspects of nucleation and growth of the solid phase in the melt. Starting from a large number of well-equilibrated entangled linear polyethylene melt configurations of narrow molar mass distribution, we perform molecular dynamics simulations under (a) quiescent and (b) stretching conditions. We calculate the evolution of the degree of crystallinity over time, analyze the mass and the radius of gyration tensor of the largest ordered cluster present, and determine the stochastic distribution of induction times from these geometric characteristics and from mean first passage time analysis. The presence of a flow field is found to have a profound impact on nucleation and growth, accelerating the emergence of the crystalline phase. Ordered clusters created under stretching are strongly oriented along the drawing direction and merge together, ultimately adopting highly cylindrical shapes, as opposed to the quasi-spherical clusters generated under quiescent conditions, whose orientation is random [1]. In other simulations, designed to mimic the formation of polyethylene films from the melt through the Machine Direction Orientation process, we have determined the crystal nucleation rates in dependence of the temperature and strain rate, identified the "kinetic elements" which assemble to form ordered clusters, and explained our findings in terms of a nucleation theory which takes into account the free energy associated with flow-induced orientation of the kinetic elements [2]. The predicted oxygen solubility in room-temperature films of semicrystalline linear polyethylene generated through our simulation protocol falls linearly with the degree of crystallinity, closely matching experimental measurements [3].

In simulating industrially relevant polymer systems, a faithful representation of broad molar mass distributions is imperative. We have reformulated our connectivity-altering Monte Carlo algorithms in a manner that allows creating ensembles of well-equilibrated molecular configurations representative of any arbitrary distribution of chain sizes [4]. When applied to bidisperse polyethylene melts, our Monte Carlo approach predicts negative deviations from ideal mixing behavior, as predicted by Flory theory and as measured experimentally [4].

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Extraction of natural compounds using sustainable solvents – What can thermodynamics bring us?

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Because of the very large diversity of natural compounds, extraction thereof from plant raw material has been almost exclusively an experimental domain. Furthermore, the emergence of concepts of sustainable chemistry principles and eco-extraction has triggered an important impulse into the field, pushing researchers to propose new processes, benefiting of innovative extraction methods assisted by microwave or ultrasounds, for instance, or using chemical approaches based on sustainable or supercritical solvents.[1]
Thanks to recent developments in thermodynamics modelling, particularly with a model such as COSMO-RS,[2] we propose explore the field of extraction of volatile and non-volatile compounds using sustainable solvents, with the general objectives of, obviously, describing experiments but also predict experimental results, thus helping in finding optimised conditions for extracting natural compounds in a sustainable way.
In this talk, we will present experimental and theoretical investigations related to new sustainable solvents, extraction of volatile and non-volatile compounds, and how thermodynamics models can help us finding suitable solvents or sets of solvents for extracting[3-6] and purifying[7-8] natural compounds.

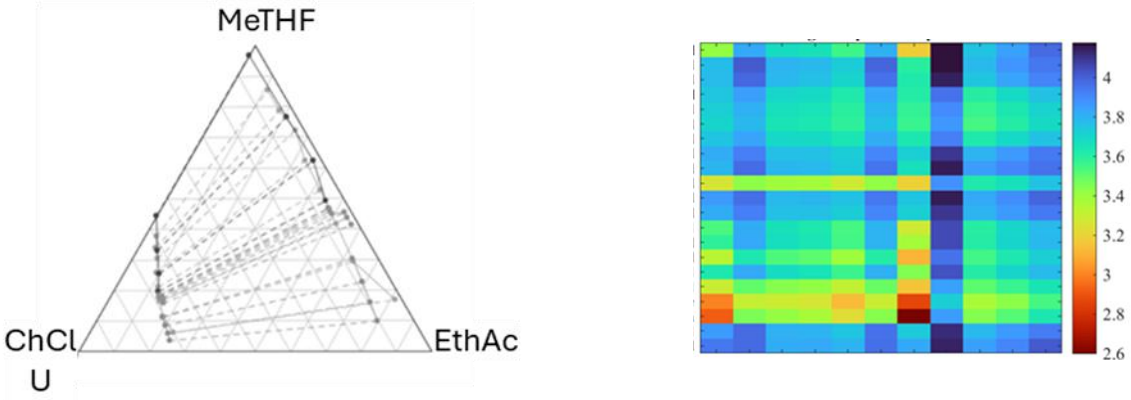

Figure 1. Left: Phase diagrams of a biphasic systems composed of 2- methyltetrahydrofuran, ethylacetate and deep euctectic solvents Choline chloride/Urea.[3] Right:. Predicted values for the logarithm of activity coefficient at infinite dilution for 2-phenylethanol, major compound in *Rosa centifolia.*

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Development of thermo-catalytic decomposition process of methane into hydrogen and graphite and other matters

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Thermo-catalytic decomposition process (TCD) splits methane to produce low-carbon hydrogen and industrial-quality solid carbon allotropes. It is based on decomposition of methane molecules with catalytic process and heat. The novel methane-splitting technology requires less energy than hydrogen production by electrolysis and enables local production of the critical material, graphite.
The source for hydrogen can be biomethane, methane from natural gas, or synthetic methane. As a cutting-edge carbon capture, utilization, and storage (CCUS) technology, TCD solution enables the creation of carbon sinks when using biomethane.
Based on years of research at the University of Oulu, Hycamite start-up independently develops industrial-quality carbon suitable for graphite and carbon fibre applications. Hycamite was founded in 2020 in Kokkola, Finland. It recently built its first industrial-scale facility in Kokkola Industrial Park (KIP). In March 2025, the European Commission selected Hycamite as a Strategic Project under the Critical Raw Materials Act (CRMA).

Adsorption of Chainlike Amphiphiles on Solid Nanoparticles from Aqueous Mixtures: Prediction from a Molecular Model

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Solid nanoparticles are widely used in many fields including medicine, electronics, chemistry and engineering. Prediction of local structure of adsorbed layers of surfactants and other complex organic molecules on the nanoparticles in solution is of key importance in drug delivery, reaction engineering, etc. Popular theoretical approaches proposed for adsorption systems [1,2] do not take into account correlations between interacting functional groups of molecules. The recently developed approach - the Multilayer Quasichemical Model (MQuM) [3,4] – describes correlations between functional groups within the Guggenheim quasichemical approximation and considers different orientations of functional groups in nonuniform fluids. MQuM takes into account specific interactions in mixtures containing chainlike and associating species. It has been tested in modelling interfacial layers between equilibrium bulk phases and mesoscopic aggregates in solution and gave quite promising results [3,4].

In this work MQuM is modified and applied to describe details of local structure of adsorbed layers on solid hydrophilic or hydrophobic particles submerged in aqueous mixtures that contain amphiphilic chainlike molecules.

We discuss predictions of MQuM for spherical nanoparticles of differing radii and demonstrate the dependence of density and orientation profiles of adsorbed chainlike molecules on the type and the radius of the nanoparticle. The model shows how the competition of polar surfactant heads with water molecules for adsorption on the hydrophilic particles determines the structural details of the adsorbed layer. We also predict profiles of local orientation of hydrogen bonds between water molecules within the adsorbed layers.

Acknowledgements We thank RSF (project No. 25-23-00040) for financial support.

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PEG/Citrate Aqueous Two-Phase Extraction of Fish Proteins

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In the fish canning industry, the principles of Circular Economy and Zero Waste drive towards the exploitation of residues to recover all valuable materials. The cooking wastewater typically carries a significant amount of valuable proteins that can be used in different food and cosmetic applications [1,2]. In this work, we have investigated the recovery and concentration of fish proteins from cooking waters using Aqueous Two-Phase Extraction (ATPE). The PEG/sodium citrate Aqueous Two-Phase System (ATPS) was selected as model biphasic system for extraction, while fishmeal was selected as model source of fish proteins (supplied by Jealsa Foods, Spain). Then, partition coefficients of fishmeal in PEG/Citrate ATPS were evaluated experimentally using the BCA method to quantify the protein content. The effect of PEG molecular weight, ATPS tie-line selected, pH and ionic strength (addition of sodium chloride) were also evaluated. The isoelectric point of the fishmeal proteins was also evaluated and comparison with partition coefficient shows the correlation between protein solubility and partitioning as function of pH. Figure 1 shows the effect of tie-line concentration and PEG molecular weight on fish protein partition coefficients (left) and the comparison of the protein solubility in water and partitioning in PEG1500/sodium citrate ATPS as a function of pH (right). There is a clear correlation between both properties, with minimum solubility and partitioning in the protein isoelectric point. Furthermore, the recovery of proteins from tuna cooking waters with different salt levels was tested and compared to the fishmeal model partitioning.

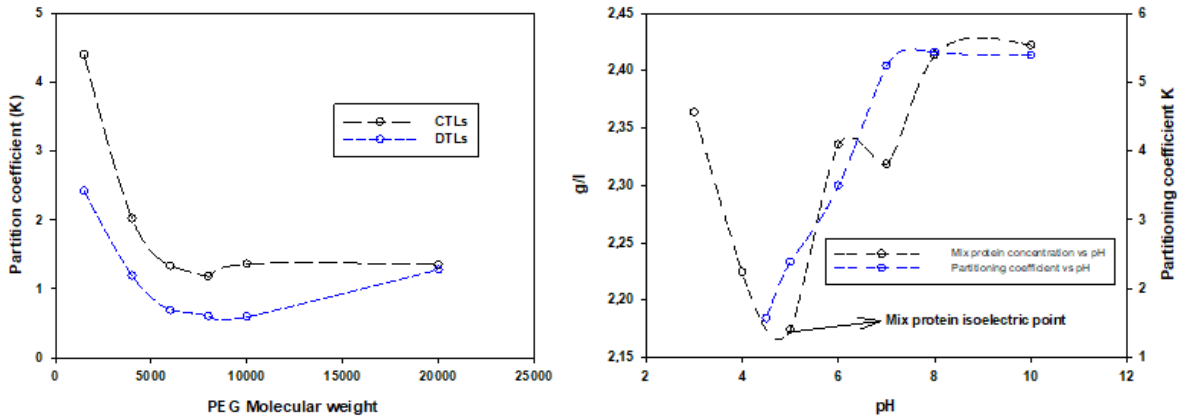

Figure 1. Left: Partition coefficients of fishmeal proteins in PEG/sodium citrate ATPS concentrated and diluted tie-lines (CTL and DTL, respectively). Right: Comparison of fishmeal proteins' solubility in water and partition coefficient in PEG1500 ATPS, as a function of pH. The minimum solubility, corresponding to the isoelectric point, provides the lowest partition coefficient.

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Separation of Azeotropic Refrigerant Mixtures using Ionic Liquids

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Refrigeration and air-conditioning systems are widespread throughout modern society, from the refrigerated cold chain that provides fresh foods and storage of medicines to the air conditioning of homes and buildings. Refrigeration is viewed as one of the most transformative engineering achievements of the 20th century and the demand for cooling will continue to increase as economic conditions improve and the climate continues to warm; however, refrigerants do come with an environmental cost.

In 1987, the Montreal Protocol phased out chlorofluorocarbon (CFC) refrigerants because of their high ozone depletion potential (ODP). The replacements, typically mixtures of hydrofluorocarbons (HFCs), are safe for the Earth's ozone layer, but most have high global warming potentials (GWPs). HFCs account for 7.8% of total global greenhouse gas emissions, with 63% of that from "indirect" emissions (i.e., energy for running the system). As a result, 197 countries signed the Kigali agreement in 2016 to phase out high-GWP HFCs, with the goal of reducing emissions by 80% in the next 20 years. Millions of metric tons (mts) of high-GWP refrigerants will need to be reclaimed, but there are no good methods for separating and recycling the individual components, given that many are azeotropic mixtures.

Currently, there is no means of separating azeotropic HFC mixtures, and the refrigerants will ultimately be illegally vented or have to be incinerated. The commercial HFC mixture R-410A containing 50 wt.% HFC-32 (GWP = 675) and 50 wt.% HFC-125 (GWP = 3500) is a prime example. The HFC-32 can be reused when separated in new low-GWP products such as R-454B (69 wt% HFC-32 and 31 wt% HFO-1234yf) with a 75% lower GWP than R-410A and HFC-125 can be used in R-449A (24 wt% HFC-32, 25 wt% HFC-125, 26 wt% HFC-134a, and 25 wt% HFO-1234yf) with a 65% lower GWP than R-404A.

This presentation will review our current efforts to utilize novel materials such as ionic liquids (Ils) to separate azeotropic HFC mixtures based on differences in solubility, the design and modelling of a new pilot-scale extractive distillation column for demonstrating at scale the separation efficiency, and highlight a new U.S. National Science Foundation Engineering Research Center called EARTH (Environmentally Applied Research Technology that is focused on creating a sustainable and circular refrigerant economy.[1]

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Transport Properties and Glass Transition Temperatures of Polymers as Determined by Macromolecular Theory and Simulations

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I have never worked with late Prof. John Prausnitz but he inspired me tremendously throughout my academic career. I first encountered his textbook on molecular thermodynamics when I was an undergraduate student at the University of British Columbia. I did not understand much of it. About thirty odd years ago when Prof. Prausnitz delivered a seminar in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto, I attended the seminar. At that time, I was a doctoral student at the University of Waterloo, a university about 80 km west of the University of Toronto. I made my effort to attend his seminar. The lecture hall was filled with hundreds of attendees. The lecture was inspirational. Since then, I have become more interested in molecular thermodynamics. Indeed, I have been using concepts and methods in molecular thermodynamics frequently in my research.

Over the past decade, our research group has developed a free volume theory for macromolecules with *linear* and *non-linear* macromolecular structures. The theory is able to predict the diffusivity and viscosity of polymers below and above the critical molecular weight [*Soft Matter*, 2019, 15, 9300; *Soft Matter*, 2020, 16, 4283; *Soft Matter*, 2020, 16, 7458]. The theory uses the intermolecular radial distribution function (RDF) as the input. Here, RDF can be determined from molecular dynamics simulation or the polymer reference interaction site model (PRISM).

More recently, our research group has applied the free volume theory and schematic mode-coupling theory to estimate the viscosity of glass-forming liquids over a wide range of temperatures including their glass transition temperatures [*Physics of Fluids*, 2024, 36, 033120]. The new method is computationally more efficient than the conventional molecular dynamics simulation. One key parameter in the calculation is the critical number density (transition point), at which particles are trapped in a cage that only segmental vibration is possible. The critical number density is also identified using the RDF.

The method can also be applied to polymer thin films [*Physics of Fluids*, 2025, 37, 042106]. In the case of a polystyrene thin film, the surface density profile is first calculated using the Euler–Lagrange Equation. The numerical results show that density at each layer of the thin film is a function of the depth from the surface into the bulk. At each layer, the RDF in the Fourier space is computed using PRISM. The structure factor and the correlation length are then determined at zero wave vector. This allows the determination of the transition point in the schematic mode-coupling theory. In agreement with experimental observations and simulation results, the presence of the mobile surface layer contributes to a reduction in the glass transition temperature of the polystyrene thin film.

Molecular Thermodynamics of Phase Equilibria for Complex Systems with Applications

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We present a few results of thermodynamic and phase behaviour properties for complex systems, ranging from molecular simulations and integral equation theory for model systems such as chain molecules, through polyelectrolytes, polymer systems, associating fluids, proteins, petroleum fluids and gas hydrate systems, with a brief sojourn through Gilman Hall. Both theoretical modelling and experimental results are presented.
We attempt to show that despite the vast differences in the types of systems studied, they can be unified through the molecular approach to thermodynamics pioneered by John M. Prausnitz and co-workers [1].
We present recent results in applications such as carbon capture, transport and storage, as well as the use of polymers for offshore pipelines and gas hydrates as energy storage materials.

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Liquid-liquid equilibrium islands in ternary systems comprising an ionic liquid

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Liquid-liquid equilibria can exist at specific overall compositions in ternary systems for which all three binary subsystems are totally miscible. Coined as 'Type 0' by Sørensen et al. [1], the liquid-liquid region of these systems forms an isolated 'island' surrounded by a single-phase region on the ternary phase diagram. In this work, liquid-liquid equilibrium islands of this unusual type of phase behaviour are reported for ternary systems comprising an ionic liquid (a salt with a liquid range overlapping that of conventional molecular solvents), water, and an organic solvent. One example is presented in Figure 1 for the case of the system constituted by water, acetonitrile, and the ionic liquid 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) at 298.2 K. By increasing the temperature, at 308.2 K the biphasic region was found to have disappeared. By decreasing the temperature, the island became gradually larger (experimentally determined at 288.2 K and 278.2 K), until no longer being an island due to the liquid-liquid demixing exhibited by the binary system water + acetonitrile (with an upper critical solution temperature of 271.8 K [2]).

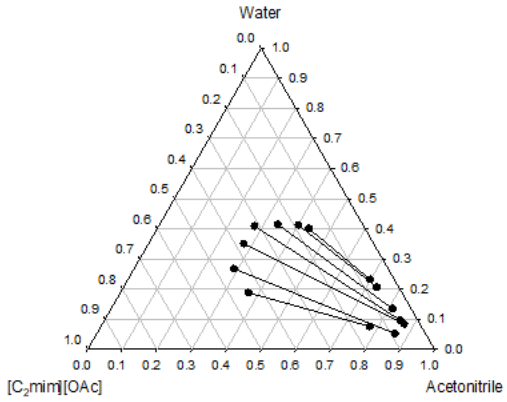

Figure 1. Liquid-liquid equilibrium diagram for the ternary system [C_2mim][OAc] + water + acetonitrile at 298.2 K and atmospheric pressure.

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Thermodynamic Contributions of Mobile and Stationary Phases to Retention in Different Modes of Chromatography

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Gibbs ensemble Monte Carlo simulations are applied to probe the molecular details of the retention mechanism in reversed-phase liquid, enhanced-fluidity liquid, supercritical fluid, and hydrophilic interaction liquid chromatography. By using a three-box Gibbs ensemble set-up with an ideal-gas transfer medium, the simulations allow to decompose the free energy of retention into separate contributions from the mobile and the stationary phases. Furthermore, the simulations provide insight on how addition of mobile-phase modifiers changes the thermodynamic contributions from both phases.

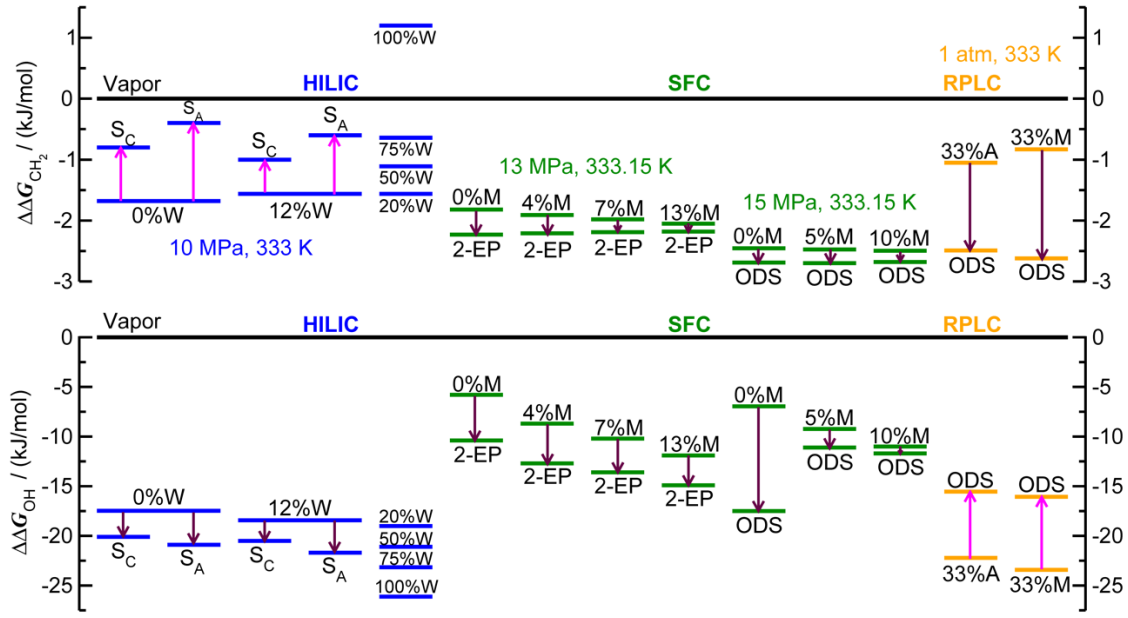

Figure 1. Incremental free energy of transfer for methylene and hydroxyl groups obtained for various chromatographic conditions.

Inference of Virial Coefficients from Experimental Data

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The virial equation of state (VEOS) relates the pressure to the thermodynamic state via a power series in density, with temperature- and mole-fraction-dependent coefficients. Among thermodynamic equations of state, the VEOS is unique in that its compound-specific modeling parameters, B_n, can be rigorously expressed in terms of the intermolecular potential-energy surface (PES).

Consequently, the VEOS can play an important role in molecular and thermodynamic modeling. The value of the VEOS has grown in recent years with advances in computational chemistry and the advent of machine-learning methods to represent the PES. Because the thermodynamic equation of state can be measured experimentally, comparison of the VEOS to experimental data can provide an assessment of the molecular model used to compute the B_n. An effective way to do this is to infer values of the virial coefficients from the experimental data and compare them to corresponding values computed from the PES. In this manner the VEOS can be applied systematically to pinpoint specific weaknesses in the PES.

A key requirement for the application of the VEOS to assess the PES is the availability of accurate values of the virial coefficients as obtained from experiment. While it may be possible to fit a polynomial to experimental PV data for a given temperature, the coefficients of the fit are not guaranteed to equal the true virial coefficients B_n, even considering experimental uncertainty. The correct values are given via a limiting process, considering the behaviour as the density goes to zero. However, experimental data are necessarily recorded at finite density, so the limit must be obtained by extrapolation. Furthermore, a full characterization of the virial coefficients must consider their temperature dependence. This dependence is non-trivial, and would not be well characterized by a simple polynomial.

Given the central role of experimentally-derived Bn in any project to assess the PES through comparison to experiment, it is worthwhile to examine methods to estimate the virial coefficients from experimental PVT data. This presentation examines and develops methods for doing so, considering new approaches made possible by recent advances in machine learning.

Modelling the Structure and Dynamics of Ionic Liquid Media

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This presentation focuses on the use of molecular modeling and computer simulation to assist on the development of new ionic liquids to be used as transport media in sustainable applications. We will show how the design of ionic liquids linked to task-specific organic moieties can be optimized with the aid of Molecular Dynamics simulations, by discovering and quantifying structural features of the media that are crucial for the development of more efficient dynamical processes.
One of the main technological disadvantages of ionic liquids is their relatively high viscosities. The central concept discussed throughout this presentation is that there are many useful "ionic liquid" media" that are not necessarily… liquid. In other words, there are applications where a highly viscous fluid, a liquid crystal or even a solid phase can present significant advantages relative to conventional, Newtonian fluids.
Three examples will be addressed: a) glyme-solvated Li-ion ionic liquids for battery electrolytes with enhanced ion mobility[1], b) anthracene-based ionic liquids as photon up-conversion chromophore media for more efficient solar energy harvesting[2], and c) cyclopropenium-based ionic liquid media as state-independent electrolytes (SIEs) for use in solid-state batteries[3].
Given the extraordinary number of possible ionic liquids and the relatively recent development of this area of knowledge, a moddeling-led effort that tries to establish links between the nano-structure of task-specific ionic liquids and the key-properties that enable their use as paradigm-shifting media in sustainable energy applications (illustrated in the three panels of the figure below) is an extraordinarily useful route that can lead to breakthrough discoveries in this area, both at the scientific and technological levels.

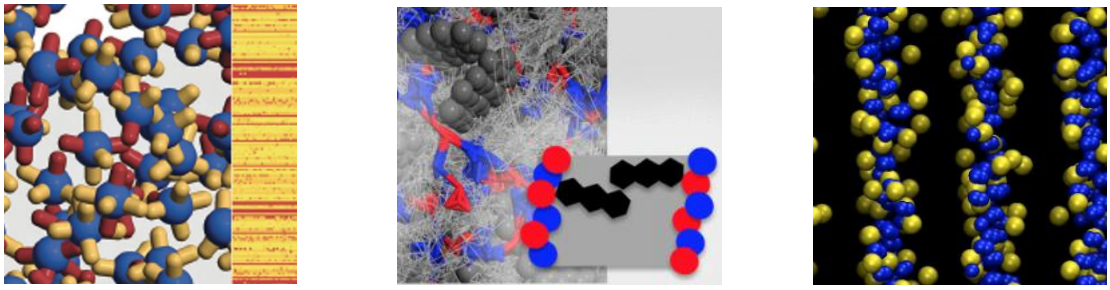

Figure: Simulation snapshots illustrating structural features that are crucial to the optimization of glyme-solvated Li-ion IL electrolytes for lithium batteries (left panel), anthracene-based ILs for up-conversion media (central panel), and cyclopropenium-based ILs for solid-state batteries composed of state independent electrolytes (right panel).

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A Density Gradient Theory of Surfactant Solutions

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A density gradient theory for solutions containing amphiphilic molecules is developed, based on a phenomenological free energy functional originally proposed by Stillinger [1], which is able to describe the various ordered mesophases, such as the lamellar phase, as well as isotropic micellar aggregates, vesicles, etc. In this approach, a non-local functional is used to enforce the chemical bonds between these chemically distinct moieties. This non-local bonding term resembles a Coulombic interaction between the two different moieties on the surfactant molecules, and this analogy with charged systems, initially recognized by Stillinger, was was later pursued by Chandler and co-workers [2,3]. In this work, the electrostatic analogy is pushed further in this approach, explicitly introducing the "electrostatic potential" into the formulation of the model. This acts as an effective one-body potential required to enforce connectivity within a surfactant molecule; its bulk value plays a role similar to the Donnan potential which is responsible for enforcing bulk electroneutrality. With this formulation, the theory reduces to a set of partial differential equations, rather a set of integral equations. This greatly simplifies the numerical evaluation of the theory, allowing the use of standard finite element or finite volume solvers. This approach enables the simulation of more complex systems and geometries, such as foams. This general approach can be combined with any bulk free energy models, such as cubic equations of state or SAFT models, and extends "standard" density gradient theories, which are often used to estimate the interfacial tension between coexisting phases, to include the influence of amphiphilic molecules. Finally, inspired by Prof Prausnitz's talk on "Chemical engineering and the postmodern world" [4], chemical engineering is examined through a postmodern lens. As an example, the formation of stable aggregates, in particular the formation of micelles in aqueous surfactant solutions, is examine through different perspectives [5,6], including isodesmic model, density functional theory, integral equation theory, and self-consistent polymer field theories.

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Recent Advancements in the Fundamental Understanding in the Role of Additives in Modulating Clathrate Hydrates

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Clathrate hydrates are fascinating materials that offer many attractive benefits for applications ranging from carbon sequestration to water desalination, from intermittent natural gas storage to separations. Several hurdles however prevent their applications, including but not limited to slow kinetics of growth and reduced loading capacity. To overcome both hurdles, chemical additives can be used. Among other additives, tryptophan has been proposed to speed up hydrates' growth. This additive is attractive because it is environmentally beneficial and performs even at low concentrations. However, the molecular mechanism responsible for its performance is not known, nor is the reason why this compound is effective at low concentrations. From a different perspective, to enhance the loading capacity, it has been proposed to use 1,3-dioxane to stabilize sII hydrates, whose larger cages could enhance gas uptake. However, the mechanism of growth is not known, nor it has been clarified whether 1,3-dioxane occupies all large cages, in which case the gas loading capacity would be low. Non equilibrium molecular dynamics simulations are used here to study these systems. The results will be discussed, with emphasis on the implications for practical applications.

Experimental and Modelling Insights into Anion Exchange Membranes for Moisture-Driven Direct Air Capture

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Direct Air Capture (DAC) has emerged as a vital technology for mitigating the impacts of global warming and accelerating the transition toward net-zero emissions by removing CO_2 directly from the atmosphere [1]. However, incumbent DAC technologies—those reliant on temperature and pressure gradients—remain limited by the unfavourable economics of these processes [2]. In this work, we investigate Moisture-Driven Direct Air Capture (MD-DAC) as a viable alternative, employing anion exchange membranes (AEMs) as the medium. Specifically, we examine two commercially available AEMs—Fumasep and Sustainion—from two complementary perspectives: (1) a phenomenological perspective, through direct experimental measurements of the diffusivity and solubility coefficients of light gases under dry membrane conditions, supported by thermodynamic modelling of gas sorption under both pure and mixed-gas environments (for example, see figure 1); and (2) a process design perspective, by elucidating the influence of various membrane parameters and operating conditions on the overall MD-DAC performance. Overall, this study highlights the potential of AEM-based MD-DAC systems and establishes a foundation for more comprehensive investigations of this emerging technology.

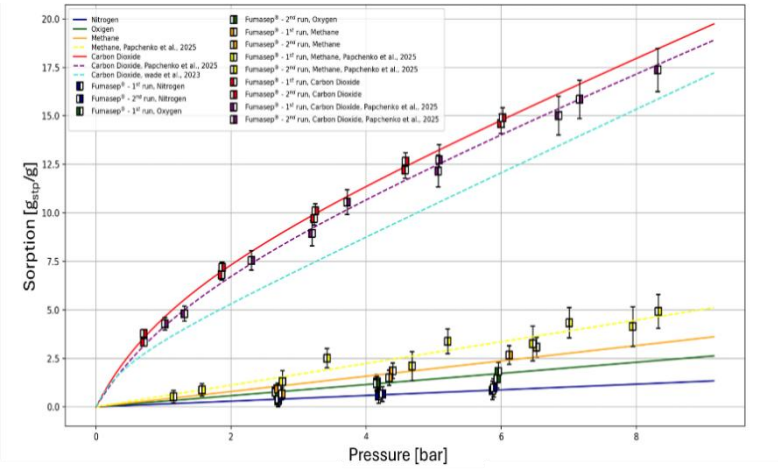

Figure 2 Gas Sorption Isotherms (35°C) in dry Fumasep.

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Thermodynamics and process modelling for a (more) sustainable chemical industry

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The imperative for a more sustainable future is driving the chemical industry, namely the polymer sector, to explore new approaches such as the use of alternative raw materials, bioprocesses, and the development of circular economy strategies. This transition sometimes involves unit operations not commonly used in traditional polymer manufacturing, as well as dealing with a range of new impurities and side-products that are often poorly characterised in terms of physical properties and chemical behaviour.

In this context, process modelling is a crucial tool for conceptual design, comparing alternative processes and different configurations for the same process, as well as for process optimization. Reliable physical property data is of prime importance. However, the magnitude of the consequences stemming from inaccurate property data is often underestimated. We have recently demonstrated with industrial examples how erroneous property data can significantly distort model outcomes and misguide the design of new chemical processes [1].

This work examines different approaches toward sustainable processes and demonstrates how thermodynamics and reliable property data can support these efforts, drawing on industrial case studies. We also highlight common misconceptions in applying circular economy principles.

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THERSAURUS: Towards a Thermodynamics of Sustainability

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Humanity is facing a profound sustainability crisis. Climate change, biodiversity loss, and resource depletion are symptoms of an unsustainable metabolism of energy and materials. The challenge is not only technological but conceptual: societies lack a coordinated scientific framework that links thermodynamic principles—the physical laws governing energy and matter transformations—to sustainability assessment and policy.

THERSAURUS (Thermodynamics for Sustainability Assessment and Universal Resource Standards) is a four-year COST Action that seeks to transform thermodynamics into a science for sustainability in the 21st century. The Action will build a shared thermodynamic language for resource management, develop harmonized methods and standards, and provide digital and educational tools to bridge science, policy, and society. The initiative departs from a key insight: economic scarcity is rooted in physical reality. All natural resources degrade irreversibly when used in economic activity, and recycling—while essential—can never be complete. Understanding these physical limits through the lens of the Second Law of Thermodynamics enables the quantification of degradation, regeneration, and irreversibility, providing a foundation for sustainability metrics beyond economic or environmental indicators.

THERSAURUS will advance four interconnected objectives: 1. Harmonize: Establish common definitions, metrics, and standards for thermodynamics of sustainability, including exergy, , exergy cost, irreversibility, regeneration potential, and resource "rucksacks."2. Educate: Redefine thermodynamics education by integrating concepts such as exergy and resource degradation into curricula and developing open-access teaching materials and Training Schools. 3. Consolidate: Create open digital tools and databases of physical resource costs and irreversibility burdens, leveraging AI and interoperability with existing LCA platforms. 4. Advocate: Promote exergy-based approaches in sustainability policy, linking physical and economic costs to support informed decision-making and evidence-based governance.

Through these pillars, THERSAURUS will connect researchers, educators, policymakers, and industry to build consensus and accelerate adoption. Its interdisciplinary network already brings together over 120 proposers from 34 countries, combining leading experts in thermodynamics, sustainability science, and ecological economics with a new generation of researchers and innovators. THERSAURUS will contribute directly to the European Green Deal and the European Research Area objectives by providing a rigorous, physics-based foundation for sustainable resource management and circular economy strategies. By harmonizing concepts, fostering education, and developing digital infrastructures, the Action will enable thermodynamics to evolve from a technical discipline into a practical tool for sustainability transition.

Just as Carnot's insights two centuries ago enabled the Industrial Revolution, THERSAURUS aims to ignite a Sustainability Revolution—one that measures progress not only by energy efficiency or economic growth, but by the preservation of the planet's finite exergy endowment for future generations.

Some recent developments in electrolyte thermodynamics

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A large European project (ElectroThermo) has given us during the last six years the opportunity to have a deeper look at electrolyte thermodynamics. The project has been formally completed by August 2025, although some final results will be published later.
The ElectroThermo project has as overall target to arrive at a fundamental understanding of electrolyte thermodynamics and thus enable the engineering of a new generation of useful, physically sound models for electrolyte solutions. These models should be general and applicable to a wide range of conditions so that they can be potentially used for many applications. The aim is both to achieve a fundamental understanding of electrolyte thermodynamics but also ensure contact with stakeholders (industry, etc) where electrolyte thermodynamics is expected to be relevant and useful. The ambition is to make advances, which can clarify major questions and misunderstandings in electrolyte thermodynamics and create a new paradigm that will ultimately pave the way for the development of new engineering models for electrolyte solutions.
The most important results from the ElectroThermo project will be presented in the form of messages from both the fundamental and the practical investigations. The topics covered will include, among others, comparison of theories for ion-ion interactions, the effect of relative static permittivity and ion pairing on the performance of the models, balance of forces against molecular simulation data and development of engineering-oriented but fundamentally based equations of state suitable for electrolytes solutions.

Acknowledgements

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Mixing Rules for Cubic Equations of State: What Works, What Fails, and What Remains to Be Investigated

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One of the most challenging aspects of using a Van der Waals type equation of state for mixtures is determining the appropriate expressions for the coefficients a (attractive parameter) and b (covolume) involved in this equation. It has been 45 years since Huron and Vidal first proposed the "EoS/g^E" advanced mixing rules. A decade after, building upon the original proposal, Michelsen subsequently derived the "zero reference pressure" (ZRP) approach and proposed the approximate ZRP mixing rules MHV1 and MHV2. Throughout the 1990's and 2000's, the Huron-Vidal and ZRP approaches were subject, often empirically, to multiple revisions in order to remedy some of their well identified shortcomings. It would appear that the debates surrounding advanced mixing rules are now over, with the latest conclusions proposed in the 2000s enjoying a degree of consensus.

The objective of this article is to reopen the debate in light of the scientific insights gained from our recent research on advanced mixing rules for cubic equations of state [1].

- The concept of deriving mixing rules by equating the excess Gibbs energy expressed from an equation of state to the same quantity expressed from an activity coefficient model was undoubtedly an appealing one. However, experience has shown that such a matching equation is not without its limitations, particularly due to the lack of sufficient constraints.
  To derive advanced mixing rules that are free from shortcomings, the best and unique solution is to modify the matching equation proposed by Huron-Vidal and Michelsen and to only equate the residual contributions. Based on this observation, we demonstrate how the demonstrations of the ZRP and HV mixing rules can be reworked to arrive at **a unique and universal (independent of the reference pressure) mixing rule**, called UHVM (Unified Huron Vidal Michelsen) mixing rule.
- We also wish to discuss the thorny issue of parameterizing the mixing rules. In particular, many equations of state use mixing rules based on the UNIFAC predictive activity coefficient model. In some cases (such as PSRK), the equation of state uses the UNIFAC parameters without re-determining them. In other cases (such as VTPR), the equation of state uses re-determined UNIFAC parameters. **We will discuss the conditions under which the same binary interaction parameters can be used in both the activity coefficient models and the equations of state employing these models.**
- Finally, in connection with the previous issues, we also wish to demonstrate and discuss **the essential role played by the chosen mixing rule for the parameter b**.

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Speciation in SAFT-γ Mie: Formulation and application for loaded aqueous monoamine solutions

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Carbon Capture and Storage (CCS) is one of the most promising technologies for reducing carbon emissions, especially for hard-to-decarbonize industries like cement and steel manufacturing and fossil-fuelled power plants [1]. Some of the most widely used solvents for carbon capture are aqueous amine solutions, that chemically absorb CO_2. To design these processes, it is necessary to have accurate models able to capture phase and chemical equilibria for these systems. However traditional equations of state struggle to accurately take into account the effect of speciation from the CO_2-amine reactions. Some modelling approaches for these systems handle the chemical speciation implicitly, like using SAFT-γ Mie [2], meaning they are not reliant on chemical equilibrium constants. Here we have extended this approach to develop a method to identify the composition of the reaction products. The approach is general for all SAFT-type models, relying on identifying the number of molecules with a specific type of site bonded to another type of site. The formulation has been applied for various systems that include solutions of monoethanolamine (MEA), diethanolamine (DEA) and aminomethyl propanol (AMP).

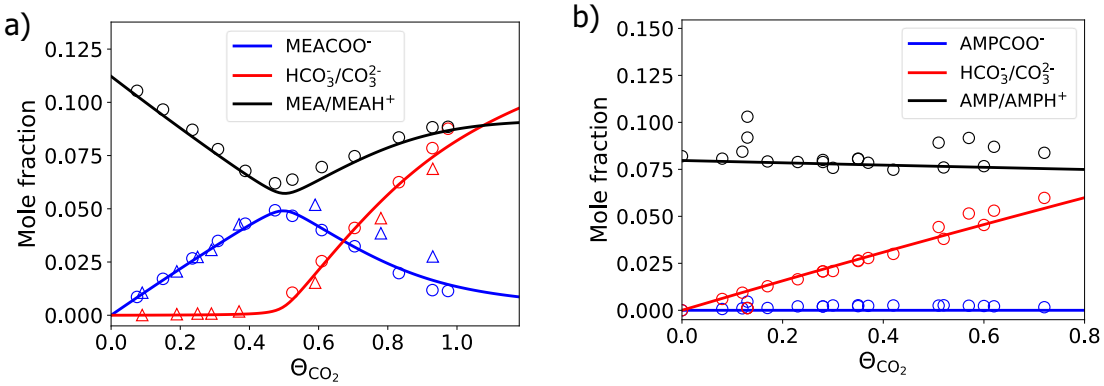

Figure 1. a) Mole fraction of carbamate, bicarbonate/carbonate, and protonated/free amine in loaded aqueous amine solution of a) MEA (30% w/w and 293.15K) and b) AMP (30% w/w and 298.15K). Curves are predictions and symbols are experimental data.

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Adsorption of Paracetamol On Graphite: A Thermodynamic Study Combining Isothermal Titration Calorimetry and Spectroscopy

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Carbon materials can be used for water decontamination purposes. The adsorption of pharmaceutical ingredients like paracetamol are therefore often studied to evaluate the ability of various materials to remove pollutant from the environment [1]. However, thermodynamic aspect is rarely explored. Activated carbons are usually the most efficient [2], but in our work, we used a pure graphite surface to study a simpler case with a chemically more homogenous surface. To better understand the energetic nature of the adsorption process, a direct experimental method is required. Unlike classical approaches based on adsorption isotherms, which only provide indirect estimations of thermodynamic parameters through model fitting, Isothermal titration calorimetry (ITC) directly measures the heat exchanged during adsorption and allows the determination of all main thermodynamic parameters (enthalpy, free enthalpy and entropy) from a single experiment [3]. In our case, ITC should be combined with UV-vis spectroscopy to determine all this thermodynamic quantity.

In fact, in ITC, the amount of heat exchanged during the experiment is directly linked to the number of molecules adsorbed and to the adsorption enthalpy. However, the physisorption of paracetamol on graphite is weak and only a partial adsorption is observed during each injection of the ITC experiment. Extracting simply the thermodynamic parameters from a single ITC experiment is therefore not likely. By combining ITC data with another experimental technique that allows the determination of the adsorbed quantity, it becomes possible to calculate the adsorption free energy and other thermodynamic parameters. This combined approach gives access to a complete thermodynamic description of the adsorption of weakly interacting molecules with surfaces.

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Molecular Investigation of CO_2 Effects on FKM Elastomers for CO_2 Transport Applications

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The integrity of polymeric sealing materials with dense CO_2 phases is a critical factor for the reliability and safety of carbon capture and storage (CCS) infrastructure. Elastomers, widely used as gaskets in CO_2 transportation, are particularly prone to CO_2-induced phenomena such as volume swelling and plasticization, which can compromise their mechanical integrity [1,2]. Experimental investigation of these effects under CO_2 transport conditions (low-T and high-p), is technically challenging. While some properties such as CO_2 sorption and diffusion can be measured in situ, others, including swelling, T_g shift, and elastic modulus, are often assessed ex-situ, limiting their relevance to real operating conditions. To address this gap, molecular-level modelling offers a valuable complementary approach.
In this study, Molecular Dynamics (MD) simulations are employed to investigate the interaction between CO_2 and Fluorine Kautschuk Material (FKM), a benchmark elastomer for sealing applications, at the atomistic scale.
Realistic polymer networks are constructed, incorporating representative low-molecular-weight additives commonly used in industrial formulations. These systems are equilibrated at CO_2 concentrations derived from experimental sorption data [2] to ensure consistency with realistic exposure scenarios. Through MD simulations, key material properties, such as volume swelling, diffusivity of CO_2 and additives, and variations in elastic modulus upon CO_2 uptake, are evaluated. The simulation results provide molecular-level insights into the physical response of FKM elastomers upon CO_2 exposure. The approach demonstrates the potential of MD-based modelling as a predictive tool for assessing the performance and reliability of sealing materials in CO_2-rich environment, contributing to a deeper understanding of sealing performance in CO_2-rich environments and supporting the development of more resilient elastomeric systems for CCS applications.

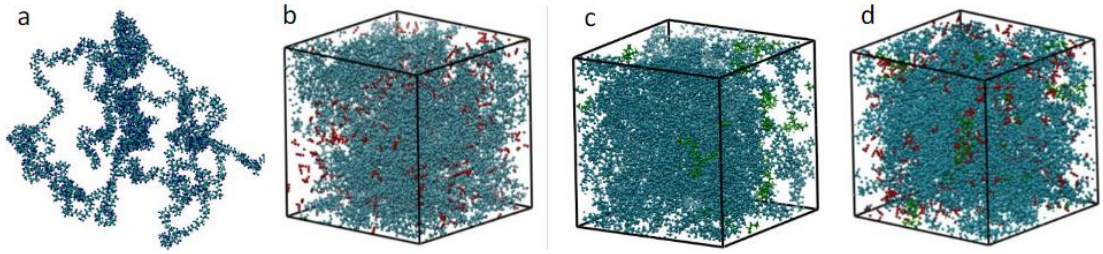

Figure 1. (a) Atomistic representation of the FKM molecular structure. (b) Simulation box of the equilibrated polymer + CO_2; (c) polymer + additive system; (d) polymer + CO_2 + additive system used for MD simulations.

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Solubility, dissolution and mixing enthalpies of metallic salts in ionic liquids

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Ionic liquids (ILs) containing dissolved metal salts are increasingly investigated as functional electrolytes for energy storage technologies, including batteries and capacitors [1]. In such systems, the solubility of the metal salt plays a central role in determining ionic conductivity, transport behavior, electrochemical stability, and ultimately device performance and safety. Beyond alkali salts, the dissolution of a wider range of metal salts in ILs is also relevant for applications such as electrochemical deposition, metal recovery, and redox-based energy technologies [2].
Reliable thermodynamic data on metal-salt solubility in ILs remain scarce. This limitation arises both from experimental difficulties associated with accurately determining saturation conditions and from the lack of predictive thermodynamic models capable of describing these highly non-ideal systems. Conventional approaches, including optical determination of solid–liquid equilibria (SLE) under excess solid conditions or calorimetric measurements using differential scanning calorimetry (DSC), often suffer from significant uncertainties due to metastable states or slow crystallization.
In this work, we propose the use of isothermal titration calorimetry (ITC) as a robust thermodynamic method for simultaneously determining solubility limits and dissolution energetics of metal salts in ionic liquids. By progressively titrating the solute into the solvent under strictly isothermal conditions, the method enables the direct construction of SLE phase diagrams while also providing quantitative measurements of dissolution and dilution enthalpies [3]. Through a carefully designed experimental protocol combined with rigorous thermodynamic analysis, a single calorimetric experiment can yield both the saturation concentration and the full energetic signature of the dissolution process. This approach overcomes the limitations of conventional techniques and provides a general methodology applicable to a wide range of solute–solvent systems. The resulting thermodynamic information contributes to a deeper understanding of dissolution mechanisms in ionic fluids and offers valuable data for the rational design of IL-based electrolytes and other functional liquid media.

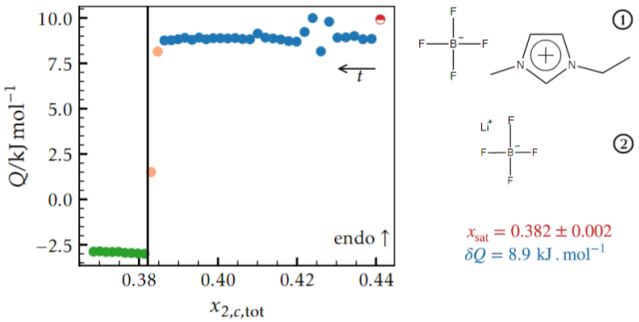

Figure 1. Heat effect calculated per mole of 1-ethyl-3-methylimidazolium tetrafluoroborate injected as a function of the composition of lithium tetrafluoroborate in the calorimeter cell.

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Electrochemically Driven Recovery of Cadmium and Tellurium from CdTe Solar Cells: A Thermodynamic Modeling and Simulation Study

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The transition toward clean energy requires technologies that not only harness renewable power efficiently but also manage their materials responsibly throughout their entire life cycle. Within this context, cadmium telluride (CdTe) thin-film photovoltaic (PV) technology represents roughly 5% of the global PV market, ranking as the second most widely deployed technology after crystalline silicon. Despite its advantages in efficiency and cost, the scarcity of tellurium (Te) and the toxicity of cadmium (Cd) pose significant sustainability and environmental challenges. Consequently, the recovery and reuse of Te and Cd from end-of-life (EOL) CdTe PV modules are essential for enhancing material circularity, reducing environmental impact, and supporting the sustainable growth of solar energy technologies. Conventional CdTe recycling technologies rely on energy-intensive thermal or chemical treatments such as oxidative leaching, which typically employ externally sourced oxidants like hydrogen peroxide (H_2O_2) along with mineral acids. These approaches not only contribute to a considerable carbon footprint but also introduce safety and cost concerns. To address these limitations, an electrochemically (EC) driven recycling process has been conceptualized by Mukopadhyay et al. at the Idaho National Laboratory, that can reduce overall energy demand by up to 96% while eliminating the need for external oxidants.

Designing such an advanced process requires a detailed understanding of the thermochemical behavior of Cd and Te species under various leaching and redox conditions. Thermodynamic modeling and simulation, therefore, serve as essential tools for identifying optimal operating windows for material extraction and recovery. In this work, key Cd– and Te–containing subsystems were identified and modeled using the Mixed-Solvent Electrolyte (MSE) framework. The established model enables systematic evaluation of oxidant and acid leachant effects, facilitating the determination of ideal reagent compositions and conditions for selective metal recovery in desired oxidation states. This integrated modeling approach minimizes acid consumption, reduces environmental impact, and enhances process efficiency, offering a sustainable pathway for the recovery of value metals from solar PV waste.

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Green Solvent Mixtures for Biomass Valorization: A Synergistic Approach Combining Experiments and Molecular Dynamics Simulations

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The development of effective and green solvent systems for biomass fractionation and valorization is one of the steps for the transition to a sustainable, circular bioeconomy. Lignocellulosic biomass, composed primarily of lignin and cellulose, poses significant challenges due to its structural complexity and low solubility in conventional solvents, therefore the theoretical studies focusing on dissolution mechanism of biomass are vital.[1,2] The present joint experimental-theoretical study investigates novel mixtures of environmentally friendly (green) solvents, including binary and ternary systems with additives, aiming to improve the solubility of biomass components while offering favorable thermodynamic and physicochemical properties.

From the experimental perspective, solubility studies were carried out using both commercial Kraft lignin and more native-like Organosolv lignin obtained by a novel fractionation process.[3] Representative model compounds were used for cellulose. In parallel, key physicochemical properties of the solvent mixtures (such as density, viscosity, heat capacity, and activity coefficients) were systematically measured in the absence of biomass to support a detailed thermodynamic description of the solvent systems. These measurements support the evaluation and comparison of solvent mixtures from both practical and theoretical perspectives.

Complementing the experiments, molecular dynamics (MD) simulations were carried out for selected solvent systems, both with and without lignin and cellulose models. For lignin, monomeric and oligomeric structures were used; for cellulose, a crystalline model was constructed to explore dissolution mechanisms. MD simulations provide molecular-level insight into intermolecular interactions, hydrogen bonding networks, microheterogeneity, and the microscopic structure of green solvent mixtures in the vicinity of of biomass interface, helping to identify the driving forces of lignin and cellulose solubility. Notably, MD simulations reveal distinct interaction motifs between solvent components and solute functional groups, that correlate with experimentally observed solubility trends.

Together, the experimental and computational results demonstrate how a synergistic approach can improve the rational design of green solvent systems for biomass fractionation and valorization. The recent findings provide a rational framework for the design of next-generation solvents that are more effective and also in compliance with principles of green chemistry and sustainability.

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Extending the SAFT-ɣ Mie approach: from polycyclic aromatic compounds to aspirin

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The prediction of the solid–liquid equilibrium solubility of pharmaceutical compounds is a major challenge for the pharmaceutical industry and solvent selection. We use the SAFT- γ Mie group-contribution equation of state [1] to predict the phase behavior and solubility of several pharmaceutical compounds, including aspirin, in a range of solvents.

The molecular modeling of aspirin relies on a recently developed group, denoted as aC for "aromatic carbon" [2], which has been initially developed to model polycyclic aromatic hydrocarbons (PAHs) and their mixtures. Literature data for the vapor–liquid equilibria, density, and enthalpy of mixing are used to characterize the new group interactions of SAFT- γ Mie that involve the aC group. In particular, the prediction of the aqueous solubility and the octanol–water partition coefficient of PAHs constitutes a challenge of environmental significance, related to water pollution issues. The range in aqueous solubility spans many orders of magnitude, from 10-5 mol/mol for naphthalene to 10-12 mol/mol for larger PAHs, which can be predicted with SAFT- γ Mie.

The new group-interaction parameters developed for the modeling of PAHs are transferred to the modeling of aspirin, such that no aspirin data is used to characterize the interactions. The transferability and predictive accuracy of the new model are assessed by comparing the theoretical predictions with available experimental solubility data. Very good agreement with the experimental data is obtained for the solubility of aspirin in 23 pure solvent systems. Our comparison includes water, alkanes, alcohols, ketones, esters, and aromatic compounds as families of solvents.

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Thermodynamic Consistency of Data for Electrolyte Model Parameterization: a Case Study Proposed by EleTher JIP

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The EleTher JIP focuses on the development of best practices for the thermodynamic description of mixed solvent electrolyte systems. The challenge of such systems is the simultaneous occurrence of phase and chemical equilibria. Very often, only a single phenomenon is considered (vapour-liquid, solid-liquid or speciation), which strongly limits the extrapolation capacity of the developed model. In this work, a follow-up on a previous paper [1] is presented, using the case study consisting of four components (water, methanol, acetic acid, potassium hydroxide). Data from several different origins (including novel, ebulliometric data) are combined using the eNRTL model that is available in both Fives Prosim and Aspen softwares.

The analysis is performed in three steps: (1) using vapour-liquid equilibrium data, the salting-in or salting-out of the volatile species is investigated; (2) using the Gibbs energies of transfer, the impact of the solvent composition on the various reactive equilibria is quantified; (3) using mean ionic activity coefficients and solid-liquid equilibrium in different solvents, the high salt concentration limit is validated. The resulting model provides a complete picture of the isothermal behaviour of a multicomponent acid-base system. The learnings from this case study will be further applied to other systems.

Thermodynamic experiments and modelling of cyclopentane hydrates in presence of pure and mixed salts from NaBr, KBr, NaCl, KCl, Na_2SO_4, K_2SO_4 and $CaCl_2$

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Water scarcity has been a major concern for many years, and hydrate-based desalination (HBD) has emerged as a promising technology to address this challenge. This study explores the use of cyclopentane (CP) as a hydrate former for desalination via crystallization at low temperature and atmospheric pressure. The main objective is to provide new phase equilibrium data for cyclopentane hydrates (CPH) in the presence of various salt systems, including NaBr, KBr, K_2SO_4, NaBr–KBr, NaCl–NaBr, KCl–KBr, Na_2SO_4–K_2SO_4, and $CaCl_2$–$MgCl_2$.
Equilibrium temperatures were determined using both rapid and slow dissociation methods [1]. Several thermodynamic models were applied to interpret the results [2]: the van der Waals–Platteeuw Kihara (Kihara) approach, the Hu–Lee–Sum (HLS) correlation, the Standard Freezing Point Depression (SFPD) method, and the Activity-Based Occupancy Correlation (ABOC).
Experimental data show that the discrepancy between rapid and slow procedures ranges from 0 to 1.2 °C. Increasing salt concentration was found to intensify the inhibitory effect on hydrate formation. Regarding cation influence, the depression of equilibrium temperature follows the order $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$, while for halide anions, Br^{-} exerts a stronger effect than Cl^{-}.
Thermodynamic modelling results demonstrate good agreement with experiments, with average absolute deviations (AAD) of ≤0.796 °C across all four models. Among them, the ABOC approach provided the best accuracy, reproducing equilibrium temperatures with an AAD of ≤0.38 °C.

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A New Method for Multiphase Isenthalpic Flash Calculations by Direct Maximization of Entropy

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Phase equilibrium calculation at pressure, enthalpy, and moles specifications (PHN) is one of the most important phase equilibrium calculation problems, beyond the widely used conventional calculations at pressure and temperature (PT) specifications. The applications range from compositional simulation for enhanced oil recovery methods to carbon dioxide storage and geothermal energy. In this work, a new method for PHN phase equilibrium calculations is presented. The problem is formulated as an unconstrained maximization of the entropy with respect to mole numbers. Enthalpy is a dependent variable and its dependence on mole numbers is taken into account by solving a nonlinear equation (the enthalpy balance equation) for temperature at each iteration level. Unlike in previous PHN formulations, the calculation framework is similar to that in PT flash. A new successive substitution iteration (SSI) method is proposed for PHN multiphase flash calculations. The iterative sequence consists of two inner loops, in which the Rachford-Rice system of equations is solved first for phase fractions and then the enthalpy constraint equation is solved for temperature. The equilibrium constants are updated in the outer loop. An ascent direction is guaranteed in the SSI method and an efficient line search procedure ensures an increase in entropy at each iteration. If non-feasible conditions are encountered at the initial guess or during iterations, a transition temperature is calculated, and the sub-phase method is used; one of the equilibrium phases is artificially split into two sub-phases having the same composition, in such a way that the enthalpy constraint is honored. The new SSI method is much simpler than various versions of the so-called direct substitution (DS) method. However, the SSI method in PHN phase equilibrium is not as robust as its PT counterpart and its limitations are discussed in detail. However, SSI does not need to be effectively converged in practice; the purpose is to bridge between a potentially poor initial guess and the domain near the solution where Newton iterations exhibit unproblematic quadratic convergence. In the second-order Newton method, a line search procedure is used to guarantee an increase in entropy at each iteration. If the Hessian matrix becomes indefinite, a diagonal correction is added using a Trust-region method. Criteria adapted to PHN flash are used for switching from SSI to Newton iterations. The proposed method is tested for several mixtures of various complexities, from binary mixtures to reservoir fluids, with emphasis on near-critical, narrow boiling cases and low-temperature conditions and proved to be rapid and robust, clearly outperforming all previous formulations. A detailed convergence analysis is provided for both SSI and Newton methods. Several domains in the P-H plane are identified where the classical Direct Substitution method and/or starting directly with Newton method (or after some partial Newton iterations) struggle to converge or diverge, while the proposed SSI-Newton converges fast, with only a few Newton iterations required after switching. In this work, it is the first time that i) SSI are formulated in PHN multiphase flash calculations, and ii) the direct maximization of entropy using a Newton method with mole numbers as independent variables is presented and analysed in detail.

Investigation of the HSA Solvation in Diverse Solvents at High Concentrations

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DL-12-hydroxystearic acid (HSA) is an important oleogelator, and its solubility in different solvents is the key of understanding and designing oleogel systems. In this work, thermodynamic models are applied to describe the solubility of HSA in solvents of very different nature, ranging from purely dispersive (triolein, cyclohexane) to polar and hydrogen-bonding solvents (ethyl acetate, acetone, acetonitrile, methanol, and water). Both equation of state (EoS) models, such as PC-SAFT, and activity coefficient models, such as NRTL-SAC and UNIFAC, are considered. These models are used to correlate solid–liquid equilibria of HSA and to analyze related thermodynamic properties, including density, association strength, activity coefficients, and Gibbs free energy of solvation. Importantly, the analysis covers not only the dilute regime but also the high-concentration range (up to ~50 mol% HSA), which is rarely addressed but is particularly relevant for oleogel formation. The comparison of EoS-based and activity coefficient-based approaches highlights their respective strengths and limitations for describing HSA solvation in complex solvents.

Keywords: PC-SAFT, NRTL-SAC, UNIFAC, Solid–liquid equilibria, Oleogel, Gibbs free energy of solvation, Activity coefficient

A Universal Activity Coefficient Model with First-Principles/Atomistic-Simulation-Driven Gibbs Energy Minimization for Predicting CO_2 Reactive Absorption

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Post-combustion reactive absorption from point sources remains one of the most mature and widely deployed technologies for CO_2 capture. However, most industrial solvents still derive from nearly century-old formulations with only incremental first-generation improvements. Conventional new solvent discovery is slow and empirical: candidates are proposed based on chemical intuition, tested experimentally for equilibrium CO_2 solubility and speciation, and fitted to complex macroscopic reaction-based thermodynamic models (e.g., eNRTL), which are then solved with commercial or in-house-developed Gibbs Energy Minimization (GEM) software. This trial-and-error cycle makes the search for novel and more efficient solvents costly and time intensive.

To overcome these limitations, we have developed a predictive molecular-based thermodynamic framework that enables large-scale solvent screening at a fraction of the time and cost of the traditional approach [1]. The framework integrates:

(1) prediction of key reaction equilibrium constants (pKa and pKc) by combining electronic structure calculations, atomistic simulations, and machine learning models;

(2) development of a universal activity coefficient model (UACM) capable of describing complex reactive aqueous electrolyte mixtures; and

(3) rapid and efficient numerical solution of the GEM reactive vapour-liquid equilibrium problem using the predicted constants and UACM to calculate CO_2 solubility.

Efficiently developing the UACM requires solving the GEM problem for an activity coefficient model of arbitrary form. To meet this need, we created a fixed-point GEM algorithm built on an underlying ideal-solution formulation and implemented it with the open-source Reaktoro software package [2], enabling rapid and stable convergence even for highly nonideal reactive systems.

We demonstrate the fixed-point GEM algorithm within the predictive framework by calculating CO_2 solubility in a range of pure and mixed alkanolamine solvents, validating against established industrial systems, and forecasting performance for untested systems. This integration of first-principles equilibrium constant prediction, a UACM, and efficient GEM solution provides a practical route to accelerate solvent discovery and guide process design for post-combustion CO_2 capture.

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Predictive Thermodynamic Modelling of Gas Sorption and Permeation in Polymers for High-Pressure Gas Handling Applications

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As essential components of gas-transportation infrastructure, polymeric materials must maintain structural integrity under extreme pressure and temperature conditions. Their resilience and durability, in turn, may be significantly affected by the interaction with transported gases. Relevant gases, associated to the ongoing energy transitions, are carbon dioxide (within the Carbon Capture and Storage infrastructure), hydrogen, the ideal energy vector H_2, as well as NH_3, a suitable alternative as H_2-carrier. Relevantly, they are characterized by different size, thermodynamic properties and chemical nature. To obtain a comprehensive understanding of solubility and transport properties of such penetrants in both thermoplastic and elastomeric polymers is of paramount importance for the development of safe gas transportation infrastructures.
Predicting transport behaviour becomes particularly challenging when penetrants differ widely in molecular size and condensability, and a particular care has to be devoted to such analysis under high pressure and/or low conditions. In this study, we inspected the solubility, permeability and diffusivity behaviours of CO_2, NH_3 and H_2 in different polymeric materials, including both elastomers and thermoplastics. To fully assess the materials' capabilities under realistic conditions, we perform a thermodynamic modelling analysis of the key transport properties (solubility, diffusivity and permeability). By coupling Lattice Fluid Equations of State (LF-EoS) with its non-equilibrium extension (NELF), we can predict gas solubility. The Standard Transport Model (STM) is then applied to estimate permeability, where solubility and diffusivity are key inputs for the transport prediction.
The modelling approach adopted proved to be very effective in describing the experimental behaviours at very different conditions, and it can be thus considered as a valuable predictive tool.
Furthermore, the comparison of the modelling description of different penetrants that cover both condensable and non-condensable behaviour in different polymeric classes, while mapping trends up to elevated pressures, can reveal complex behaviours and key contrasts. For instance, while carbon dioxide and ammonia exhibit higher solubilities and pressure-activated deviations linked to plasticisation effects, hydrogen shows lower solubility but a different transport behaviour, given by the high constraining pressure. The model outcomes enable predictive simulations of transport properties over broad conditions.
These findings can also provide a guideline framework for polymer selection in carbon dioxide and hydrogen handling applications.

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Thermophysical properties of binary mixtures amine + carbon dioxide for the deployment of carbon capture

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The European Green Deal (2019) was introduced to achieve the objectives of reducing greenhouse gas emissions by 55 % by 2030 and becoming carbon neutral by 2050. Among the different priorities established in it, the strategies of carbon capture, utilisation and storage (CCUS) are identified as a measure which can play an important role in clean energy transition.

CCUS involves the capture of CO_2, from large point sources, like industrial facilities or power generation, which consume fossil fuels or biomass allowing for their continued operation. Except when it is used on-site, the captured CO_2 is compressed and transported to be used in different applications or injected into deep geological formations such as saline aquifers or depleted gas and oil reservoirs.

CCUS is an enabler of least-cost low-carbon hydrogen production, which can support the decarbonisation of other parts of the energy system, such as industry, trucks and ships. Besides, it can remove CO_2 from the air to balance emissions that are unavoidable or technically difficult to abate.

However, CCUS deployment is below what is required in the net zero scenario and some standardisation requirements were identified for the involved agents to achieve carbon dioxide quality assurance.

In order to facilitate efficient and safe usage of this technology across Europe and to support the CCUS industry, funded by EURAMET, the "Metrology Support for Carbon Capture Utilisation and Storage (MetCCUS)" project [1] address key measurement challenges related to flow metering, emissions monitoring, chemical metrology and the physical properties of CO_2. The overall aim of the project is to develop new metrology tools in the form of Primary Standards and methods, as well as the relevant best practice/guidance, necessary to support industry in carbon capture, utilisation and storage.

Our contribution is to provide accurate measurements related to thermophysical properties of CO_2 with the purpose of improving thermodynamic models based on these original experimental measurements. Since the most mature technology for CO_2 capture is the chemical absorption with amines. A deeper knowledge of models for these reactive systems is required.

The tasks involve the measurement of density, viscosity and heat capacity of the binary mixtures composed by (carbon dioxide + monoethanolamine) and (carbon dioxide + diethanolamine) at wide temperature and pressure ranges. Those data will be presented in this contribution.

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Extension of RAND-Based Chemical Equilibrium Calculation to Multiple Electrolyte-Containing Phases in CO_2 Capture Modeling

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CO_2 capture is essential for deep emission reductions, particularly from large point sources. Post-combustion absorption with amine-based solvents remains the dominant method, while emerging phase-change solvents show promise by reducing regeneration energy through liquid–liquid separation. A key bottleneck in simulating such systems is the reactive flash algorithms for multiple electrolyte-containing phases.

RAND-based algorithms provide an efficient framework for reactive flash by simultaneously solving chemical and phase equilibria using elemental potentials. In its modified form [1] for non-ideal, multiphase systems, composition derivatives of fugacity coefficients are utilized to achieve quadratic convergence, with Gibbs energy monitoring providing robust performance. The modified RAND formulation implicitly enforces electroneutrality through elemental balances, provided there is only a single electrolyte-containing phase [2,3]. However, this approach cannot be directly extended to systems with multiple electrolyte-containing phases, where electroneutrality must be satisfied in each phase. Tsanas et al. [4] addressed this by adding the electric-potential contribution in the objective function, but this enlarges the equation system and alters the RAND formulation.

Here, we extend RAND to enforce electroneutrality in each individual phase without introducing explicit electroneutrality constraints. This is achieved by reformulating the problem in terms of neutral artificial species formed by pairing oppositely charged ions. This guarantees per-phase electroneutrality, avoiding additional constraints and the dimensionality penalty associated with electric-potential variables.

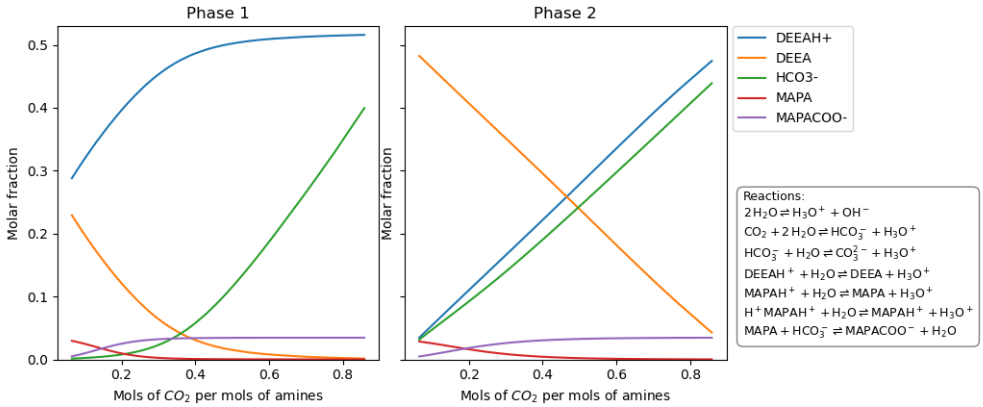

Figure 1. Liquid-liquid equilibrium of H_2O–CO_2–DEEA–MAPA mixture with two electrolyte-containing phases at DEEA = 6.3 M and MAPA = 0.42 M with varying CO_2 loading.

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COSMOtherm prediction of carbon dioxide solubility in bio-based solvents

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In this study, the Conductor-like Screening Model for Real Solvents (COSMO-RS) method, implemented in COSMOtherm, has been employed to predict the solubility of CO_2 in Dihydrolevoglucosenone (Cyrene). This compound has recently attracted attention as a potential bio-based alternative to N-methyl-2-pyrrolidone (NMP) [1,2] for physical absorption processes aimed at CO_2 removal. However, because Cyrene is a relatively new solvent, only a limited number of experimental data is available in the literature regarding the solubility of gases, including CO_2 [3,4], in it. To address this lack of data, an experimental campaign has been conducted at the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano to obtain additional CO_2 solubility measurements [5]. The experimental activity has been supported by predictive calculations performed using the COSMO-RS method, which combines quantum chemical information with statistical thermodynamics to describe intermolecular interactions and to predict thermodynamic properties of pure compounds and mixtures. Therefore, COSMO-RS has been employed to predict new CO_2 solubility data, which have been subsequently integrated with the experimental results obtained at the PT lab. Prior to its application to the CO_2–Cyrene system, the model has been validated by reproducing experimental solubility data of CO_2 in five bio-based solvents available in the literature [6]. The objective of this work is to expand the available dataset on CO_2 solubility in Cyrene, providing a solid basis for the regression of thermodynamic model parameters and for the simulation of CO_2 absorption processes using Cyrene as solvent.

This work has been carried out in the context of the PRIN 2022 project "GREEN-based water-lean SOLvent for CO_2 capture" (GREENSOL), funded by the European Union – NextGenerationEU, CUP D53D23003100001 – and we acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component C2, Call for tender No. 104 published on 2.2.2022 by the Italian Ministry of University and Research (MUR).

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Calculation Methods for COSMO-Based Activity Coefficient Models

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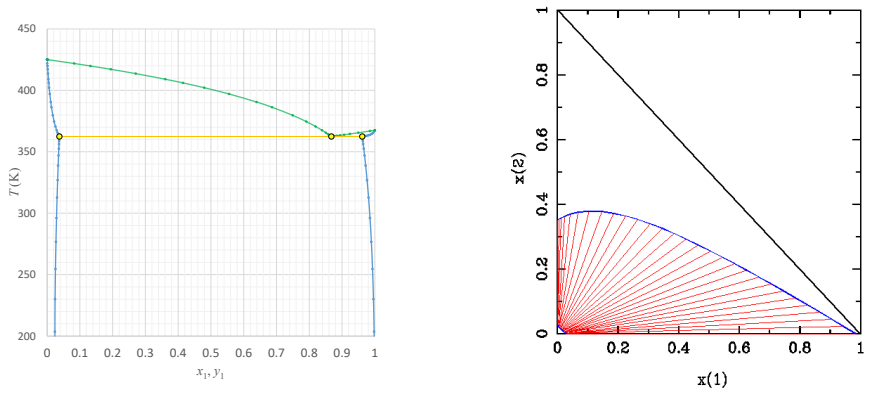
COSMO-based activity coefficient models, such as COSMO-RS [1] and COSMO-SAC [2], offer a powerful tool that bridges quantum chemical calculations with macroscopic phase equilibrium calculations. These models utilize a group contribution methodology similar to UNIFAC but require an expensive numerical solution of the self-consistency equation for interactions among all surface segments, representing a primary bottleneck in their application to analyses that involve extensive phase equilibrium calculations. This work demonstrates that the self-consistency equation can be derived by minimizing the system energy from all pairwise segment interactions. The derivation leads to an optimization-based second-order solution procedure that ensures convergence and enhances efficiency [3]. We demonstrate the robustness and efficiency of the proposed solution using various examples, including a comparison with the classical successive substitution method, and illustrate that COSMO-based models can be coupled with modern second-order convergent algorithms for phase equilibrium calculations. Furthermore, this work reveals the similarity between COSMO-based models and the SAFT method. Finally, we discuss the challenges and opportunities implicated by the energy minimization-based solution method.



A **B**

Figure 1. Phase diagrams generated by coupling the phase equilibrium calculation algorithm with the COSMO-SAC model: Txy diagram for dichloromethane (1) — water (2) at 5 bar (**A**) and ternary diagram for dichloromethane (1) — 1-butanol (2) — water (3) at 298 K and 5 bar (**B**).

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Thermodynamic Modeling of PFAS Physicochemical Properties with COSMO-RS

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Per- and polyfluoroalkyl substances (PFAS) are of growing concern due to their environmental persistence, toxicological effects, and potential for bioaccumulation [1]. Experimental detection is challenging because of their typically low concentrations, while systematic testing of the vast number of possible PFAS mixtures is impractical. Reliable predictive modeling is therefore essential to assess their environmental fate and support remediation strategies. One promising approach to address these challenges is the Conductor-like Screening Model for Realistic Solvents (COSMO-RS) [2], a thermodynamic predictive model grounded in quantum chemistry.

In this work, to predict key physicochemical properties of representative PFAS, we evaluated different implementations of COSMO-RS, including the commercial software COSMOtherm and the open-source variant openCOSMO-RS [3]. Examples include octanol–water partition coefficients and aqueous solubilities, as illustrated in Figure 1. We further assessed modifications of openCOSMO-RS, including incorporation of the dispersion term, which significantly improves model performance for fluorinated compounds [4,5]. In addition, we explored alternative data-driven predictive approaches to examine their potential in PFAS property estimation. Our findings provide insights into the applicability and limitations of predictive thermodynamic methods for PFAS modeling, while highlighting opportunities for methodological refinements.

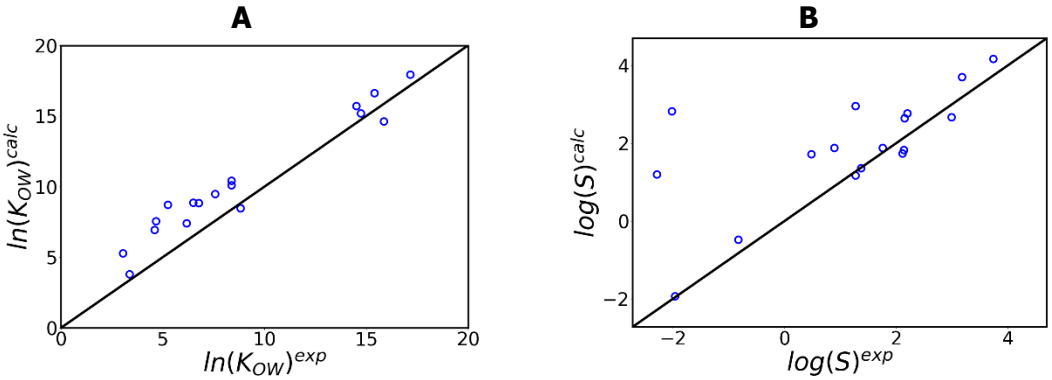

Figure 1. Parity plots comparing experimental (*exp*) and calculated (*calc*) values obtained with openCOSMO-RS [5] for PFAS octanol-water partition coefficients (**A**) and aqueous solubilities (**B**).

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Boosting thermophysical property predictions with graph neural networks

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This contribution presents a scalable solution for improvement of thermophysical property predictions in industrial applications based on the established COSMO-RS[1] method as implemented in BIOVIA COSMOtherm[2] by means of machine learning (ML).
COSMO-RS is a method, that, in contrast to many others, can be applied to arbitrary complex mixtures of compounds and is not limited to certain classes of molecules. Additionally, it provides access to a multitude of experimental observables ranging from pure compound properties such as boiling points to properties derived from interactions of multiple compounds such as octanol-water partition coefficients. This creates a challenging regime for ML applications, since any ML model used for boosting prediction accuracy, needs to be applicable to a similarly broad range of problems. The presentation will show an efficient approach based on graph neural networks[3], that encodes complex molecular setups of diverse experiments from simple input features.
Special attention is given to uncertainty quantification from aleatoric and epistemic contribution channels, as reliability and error quantification are of high importance in industrial applications.
Results are presented for the simultaneous prediction of multiple thermodynamic observables, ranging from pure liquid phase properties such as activity and partition coefficients, to gas phase related properties such as vapor pressures and solvation free energies.

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Enhancing the PR Equation of State for the Hydrogen Economy with a novel hybrid Neural Network framework

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Accurately predicting the properties of hydrogen-enriched natural gas (H_2/NG) mixtures is vital for optimising industrial processes. Widely used two-parameter cubic equation of states (CEoS), such as the Peng-Robinson (PR) model, struggle to calculate precisely the thermophysical properties of Hydrogen-hydrocarbons at temperatures far above hydrogen's critical temperature using standard alpha functions[1]. This inadequacy necessitates the use of large, temperature-dependent binary interaction parameters, which reduces the reliability of predictions.

To address these limitations, this study first enhances the foundational PR EoS by incorporating a dedicated temperature-dependent alpha function for hydrogen and advanced CEOS/A^E mixing rules [2,3]. This improved thermodynamic model is then integrated as a foundational layer within a deep learning framework, creating a Thermodynamics-informed Neural Network (TINN). As illustrated in Figure 1, the hybrid PR-NN model architecture consists of:

- A preprocessing layer to scale the input experimental density values.
- A core physics-informed layer that computes the vectorised PR-EoS.
- Fully connected hidden layers that learn to correct the PR model's deviations in predicting fluid density.

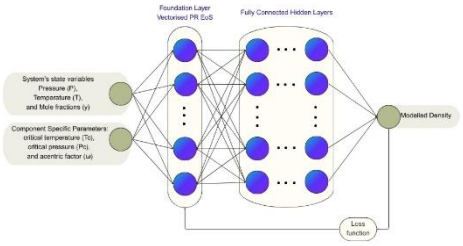

Figure 3. The architecture of hybrid PR-NN for the binary hydrogen-methane mixture

The model was trained and validated against experimental data for hydrogen-methane (H_2-CH_4) mixtures with hydrogen content below 20 mol%, pressures up to 68 MPa, and a temperature range of 140 K to 398 K.

The hybrid PR-NN model demonstrated a significant improvement in predictive accuracy compared to the enhanced PR EoS alone. Specifically, the average absolute relative deviation for density ($\mathrm{AARD\%} = \frac{|\text{Observed density} - \text{Predicted density}|}{|\text{Observed Value}|} \times 100$) was reduced from 2% to less than 1%, with notable improvements at low reduced temperatures ($Tr = T/Tc$). This study successfully demonstrates that integrating data-driven AI techniques with classical thermodynamic models is a powerful strategy. This resulting hybrid approach offers a more robust and accurate tool for thermophysical modelling, paving the way for improved efficiency in industrial applications involving hydrogen.

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Process Intensification and Optimization of Aroma Compounds Preservation in Thermal Dealcoholisation of Beer

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Thermal dealcoholisation of beer via vacuum distillation effectively reduces its ethanol content. However, this process also removes volatile aroma compounds, which compromises the beer´s sensory quality [1]. Despite this drawback, vacuum distillation remains the most widely used method for beer dealcoholisation. Improving the process design therefore requires a detailed understanding of the vapor-liquid equilibria (VLE) of aroma compounds in beer—a task made challenging by the system's chemical complexity.

This study explores the thermodynamic mechanisms behind aroma compound loss during dealcoholisation of beer and evaluates process modifications aimed at increasing the concentration of aroma compounds in non-alcoholic beer, without the use of additives.

The VLE of a model beer mixture made of water, ethanol and key aroma compounds was modelled using the Non-Random Two-Liquid (NRTL) model [2]. NRTL model was then combined with the equilibrium-cell model and employed to simulate the dealcoholisation process in a vacuum distillation column. The simulations were carried out using Aspen Plus v14, a process modelling software. The ability of the model to reproduce experimental data was assessed by simulating an operating pilot-scale plant, showing good agreement in the distribution of aroma compounds across process streams.

Subsequently, alternative process configurations, including combinations of a second distillation column, an absorption column, and side-streams, were analysed through simulations. An optimisation workflow was developed to evaluate these configurations. A Random Forest surrogate model was trained on a set of different operating conditions simulations and then used to predict process performance across a broader design space. This surrogate-based approach was used to identify optimal operating parameters within the best configurations of each of the studied process modifications. The optimisation results revealed operating windows that increased total concentration of aroma compounds while preserving the balance among aroma compound chemical families, under the constraint of less than 0.5 % v/v ethanol. Finally, the results were interpreted using sensory-relevant indices from a flavour database [3], providing a direct link between process design and dealcoholized beer sensory profile.

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One EOS to Rule Them All? Systematic Review of Equations of State for Pure Component Prediction

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Equations of state (**EOS**) are fundamental tools in chemical engineering and thermodynamics for predicting fluid behavior under varying conditions. Despite their widespread use, a consistent and comparative evaluation of a larger set of EOS accuracy—particularly regarding pure component properties—has remained limited to some non-polar components in recent literature[1].

In this study, **we systematically evaluated 15+ EOS across 110+ different compounds**. Five key thermodynamic properties were analyzed: **density**, **residual entropy**, **fugacity coefficient**, **enthalpy of vaporization**, and **saturation pressure**. These properties were examined over a broad range of temperatures and pressures, encompassing the subcritical, supercritical, and saturated regions, using the **Clapeyron.jl**[2] Julia package.

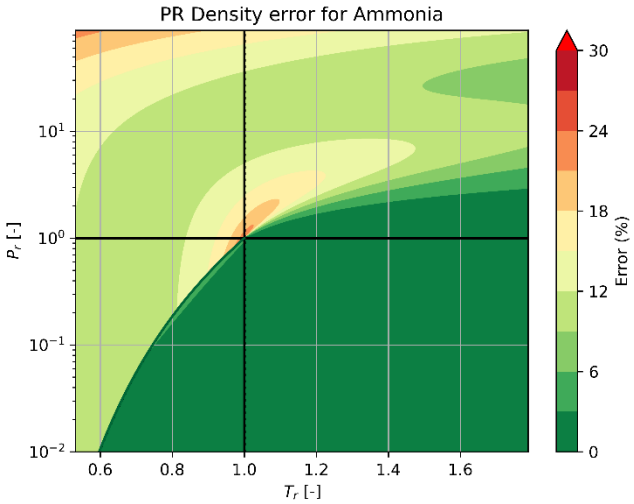

Figure 1: Density error for Ammonia with PR EOS

Errors were calculated compared to fundamental equations of state implemented in **CoolProp**[3] or experimental data. **Figure 1** shows one example of the density error for ammonia using the Peng–Robinson EOS.

The evaluated data points were categorized into five distinct thermodynamic regions based on temperature and pressure relative to the critical point. Within each region, error values were computed for the five properties to better compare the performance of the EOS.

The evaluation **compares cubic with SAFT** based EOS and shows their advantages and disadvantages emphasizing the importance of parameterization strategy for SAFT based EOS.

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Comparative 3D visualization of processes in power-to-heat and heat-to-power cycles using various types of working fluids

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The efficiency of heat-to-power and power-to-heat cycles is greatly influenced by the thermodynamic behaviour of the chosen working fluid. Traditionally used temperature - specific entropy diagrams and cycle simulations serve well for a basic understanding of the underlying phenomena. However, they often only capture the broad outlines of differences between working fluids, rather than their detailed behavior. This work presents and extends a three-dimensional visualization method that depicts simple thermodynamic state changes between saturated states in a unified framework based on entropy difference, initial, and final temperature.

Previous research has focused mainly on wet and dry working fluids, while the novelty of the present study is that it also includes isentropic fluids. This allows for a comparative study of the three main categories of working fluids—wet, dry, and isentropic—revealing the differences between isothermal, isobaric, isenthalpic, and isentropic processes. The 3D representations created in this way clearly show which state changes can be achieved with a given fluid and what entropy differences characterize them.

The results may contribute to a more conscious selection of working fluids and the adaptation of cycles to heat sources, and they may also be helpful in education for a more intuitive understanding of thermodynamic concepts. This method therefore provides support for research, industrial, and learning processes, and opens up new perspectives in the design of energy conversion systems.

A Hybrid Computational Framework for the Discovery and Thermodynamic Characterisation of New Working Fluids

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Fluorinated working fluids, such as hydrofluorocarbons (HFCs), used in the refrigeration and energy production industries, represent a significant environmental concern due to their high Global Warming Potential (GWP), with projected CO_2-equivalent emissions of 6 – 9% by 2050 [1]. In response, increasingly strict environmental regulations are being implemented to progressively phase out the use of HFCs, promoting the transition towards low-GWP alternatives [2].
In this work, we propose a new hybrid framework combining deep learning techniques with classical thermodynamic methods to find new working fluids able to meet the market performance requirements. For this purpose, we trained a generative deep learning diffusion model on a database of over two million chemical compounds [3]. We then used the diffusion model to generate new chemical compounds with potentially good properties from a technical and environmental perspective. Ultimately, a subset of promising candidates was selected and modelled through a multiscale computational approach. The molecular surface charge density distributions were obtained from COSMO-RS calculations and used to predict the flammability of the candidates through an artificial neural network [4]. Atomistic molecular dynamics simulations were performed to estimate vapour-liquid equilibrium densities, vapour pressure, surface tension, enthalpy of vaporization, diffusivity, and viscosity. The simulation results then served as the basis for developing a thermodynamic model within the soft-SAFT equation of state framework. Finally, the thermophysical and transport properties, as well as the flammability predicted for the new compounds, were compared with those of the most common 3rd-generation refrigerants. The results show that several compounds exhibit favourable performance, suggesting that they could serve as promising 4th-generation working fluids.

Acknowledgements
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Role of acids in stabilizing Reverse Micelles: the case of Dodecyl Sulfate

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The anionic surfactant Sodium dodecyl sulfate (SDS) can form reverse micelles (RMs) in two non-miscible components above the critical micelle concentration [1]. Although the RMs in salt or alkali solution has been investigated in previous studies [2,3], less is known on the working mechanism of acids in SDS RMs. Here, we employ all-atom (AA) and coarse-grained (CG) molecular dynamics to investigate the effects of chloroauric acid (HAuCl4), fluoroboric acid (HBF4) and phosphoric acid (H3PO4) solutions on the stability of the RMs through spontaneous self-assembly in toluene. We find that investigated acids can stabilize micellar structure, particularly H3PO4 due to the stable hydrogen-bonds it forms with the SDS headgroups. In addition, HAuCl4 can significantly influence micelle shape because of its strong polarizability at the water-toluene interface, while HBF4 causes the highest interfacial tension as a result of its significant hydrophilicity. Moreover, scission free energy calculations from CG simulations [4] reveal important differences, which along with the viscosity can explain how different acids affect the size of RMs. Our findings can help to rationalize the impact of different acids on the RMs stability and morphology and, in turn, on the metallic nanoparticles synthesis where the RMs are used as nanoreactors.

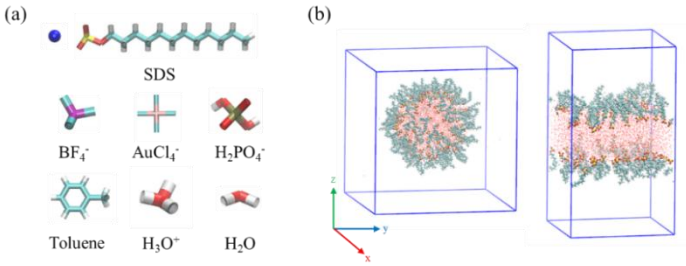

Figure 1. (a) Molecular configurations for all species and molecules in this work. (b) Snapshots of the simulation boxes for the reverse micelle (RM) and bilayer (BI), while the toluene molecules are not shown for clarity.

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First Application of Membrane-Absorption Integration for the Separation of Azeotropic Refrigerant Blends

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Hydrofluorocarbons (HFCs) are major components of refrigerant blends commonly used in refrigeration and air-conditioning systems. These compounds exhibit very high global warming potentials (GWPs > 675 kg CO_2-eq/kg), prompting international agreements such as the Kigali Amendment to the Montreal Protocol to mandate a gradual reduction in the production of virgin HFCs. Consequently, recovering and reusing existing refrigerants has become critical for minimizing their environmental impact. Although the (near) azeotropic behavior of these blends improves thermodynamic efficiency, this feature significantly complicates their separations. This underscores the need for advanced separation technologies to support sustainable refrigerant management. Among these, extractive distillation (ED) using ionic liquids (ILs) as entrainers has received special attention due to its industrial applicability and effectiveness, though it remains highly energy-intensive. [1]

As a step toward low-energy separation processes, this research proposes, for the first time in the field of separation of refrigerant blends, the intensification of the ED process using membrane contactors. This approach offers several advantages, as it avoids the need to disperse the gas phase in the liquid phase, thereby avoiding operational issues such as preferential pathways and flooding commonly observed in packed columns. Additionally, membrane contactors provide a very high specific surface area for mass transfer (5,000–10,000 m^{-1}), which is expected to result in a significant intensification of the process. To validate this approach, a pilot plant was design and built to perform absorption-membrane based separation of the R-410A refrigerant mixture (69.8/30.2 mol % difluoromethane (R-32)/pentafluoroethane (R-125)). Based on the solubility data reported in previous works [2], two ILs were selected as absorbents given their great selectivity towards R-32. Mass transfer was experimentally evaluated over a range of temperatures, gas pressures, and flowrates, enabling the development of a predictive model integrating the thermodynamic and kinetic properties of the mixture compounds and the IL. Remarkably, under mild temperature and pressure conditions, the most selective ILs achieved more than 50% recovery of R-32 with gas purity approaching 99.5 mol %, representing a major advance toward highly efficient, low-energy, and sustainable refrigerant recovery. Building on this success, this work introduces a groundbreaking approach in which the selective absorption in ILs is coupled with membrane technology to intensify the conventional ED process, thus setting a new benchmark for energy-efficient, high-performance, and sustainable separation of refrigerant blends.

Acknowledgements

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Liquid-Liquid Equilibria for the Binary Systems g-Valerolactone + Hydrocarbon: Experimental Data and Modelling

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g-Valerolactone (GVL) is a compound naturally occurring in fruits and other sources, attracting attention as a sustainable solvent that can be produced from biomass, e.g., lignocellulose. It has a wide range of applications such as liquid fuel, green solvent, food additive, intermediate material in producing valuable chemicals, and fuel additive[1,2]. We focus on GVL as a fuel additive. Adding GVL to fuel has little effect on engine performance and NO_x emissions. Furthermore, GVL exhibits nearly equivalent performance to ethanol, which is also used as a fuel additive[1,2]. To use GVL as a fuel additive, GVL and the fuel should form a single liquid phase[3,4]. Therefore, it is necessary to understand the liquid-liquid equilibrium (LLE) data for binary systems containing GVL and hydrocarbons. However, these experimental LLE data are not enough.

The objective of this work is to obtain the experimental LLE data for the GVL + hydrocarbon systems necessary for utilizing GVL as a fuel additive. LLE measurements were performed up to the upper critical solution temperature (UCST) using the cloud point method based on laser light scattering technique. Octane, dodecane, tetradecane, and 2,2,4-trimethylpentane were selected as hydrocarbon. Figure 1 shows the experimental LLE data for the binary systems GVL (1) + octane, dodecane, or tetradecane (2) with the literature ones[3,6]. Based on the experimental LLE data, the behavior of LLEs was compared as the carbon number of alkanes increased. Modelling of the experimental LLE data was performed using the NRTL model. The regressed NRTL parameters obtained in the modelling were validated using the Gibbs energy common tangent criterion along with the Gibbs stability test[7].

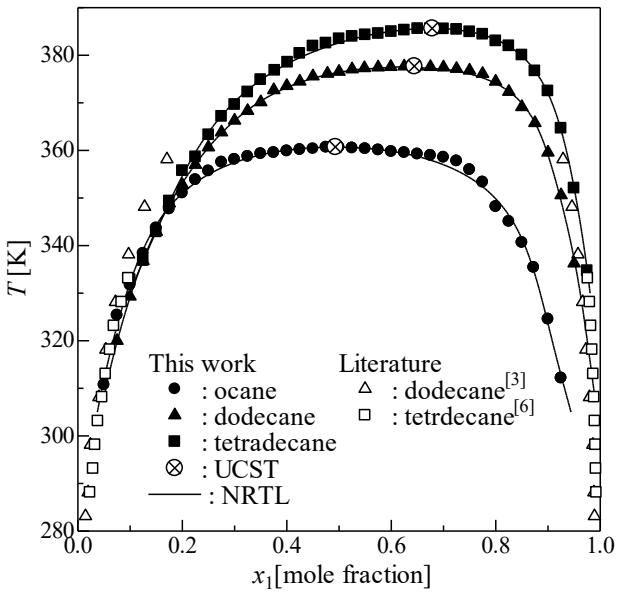

Figure 1. Experimental LLE for the binary systems GVL (1) + alkane (2).

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Advancing Thermodynamic Aproches to Model the Phase Behaviour of Peptides in Aqueous and Mixed Solvents

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The development of therapeutic peptide drugs has vastly accelerated, and they currently account for a significant proportion of the pharmaceutical market with worldwide sales of $53 billion in 2025. Accurate prediction of solubility plays a central role in drug development, since it directly influences bioavailability and formulation development. For peptide-based therapeutics, however, experimental determination of solubility presents significant challenges. Many peptides exhibit poor solubility in common organic solvents, and their tendency to undergo phase transitions often leads to formation of metastable gels, complicating reliable measurements. These limitations highlight the need for complementary approaches. From a modelling standpoint, molecular thermodynamic approaches such as COSMO-based methods and the SAFT-g Mie group contribution equation can deliver accurate predictions of complex phase behaviour, including solid–liquid solubility and liquid–liquid de-mixing, and can account for detailed molecular features. These approaches however rely on accurate experimental data, particularly the melting properties of pure peptides. Direct measurement of the melting properties of peptides is challenging due to their high melting temperatures. To overcome this, we employ fast-scanning calorimetry to determine these properties. Additionally, we measure the solubility of diglycine, dialanine, alanylglycine and glycyl-L-alanine in pure water and water + alcohol mixtures in a range of temperature (260-360 K) and at different weight ratios of the two solvents. The measurements indicate that the solubility of dipeptides decreases as alcohol concentration increases in the solution. Furthermore, the presence of alanine in the dipeptide leads to higher solubility in all the mixtures considered. We implement the SAFT-γ Mie group-contribution approach, which has been shown to deliver accurate predictions of the solubility of amino acids including the pH-solubility profiles.[1]
Here we extend the development of SAFT-γ Mie models to predict the solubility of dipeptides in the mixed solvent system of water + alcohol. The model successfully reproduces the experimentally observed trends: the predicted solubility decreases with increasing alcohol content and increases with temperature, in good agreement with the experimental data. The overall average deviation between predicted and experimental solubility is 0.011 in mole fraction, which confirms the accuracy of the SAFT-γ Mie. This agreement of the predictive calculations in turn helps in confirming the reliability of experimental data available.

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Insights on the Molecular Mechanisms Underlying Property Differences in Structurally Similar Compounds

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Polyols such as sorbitol and mannitol are widely employed in pharmaceutical, food, and cosmetic formulations. Despite differing only in the stereochemistry of the hydroxyl group at carbon 2, these diastereoisomers display strikingly different behaviours in aqueous solution. At 25 °C, for example, sorbitol is highly soluble in water (2.5 kg/kg), while mannitol dissolves much less (0.25 kg/kg). To understand the molecular mechanisms underlying these differences, molecular dynamics simulations were performed to probe hydrogen bond kinetics [1], since many differences in the behaviour of these polyols in aqueous media are often attributed to their distinct hydrogen bonding patterns [2], and several thermodynamic properties. Predicted viscosities, diffusion coefficients, vaporization enthalpies and other properties showed excellent agreement with experimental data, with deviations as low as 0–4% and correlation coefficients exceeding 0.9. Analyses of hydrogen bond lifetimes, forward and backward rate constants, and temperature-dependent Van't Hoff and Eyring relationships, as well as complementary analyses of solvent structuring and molecular fluctuations, revealed clear stereochemical effects on interactions within the systems. For instance, sorbitol forms longer-lived, disorder-prone hydrogen bonds, while mannitol faces higher barriers and slower dynamics. These insights not only rationalize the contrasting aqueous properties of sorbitol and mannitol but also demonstrate the capability of molecular simulations to capture both quantitative physicochemical differences and their molecular origins. Beyond providing understanding, the results highlight the potential of such approaches to refine predictive thermodynamic models, such as COSMO-based methods, for complex formulation of systems involving hydrogen-bonding compounds, ultimately contributing to the optimization of industrial processes.

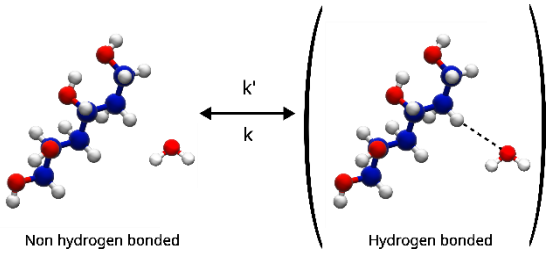

Figure 1. Schematic representation of the formation and disruption of polyol-water hydrogen bonds.

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Predictive Methods for Estimating the Thermal Conductivity of Pure Substances and Mixtures using Entropy Scaling

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The prediction of transport properties is essential for process and apparatus design. Entropy scaling has shown to provide a powerful framework for developing predictive models for transport coefficients, such as thermal conductivity. Entropy scaling was introduced by Rosenfeld[1], who showed that dimensionless transport coefficients show a univariate behavior with residual entropy, to surprisingly good approximation. Our work shows that an entropy scaling model can be extended to also account for critical enhancement of thermal conductivity. The critical enhancement is described through mode coupling theory using an analytic model by Perkins et al.[2]. When pure substance model parameters are available, the mixture thermal conductivity can be predicted using suitable mixing rules.

Where experimental data is missing predictive methods are needed to determine the thermal conductivity for unknown or poorly measured substances. This work explores two options: a traditional group contribution approach where molecules are decomposed into predefined groups with their respective contributions to the model and a machine learning approach based on neural networks. The neural network approach explores different feature vectors as well as network architectures.

Our results show that coupling entropy scaling with predictive methods yields accurate predictions of the thermal conductivity across the entire fluid region, including near-critical conditions, for both pure substances and mixtures.

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Surfactant-Based Remediation of Contaminants on Solid Surfaces and in Aqueous Environments: A Molecular Dynamics Study

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Molecular simulations were conducted to investigate the removal of contaminants from aqueous media and solid surfaces using both synthetic and biosurfactant molecules. Surfaces such as graphite, dolomite, and cellulose were contaminated with hydrocarbon molecules, and desorption studies were carried out at various surfactant concentrations.
Both ionic and non-ionic surfactants were evaluated. The results showed that anionic surfactants were more effective than non-ionic ones; however, biosurfactants outperformed both types. The analysis was based on density profiles, pair correlation functions, and adsorption isotherms.
Gas removal from aqueous media was also studied, both in the presence and absence of surfactants. Sodium dodecyl sulfate (SDS) and surfactin were used as the representative synthetic surfactant and biosurfactant, respectively, to assess their potential. The adsorption isotherms revealed that surfactin exhibited superior contaminant removal efficiency compared to SDS.
The simulations demonstrated that surfactants significantly enhance the removal of various contaminants, highlighting their potential as alternative agents in decontamination processes.

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Thermodynamics and Structures in Self-Assembly Processes of Soft Matter

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Self-assembly processes are ubiquitous in soft matter they are involved in biological processes, have important applications in chemistry, synthetic biology and in material science. The simulation at molecular level of these processes and their thermodynamic characterization is difficult especially when detailed models (atomistic or close to an atomic resolution) are used. The talk will first introduce hybrid particle-field molecular dynamics (hPF-MD).[1,2] This simulation technique car reach large length and timescales even using molecular models of high level of molecular details and systems characterized by long-range forces such as electrostatic interactions. By using this technique, it is possible to predict complex phase structures formed in aqueous solutions or in polymer melts. Several examples will be shown regarding assemblies of charged surfactants,[3] bacterial lipids,[4] and nanoparticles.[5] Moreover, recent applications of hPF-MD aimed to understand the structures of nanoplastics in water and their colloidal stability will also presented.[6]

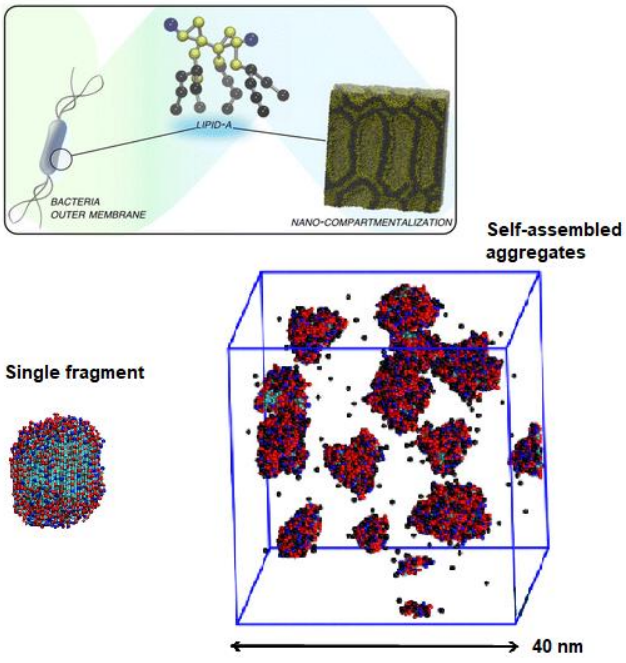

Figure 1. Top panel: schematizations of the molecular models used to describe bacterial lipids and self-assembled structures obtained. Lower panel: molecular model of a nano-fragment of polyethylene and aggregates of fragments in water solution.

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Revisiting the classification of physisorption isotherms with classical density functional theory

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The theoretical study of confined fluids is relevant for applied problems, such as the characterization of porous materials, and fundamental questions, such as understanding the mechanism of adsorption and desorption. The physisorption of gases is analysed typically at constant temperature for various pressures, and the corresponding isotherms have been classified in standard IUPAC reports [1], mainly based on empirical considerations. We propose to reorganize and extend this classification, based on fundamental thermodynamic considerations. The effect of temperature, pore size, and intensity of the fluid–solid interactions is systematically studied [2]. Classical density functional theory (cDFT) [3] is used to predict the microscopic structure of the confined fluids and determine the physisorption isotherms over a large range of thermodynamic conditions.

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From AI to Thermodynamics: Predicting Pure-Component EOS Inputs with Ensemble Learning

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Equations of state (EoS) play a central role in thermodynamics and chemical engineering, as they provide a fundamental relationship between pressure, temperature, and molar volume of pure fluids. They form the backbone of phase equilibrium calculations and are indispensable for predicting vapor pressures, boiling points, and property changes during vaporization or condensation. When coupled with suitable expressions for ideal-gas heat capacities, EoS also allow the estimation of enthalpy, entropy, and exergy variations. This makes them essential components of industrial process simulators, which rely on accurate thermodynamic predictions for the design, optimization, and safety analysis of chemical processes.

Among the many EoS proposed in the literature, cubic models have retained a pivotal position because of their simplicity, robustness, and proven accuracy for many fluids. The Peng–Robinson and Redlich–Kwong–Soave equations are the most widely used representatives of this class. Their relatively simple mathematical structure enables straightforward implementation and parameterization. However, their predictive accuracy crucially depends on three input parameters: the critical temperature (Tc), the critical pressure (Pc), and the acentric factor (ω). These quantities are not always available experimentally, especially for novel or scarcely studied molecules, which creates a strong need for accurate and reliable estimation methods.

To address this challenge, we have developed an ensemble learning approach that leverages the combined strengths of multiple machine learning algorithms. Ensemble methods are known to reduce bias and variance compared to single-model approaches, thereby improving robustness and generalization capabilities. In our work, the input space is defined by molecular descriptors automatically generated from the open-source Python library MORDRED, which computes more than 1,800 descriptors capturing structural, topological, and physicochemical features of a molecule. The learning database is composed of experimental Tc, Pc, and ω values for over 1,700 compounds, spanning a wide diversity of chemical families.

The performance of the proposed model has been rigorously evaluated. Cross-validation procedures and external test sets were used to assess its generalization capability, and results were compared against those of several machine learning approaches recently reported in the literature. Our ensemble model consistently outperforms alternative methods, achieving lower prediction errors and improved reliability across different chemical families. These results highlight the advantage of combining multiple algorithms to capture the complex, nonlinear relationships between molecular structure and critical properties.

In addition to its scientific contribution, this work also aims at providing a practical tool to the community. We have therefore implemented our model in a freely accessible web application that allows users to predict Tc, Pc, and ω directly from the SMILES (Simplified Molecular Input Line Entry System) notation of a molecule. The tool is available at: https://lrgp-thermoppt.streamlit.app/

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COSMO-NET: Efficient Graph Neural Network Surrogates for COSMO-Based Molecular Descriptors

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Predictive thermodynamic models are crucial for exploring chemical space in molecular design and discovery across diverse applications, including but not limited to the chemical and pharmaceutical industries [1]. Among the most widely used are COSMO-based approaches, including COSMO-RS [3] and COSMO-SAC [3]. At the core of these models is a quantum mechanics (QM) calculation in a perfect conductor used to obtain the molecular surface screening charge density. From this, the surface charge density distribution ($p(\boldsymbol{\sigma})$) and, when required, its non-hydrogen bonding ($p^{NHB}(\boldsymbol{\sigma})$), hydrogen bonding of OH functional groups ($p^{OH}(\boldsymbol{\sigma})$), and hydrogen bonding of other functional groups ($p^{OT}(\boldsymbol{\sigma})$) components, along with the COSMO surface area (A) and cavity volume (V) are obtained. The statistical thermodynamic layer uses these descriptors, via surface-segment interactions (electrostatic misfit and hydrogen bonding), to compute chemical potentials, activity coefficients, partition coefficients, and related properties. The workflow is accurate but computationally demanding because of the QM step (often involving conformer sampling and geometry optimization). To address this limitation, we have developed graph neural network surrogates, specifically a Directed Message Passing Neural Network (DMPNN) [4] and a Graph Convolutional Network (GCN) [5], that predict COSMO descriptors ($p(\boldsymbol{\sigma})$, A, V) with high accuracy as drop-in replacements for the costly per-molecule QM COSMO calculations, delivering both speed and precision. Training was performed on a dataset of more than 16,000 molecules generated through an automated quantum chemistry workflow. The results indicate that DMPNN yields superior accuracy for surface charge density distributions, whereas GCN performs better for surface area and volume predictions. We therefore propose COSMO-NET, a hybrid that uses GCN for A and V and DMPNN for $p(\boldsymbol{\sigma})$, $p^{NHB}(\boldsymbol{\sigma})$, $p^{OH}(\boldsymbol{\sigma})$, and $p^{OT}(\boldsymbol{\sigma})$. In downstream evaluation, COSMO-NET attains a mean absolute error of 0.31 for the octanol–water partition coefficient of the test set containing 20% of all compounds in the database. Our findings demonstrate that ML surrogates remove the main QM bottleneck, enabling high-throughput screening across a far larger chemical space.

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Prediction of the Surface Tension of Amine-Based Solvents with a New Group-Contribution Machine-Learning Model: GriTo

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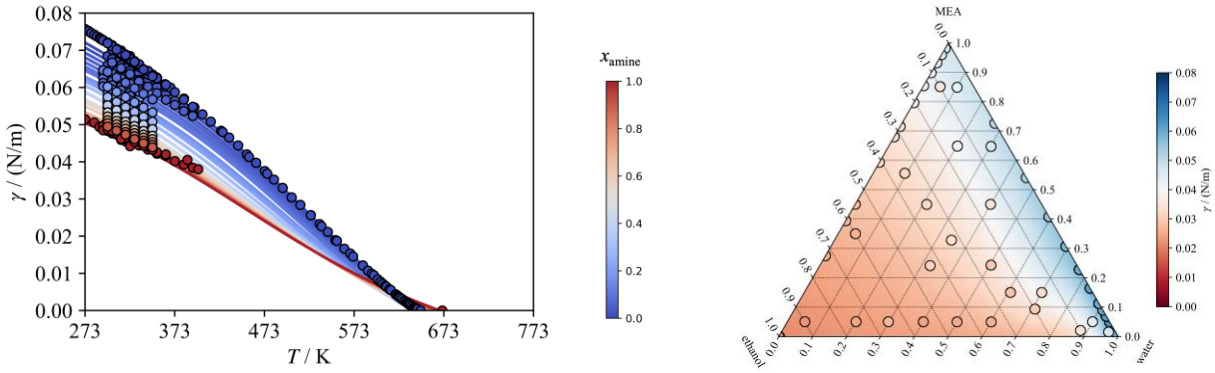
The prediction of the surface tension of mixtures is a challenge for standard approaches based on statistical physics, as well as for empirical and machine learning (ML) methods. Following a rigorous methodology, we present a new group-contribution ML model, GriTo (for "Groups in, Tension out"), that can be used to predict the surface tension of complex fluids and their mixtures. The only inputs of the model are the temperature and group composition that characterize the system (using the groups defined for use in the SAFT-g Mie equation of state [1]), enabling predictions for new compounds. In addition to hydrocarbons, alcohols, and water, amine-based solvents are considered as they constitute a significant solvent family used in carbon capture processes [2]. The surface tensions calculated with GriTo are in very good agreement with the experimental data for a large range of thermodynamic conditions. Examples of surface tension calculations are shown in Figure 1(a) for a binary mixture and Figure 1(b) for a ternary mixture.



(a) (b)

Figure 1. (a) Surface tension of monoethanolamine (MEA) + water as a function of temperature. The experimental data points are represented with circles. The calculations with GriTo are represented with the curves at each composition for which experimental data are available. (b) Surface tension of MEA + ethanol + water at 303 K, on a mole fraction basis. The colour of the circles represents the experimental surface tension. The background map colour represents the surface tension calculated with GriTo.

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Confidentiality-preserving Training of Thermodynamic Models with Federated Learning

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Accurate thermodynamic models are essential for the design of chemical processes. However, many of the high-value experimental data required for model development and training remain locked in proprietary industrial databases, which are rarely shared due to concerns about revealing business-sensitive information.

In this work, we introduce federated learning (FL) [1] into the development of thermodynamic models, enabling the confidential integration of proprietary data into the training process. We investigate the practically relevant problem of parameterizing models of the excess Gibbs energy, whereby we study two cases: parameterizing the physical group-contribution model UNIFAC [2] and training the hybrid physics-informed machine-learning model HANNA [3]. In both cases, the database was drawn from the Dortmund Data Bank, and we created a synthetic scenario with multiple clients, each representing a hypothetical company. Each client had exclusive access to a local dataset (as a proxy for its proprietary data) as well as to a shared dataset (as a proxy for public data).

In the FL approach, each client fits the model parameters to its local and the shared data, and sends only the fitted parameters – not the data – to a central server. There, the parameters are aggregated into a global model, which is redistributed to the clients, where it is used as prior knowledge. We explore different options for incorporating the prior knowledge, specifically using the global model to generate informed prior distributions over the model parameters in a Bayesian refitting process, as well as using the global model's parameters as initialization for the local retraining step. In all cases, the procedure was repeated for 10 FL epochs, during which the global model parameters converged.

The global and local models were evaluated on independent test sets at each epoch, showing increasing prediction accuracy throughout the FL process. The final global models outperform models trained only on local data and match reference models trained on the full combined dataset. These results highlight the strong potential of FL to enable collaborative thermodynamic model development using confidential fluid property data—without requiring disclosure of the data, components, or systems involved.

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Terpene-Based Eutectic Mixtures as Green Solvents for CO_2 Capture: Experimental Characterization and Molecular Insights

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The search for sustainable solvents for CO_2 capture represents a prominent challenge in the development of environmentally friendly separation processes. Terpene-based eutectic mixtures constitute a promising class of candidates owing to their renewable origin, low toxicity, and favorable safety profile [1]. Among terpenes, camphor has been identified through COSMO-RS screening as exhibiting a strong affinity toward CO_2 [2]. However, its elevated melting point (≈ 175–180 °C) hinders direct application under practical conditions. To overcome this limitation, eutectic mixtures of camphor with menthol, thymol, carvone, and 1,8-cineole were prepared, resulting in stable liquids near ambient temperature and thereby enabling their thermodynamic characterization as a solvent. Density and viscosity of the eutectic mixtures were measured over a temperature range of 30–60 °C, while CO_2 solubility was determined isothermally in the same interval at pressures up to 20 bar. To complement the experimental measurements, the perturbed chain–statistical associating fluid theory (PC-SAFT) was employed to model the mixtures as multicomponent systems [3], allowing the exploration of different molar compositions and their influence on solvent performance across a broad range of thermodynamic conditions. In parallel, molecular dynamics simulations are being conducted to reproduce macroscopic observables such as density, viscosity, and solubility, while also providing microscopic insight into the structural organization of the eutectic network and the local environment of CO_2 within the liquid phase.

The combination of targeted experiments, molecular thermodynamic modelling, and atomistic simulation establishes a coherent framework for understanding structure–property relationships in terpene-derived eutectics. This integrated approach demonstrates the potential of these mixtures as a versatile platform for the rational design of next-generation green solvents, while laying the thermodynamic foundation necessary for future evaluation of their performance in large-scale CO_2 separation processes.

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Twenty Years of Deep Eutectic Solvents: Are Thermodynamic Models Ready for Industry?

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More than two decades have passed since Deep Eutectic Solvents (DESs) were introduced as a novel class of green solvents in 2003 by Abbott et al. [1], offering unique physicochemical features and attracting worldwide scientific attention. By September 2025, more than 16,700 publications had been indexed in Scopus, demonstrating the rapid expansion of this research domain. Despite this remarkable growth, a fundamental question persists: have DESs successfully crossed the boundary from laboratory-scale studies to industrial-scale deployment, or do they remain largely confined to academic investigations?

A thorough understanding of their physical and thermodynamic properties is essential for answering this question. Industrial adoption of any solvent relies on reliable knowledge of physical and thermodynamic properties. Accurate prediction of these properties forms the foundation for solvent design, process simulation, and optimization. Without robust models, the transition of DESs from promising green media to practical industrial tools remains uncertain. Since 2019, our research group, Des.Solve, has been dedicated to building predictive and correlative frameworks to address these gaps. Over the past six years, we have developed and validated more than 20 thermodynamic models encompassing classical group and atom contributions, semi-empirical correlations, EoS-based models, and hybrid machine learning approaches. These models have been applied to a wide range of properties, including density, viscosity, surface tension, thermal and electrical conductivity, refractive index, speed of sound, heat capacity, and the solubility of critical gases such as CO_2, H_2S, and SO_2. In this presentation, we will offer a panoramic overview of two decades of progress in the thermodynamic modelling of DESs, with emphasis on the interplay between theory, data, and application. We will discuss the current strengths and limitations of existing models, identify key knowledge gaps that hinder industrial adoption, and propose directions for future research that could strengthen collaboration between academia and industry. Particular attention will be given to the role of machine learning and data-driven models as a complement to traditional thermodynamic approaches. By drawing on our accumulated experience, this work aims not only to summarize the state of the art but also to stimulate dialogue on how DES research can evolve over the next decade, transforming DESs from an academic trend into viable industrial solvents for sustainable chemical processes.

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A thermodynamic framework to design greenhouse gas capture units using phosphonium-based ionic liquids

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The growing concern over global greenhouse gas (GHG) emissions has prompted the development of advanced methods for their recovery, separation, and potential reuse. Carbon dioxide (CO_2) and fluorinated gases (F-gases) are among the main targets of these strategies. Absorption into novel liquid solvents—particularly ionic liquids (ILs)—has emerged as a promising approach for removing harmful compounds from the atmosphere and transforming them into valuable, more sustainable products.

Ionic liquids are of special interest due to their low vapor pressure and the ability to tailor their solvent power by tuning cation–anion combinations according to the composition and operating conditions of the target gas stream. Although several phosphonium ILs have shown promising performance for GHG absorption, a comprehensive thermodynamic characterization is still needed to identify the most suitable candidates.

In this work, the solubility of CO_2 and F-gases in quaternary phosphonium-based ILs was investigated using the soft-SAFT equation of state [1]. New molecular models were developed within the soft-SAFT framework, with association parameters estimated through DFT calculations [2,3]. The analysis of molecular charge distributions enabled the identification of relevant interaction sites. Soft-SAFT was then employed to predict thermodynamic and absorption properties over a wide range of conditions, while the free-volume theory was used to estimate viscosities. The analysis included ternary systems where the competition between gases is evaluated.

Finally, solvent selection criteria were established considering, not only absorption capacity but also: (a) working capacity upon cycling, (b) selectivity toward the target gas, (c) viscosity, and (d) desorption enthalpy. These indicators were evaluated to identify the most suitable phosphonium-based ILs for efficient greenhouse gas capture at different flue gas compositions.

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Inclusion Complexation of Native and Functionalized α-, β-, and γ-Cyclodextrins with PFAS

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β-Cyclodextrin (β-CD)-based polymers have been widely used for per- and polyfluoroalkyl substances (PFAS) removal from drinking water, showing high adsorption capacity. Although the mechanism of PFAS capture by these polymers involves the synergistic effect of different physical and chemical phenomena, it is important to understand the host-guest binding between β-CD and PFAS, as it governs the primary removal process. In this study, we performed molecular dynamics simulations using the attach-pull-release method[1] to model CD-PFAS inclusion complexes in aqueous solution. To study host-guest binding, we computed the Gibbs free energies, enthalpies, and entropies of the process.

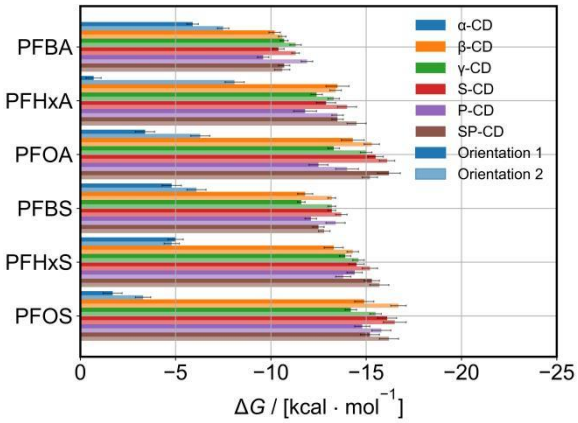

Figure 1. Gibbs free energies of host-guest binding systems using the explicit solvent model.

For all PFAS studied, our results exhibited trends consistent with physicochemical intuition. To explore how the local environment influences guest behavior in the absorbent matrix, we functionalized β-CD with one or two hexafluorobenzene groups, which are commonly used as linkers in CD-polymers. Finally, we utilized empirical linear free energy relationships to estimate reactivity constants for the CDs variants interacting with PFAS. Overall, this study investigates the interaction developed between PFAS and CD variants (native and modified) in silico, using computational calorimetry methods, probing the underlying molecular mechanisms, and laying the framework for future research into PFAS removal using CD-based polymers.

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Sustainable Epoxy Network Design by Multiscale Simulation: Towards High-Performance Membranes for Gas Separation

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The decarbonisation of industrial gas separation remains a central challenge for sustainable process engineering. Conventional separation methods are energy intensive, motivating the development of next generation membranes with high selectivity, stability, and scalability. In this study, we present a computationally driven framework for the design of epoxy networks derived from plant-based phenolic acids as sustainable candidates for carbon dioxide separation from nitrogen and methane streams.

The work integrates a hierarchical crosslinking algorithm with multiscale molecular simulations to establish quantitative structure-property relationships in highly crosslinked polymers. In this work, the crosslinking is initiated in a coarse-grained (CG) representation, where thermally activated proximity-based bonding efficiently generates high-conversion networks. These CG structures are subsequently reverse-mapped to atomistic resolution, enabling precise evaluation of the glass transition temperature, density, free-volume topology, and elastic moduli. This approach circumvents the limitations of traditional all-atom crosslinking while preserving atomistic simulations accuracy in property prediction. This computational strategy provides a transferable platform for screening and optimising sustainable network polymers.

Gas transport behaviour is evaluated using equilibrium molecular dynamics and grand canonical Monte Carlo simulations to obtain solubility, diffusivity, and permeability for carbon dioxide/nitrogen and carbon dioxide/methane mixtures. A data-driven analysis is then employed to correlate chemical functionality, curing agent type, and crosslink density with transport performance, identifying molecular motifs that enhance carbon dioxide selectivity through electrostatic interactions. The results reveal that fine-tuning crosslink architecture, local free-volume connectivity and incorporation of some high carbon dioxide affinity groups can yield substantial improvements in carbon dioxide permeability without sacrificing mechanical integrity.

From Small Molecules to Colloidal Assemblies: Towards a Unifying Theory of Nanoscale Matter

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Currently, there exists a large space of experimental parameters that can be employed to direct nanoscale assemblies. Tuning such experimental handles produces different modes of inter-particle associations such as hard particle packing, soft inter-penetrable ligand shells, or patchy/selective attraction. Such synthetic strategies have been leveraged to create nanoscale synthons with predictive control over shape, size, and interparticle interactions. However, due to this expansive suite of experimental handles available for particle synthesis, no theoretical framework exists that is capable of performing rational design across the entire experimental phase space. Here, we present a unifying theory of nanoscale matter that addresses the above limitations. We first discuss insights into how to imbue selective, directional, and/or symmetry breaking interactions into nanoscale building blocks. We then show how such interactions can be toggled on/off via experimentally relevant stimuli such as temperature, external field, and/or solvent modulation and predict how synthon reconfigurability shifts the thermodynamically stable assembly structures. Our works provide unique insights into nanoscale synthesis that can be leveraged to guide the future design of complex building blocks capable of accessing novel and reconfigurable assemblies.

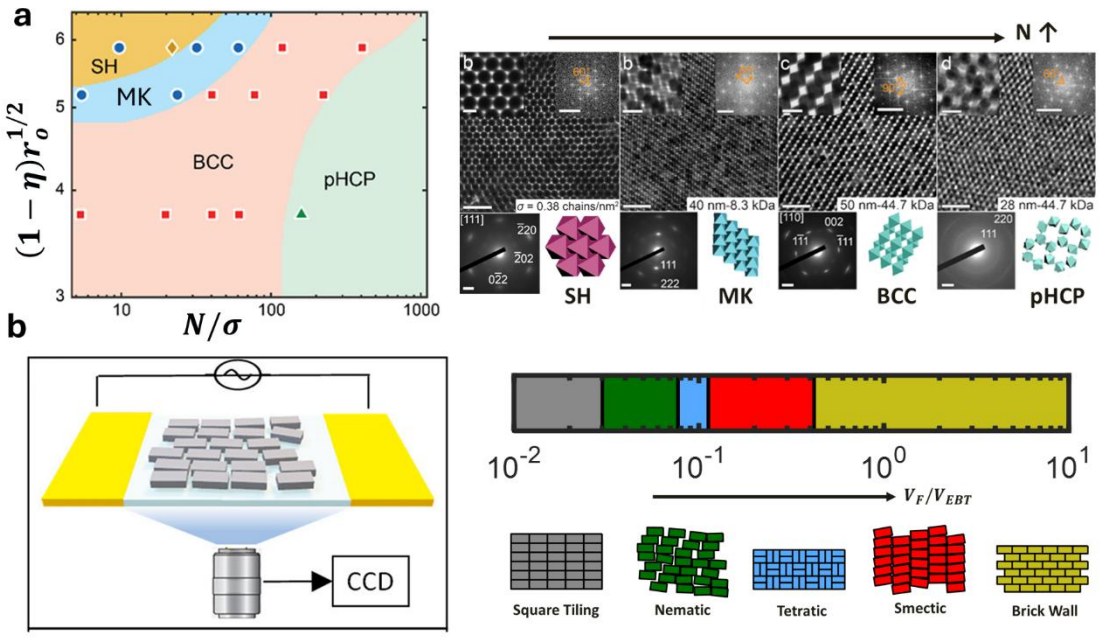

Figure 1. Computational design of a) polymer coated nanooctahedra with tuneable superstructural phase transition[1,2] and b) field-mediated symmetry breaking and directed assembly of nano-rectangles.

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Mechanical Behavior of Polymers under Shock Loading: a Molecular Dynamics Study

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Understanding the behavior of polymers under shock loading is essential for their applications in car equipment, aircraft, space structure and plastic bonded explosives. Despite much effort, both experimentally and numerically over the last twenty years [1,2], there are specificities of the shock behavior of polymers that are still unclear. These include the relation of the shocked state to the dynamic glass transition. Direct shock simulations of three different polymers, cis-1,4-polybutadiene, polystyrene and phenoxy resin, with different glass transition temperatures, were performed [3]. First, I will show that the polymer melts created in this work have a structure factor and a Hugoniot locus very close to their experimental counterparts. Second, I will focus on the shear stress relaxations behind the shock front. It is found that the polymers with the highest glass transition temperature have the most slowly relaxing shear stress behind the shock front. Finally, to refine the local stress behavior around the shock front, I will present a new expression of the local stress tensor for molecular systems which verifies by construction the local balance of linear momentum [4,5].

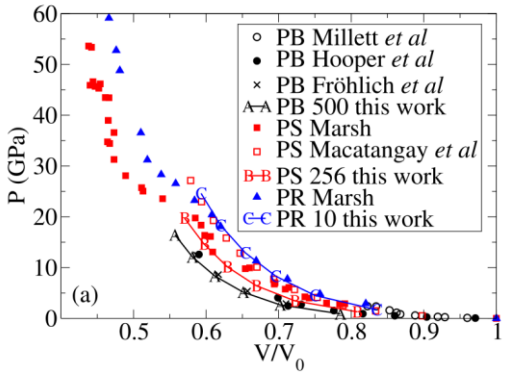

Figure 1. Hugoniot locii of polybutadiene (PB), polystyrene (PS) and phenoxy resin (PR).

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Ready-to-use Durvillaea incurvate extracts using edible deep eutectic solvents

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The increasing prevalence of non-transmissible chronic diseases related to sedentary lifestyles and unbalanced nutrition, such as cardiovascular diseases and metabolic syndrome, has driven the search for emerging strategies aimed at prevention. In this context, natural ingredients with bioactive properties have emerged as a promising alternative. Seaweeds are a particularly rich source of bioactive compounds, including polyphenols and polysaccharides, which have been reported to exert diverse biological activities [1]. In Chile, Durvillaea incurvata is a brown seaweed distributed along the entire coast and has recently attracted attention due to its wide range of health-promoting effects. Previous studies have demonstrated its strong antioxidant capacity [2], antihyperglycemic properties [3] and antimicrobial potential [4]. These bioactivities are particularly associated with the presence of polyphenols, which in brown seaweeds can account for up to 30% of their dry weight. Nevertheless, most studies rely on extracts obtained with organic solvents, which are potentially toxic for human consumption and environmentally hazardous. To overcome this limitation, this work proposes the use of food-grade deep eutectic solvents (DES) as a sustainable alternative for the production of ready-to-use D. incurvata extracts with bioactive properties.

In this study, betaine- and choline bitartrate-based DES combined with different organic acids were designed and pre-selected using COSMO-RS computational screening, which allowed the prediction of infinite dilution activity coefficients to identify the most suitable solvent systems. Extractions were subsequently carried out under different operational conditions, varying temperature and extraction time. As conventional controls, 75% ethanol, 70% acetone, and 70% methanol solutions were employed. The resulting extracts were characterized in terms of total phlorotannin content, antioxidant capacity (DPPH and ORAC assays), and in vitro α-glucosidase inhibition. Furthermore, extract stability was evaluated by monitoring phlorotannin content over one month of storage under ambient, refrigerated, and frozen conditions. Finally, toxicity and in vivo α-glucosidase inhibition were assessed using zebrafish as a model organism.

Preliminary results show that seaweed extracts obtained with DES presented higher phlorotannin content and superior antioxidant capacity compared to conventional controls. Both in vitro and in vivo evaluations revealed a consistent inhibitory effect on α-glucosidase, with DES extracts achieving 50% inhibition at lower concentrations than acarbose, a standard antidiabetic drug. Overall, these findings demonstrate that betaine- and choline bitartrate-based DES provide a promising strategy for the production of ready-to-use functional seaweed extracts with potential applications in the prevention and management of chronic metabolic disorders.

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From Molecular Simulation to Equation of State: CO_2 Adsorption Enthalpies on CALF-20

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We evaluate two methodologies to compute the enthalpy of adsorption (ΔH_{ads}) of CO_2 on CALF-20, namely, molecular simulations and a molecular-based equation of state (EoS) [1], originally developed from the SAFT-VR Mie EoS. Using Grand-Canonical Monte Carlo (GCMC) simulations, ΔH_{ads} is computed from energy/particle fluctuations. A transferable three-site model is used for CO_2 [2], with the framework treated as rigid and described using the DREIDING force field [3]. The EoS is initially used to correlate the isotherms obtained from the GCMC simulations. Such a formalism allows for the calculation of ΔH_{ads} directly from the EoS through classical thermodynamic relations that connect the enthalpy and the Helmholtz energy of each phase. ΔH_{ads} at low-coverage CO_2 obtained from GCMC simulations (-36 kJ·mol^{-1}) is comparable with the reported experimental value (-39 kJ·mol^{-1}) [4]. The loading-dependent decline reported in the literature [4] is also reproduced. Results obtained from the EoS underestimates the GCMC results by approximately 16%.

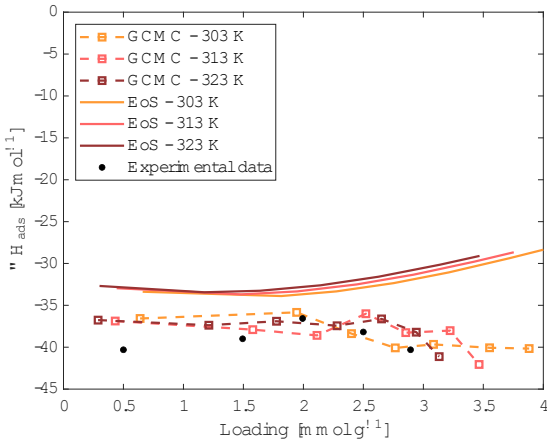

Figure 1. CO_2 adsorption enthalpy on CALF-20 at 303–323 K and 0.01–1.5 bar. Full lines correspond to EoS predictions, dashed lines with square markers to GCMC simulations, and solid dots to experimental data [4].

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Thermodynamic and dynamic aspects of glass transition of water and aqueous systems

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The glass transition remains one of the most intriguing problems in applied thermodynamics, with relevance to fields such as polymer chemistry and pharmaceutical formulations. The glass transition of water, which is exceptionally difficult to observe experimentally, continues to fuel active scientific debate. Two primary approaches have traditionally been employed to investigate the glass transition in pure glass formers and their mixtures: the thermodynamic approach and the relaxation dynamics approach. Despite decades of research, no physically rigorous link between these approaches has been established.

This study combines molecular dynamics simulations with theoretical analysis to examine the glass transition in water and water-based systems. Using analytical equations that connect the glass transition temperature to the relaxation time, the dynamic and thermodynamic facets of the glass transition in aqueous systems are explored. The analysis demonstrates that accurate interpretation of glass transition behavior in water requires accounting for the interplay between the glass transition and the transition between high-density and low-density liquid states [1] in supercooled water. Extending this approach to mixtures of glass formers reveals how the Gordon–Taylor equation emerges naturally within both the thermodynamic and relaxation dynamics approaches. Nonetheless, precise prediction of glass transition properties in mixtures demands a thorough understanding of the thermodynamic and dynamic aspects of mixing.

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How renewable can green ammonia be? How Exergy Costs affect Natural Resources Availability and Impact Planetary Boundaries

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The importance of renewable infrastructures on the development of new production systems (energy and chemicals) has been significantly increasing. Consequently, a product's degree of renewability and levelized lifetime production efficiency must account for all natural resources' and raw materials lifecycle production chains. Therefore, this study investigates how renewable green ammonia production can be based on renewable and non-renewable exergy costs. Firstly, we verify how the exergy costs of renewable (sunlight, wind, water, soil, and air) and non-renewable resources (fossil fuels, white hydrogen, and critical raw materials) affect the physical requirements for ammonia production via the Haber-Bosch process under different weather and resources availability conditions. Then, we evaluated the current and future physical costs of producing ammonia up to 2050 under different plant load operation conditions with the stream recirculation strategy and checked how the hybridization of electricity sources affect both the plant's load strategy and flexibility *versus* efficiency dilemma. The circular thermoeconomic model developed on Aspen Plus v14 and integrated with TAESLab explores ammonia production on a small-scale integrated multi-product ammonia plant with different sources of electricity (based on IEA NZE for solar PV, wind, hydro, and grid), hydrogen (white and green via alkaline, proton and anion-exchange, and solid oxide electrolysis), nitrogen (cryogenic and pressure swing adsorption), water (natural and desalination), soil (exergy) and air. This innovative methodology includes the exergy costs of all materials required for each technology infrastructure commissioning. Our findings shed a light on how the green ammonia's physical costs will affect future projected applications on the fertilizers sector, as an energy vector, and as a fuel. They also emphasize how natural renewable and non-renewable resources, and infrastructure costs propagate through the ammonia and by-products chain production. Therefore, this work highlights the required energy transition impact on the small-scale ammonia production for regions with different natural resources availability on the world and on the planetary boundaries.

Keywords: Thermodynamics of sustainability, Exergetic life-cycle analysis, renewable energy sources, critical raw materials, green ammonia, green hydrogen, planetary boundaries

Third Virial Coefficient of Hydrogen from First Principles

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Hydrogen is expected to play a key role in the transition to renewable energy sources, which requires accurate and comprehensive thermophysical property data. In this context, theoretical methods can complement experiments with the advantage that they can cover the temperature regime below the boiling point of liquid nitrogen without excessive difficulty and can also be extended to high temperatures.
In this work, a nonadditive three-body potential for hydrogen is developed. The interaction energies are obtained at the complete basis set limit using supermolecular coupled-cluster calculations with up to single, double, triple, and quadruple excitations (CCSDTQ). The potential energy surface (PES) is described by a spherically-averaged extended Axilrod–Teller–Muto (EATM) potential in combination with an analytical treatment of the long-range induction [1,2].
We use this potential in combination with the existing *ab initio* pair potential of Patkowski *et al.* [3] to calculate the third virial coefficient of *para*-hydrogen in the temperature range 20–2000 K by means of path-integral Monte Carlo calculations. The results are compared with experimental and theoretical data from the literature. The developed potential can be used in future work to investigate thermodynamic properties at higher pressures by means of path integral Monte Carlo simulations of bulk phases.

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Novel Computation of the CO_2 Hydrate Phase Diagram: Identifying the Hydrate-Liquid-Vapor Coexistence and Quadruple Point Q_2

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Carbon dioxide (CO_2) hydrates hold promising applications in capturing and separating CO_2 for climate change mitigation, while computer simulations are increasingly used to study their formation and stability, provide valuable insights into their underlying mechanisms. In this work, we perform Molecular Dynamics simulations to compute the three-phase coexistence line: CO_2 hydrate - Liquid water - Vapor CO_2, a computation that was previously inaccessible. To achieve this, we employ a novel solubility-based method [1,2], which allows us to accurately evaluate the coexistence line. Water and CO_2 are modelled using the TIP4P/Ice [3] and TraPPE [4] force fields respectively. Our results exhibit excellent agreement with experimental data [5], successfully reproducing the Hydrate-Liquid-Vapor equilibrium line of CO_2 + water phase diagram for the first time. Finally, we have determined the quadruple point (Q_2) where the four phases, namely Hydrate, Liquid water, Liquid CO_2, and Vapor, coexist. Our result for Q_2 show remarkable agreement with experimental observations [5], validating the accuracy of our findings.

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Monte-Carlo simulations of vapor-liquid phase equilibria of the argon-xenon binary system in the context of noble gases detectors

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Liquid Argon (LAr) detector technology has undergone impressive development in recent years in astroparticle physics and medical applications. In the liquid Argon (LAr) detector technology, the effect of doping Argon with Xenon improves the efficiency of the detectors. Argon-xenon detectors operate at atmospheric pressure and at temperatures for which the mixture Ar+Xe is in the liquid phase. Although noble gases have been widely studied, only few experimental data and some modeling attempts to describe the system phase diagram have been reported in the literature[1,2]. The aim of this study is to describe the phase diagram, accuratly determining the solubility of xenon in the liquid phase and well identify the liquid zone by using classical molecular simulations and new experiments. In this work, we investigate vapor-liquid equilibria of the argon-xenon mixture at atmospheric pressure with Gibbs-Ensemble Monte-Carlo in the isothermal-isobaric ensemble. Appropriate Mie potentials optimised for vapor-liquid phase equilibria simulation were taken from the litterature[3]. Vapor-liquid equilibria in the Ar+Xe mixture are very restrained domains of the phase diagram with composition that can be of the order of magnitude of ppms. This constitutes a challenge for molecular simulation methods. Our results are in quite good agreement with predictions from the Peng-Robinson equation of state[4]. This study will be extended to phase equilibria involving solid phases in order to have a complete knowledge of the thermodynamic behavior of the argon-xenon system.

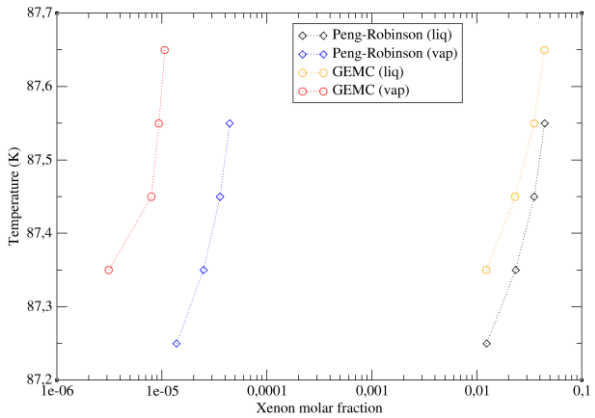

Figure 1: Comparison between liquid-vapor equilibria predicted by Peng-Robinson equation of state and Gibbs-Ensemble Monte-Carlo simulations for the argon+xenon binary mixture.

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Confined active colloids: Wall accumulation and motility-induced phase separation

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Active Brownian particles (ABPs) serve as a versatile model for synthetic active matter, such as self-propelled colloids, combining persistent propulsion with Brownian motion. The interplay between self-propulsion and thermal fluctuations gives rise to emergent behaviors that are distinct from those of equilibrium systems. When confined, ABPs exhibit propulsion-induced wall accumulation. At high confined densities and particle activities, they also display pronounced structural phenomena, including confined and surface motility-induced phase separations (MIPSs). Confined MIPS manifests as the coexistence of solid and dense phases, whereas surface MIPS involves the formation of lattice-like structures near the confining walls. We investigate ABPs confined in slit pores using overdamped Langevin dynamics, analyzing their wall accumulation and MIPS behavior as functions of particle activity and slit width, at both gas and liquid densities. Furthermore, we examine the correspondence between confined ABPs and their equilibrium counterparts, confined fluid particles capable of completely wetting the slit walls. This study provides insights into the mechanisms governing wall accumulation and phase behavior in confined active matter, thereby deepening our understanding of how nonequilibrium activity influences collective organization. Our findings are relevant to microfluidic and lab-on-a-chip applications, where controlled manipulation of active particles can be exploited for targeted transport, sorting, and trapping.

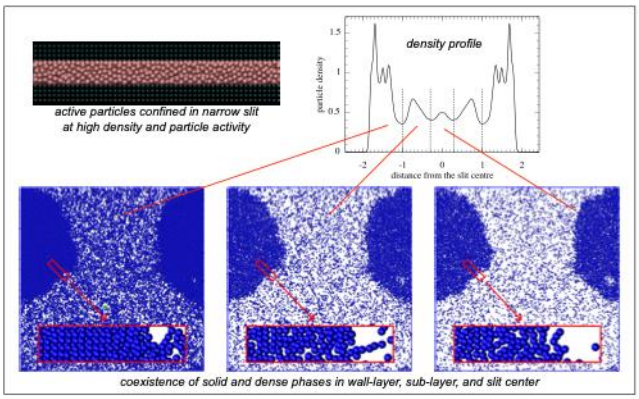

Figure 1. ABP propulsion-induced wall accumulation and MIPS under slit confinement.

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Predicting equilibrium and kinetics of esterification reactions using electrolyte thermodynamics and the importance of H_3O^+ activity

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Esters play an important role in the chemical industry such as in the biofuel production, polymer synthesis, food production and washing powder. It is therefore of great interest to optimize the reaction conditions to boost the reaction equilibrium as well as the reaction kinetics of these esterification reactions. In past works, PC-SAFT was used to predict the reaction equilibrium very well but showed problems at predicting the reaction kinetics at different system conditions and compositions [1,2]. In this work, ePC-SAFT was employed to predict the effect of different additives (especially strongly non-ideal solvent mixtures (SNISMS)) on the equilibrium and kinetics of several homogeneously catalysed esterification reactions (e.g., acetic acid or formic acid esterification with ethanol). Thermodynamic activity-based approaches were used for modelling of equilibrium and kinetics, and the latter also included the thermodynamic activity of the catalytically active species. This approach was chosen to overcome the shortcomings of earlier kinetic approaches used in (e)PC-SAFT modelling. The dissociation of the catalyst (strong acid) was also accounted for by using the dissociation constant of the strong acid in the model framework and treating the dissociation as instantaneous (always in equilibrium) compared to the esterification reaction. In this context, the modelling of ions in the reaction systems was given special attention since the catalytically active species is ionic in nature. A modified Born term was used in ePC-SAFT that includes effects like the solvation shell around ions and a new mixing rule for the dielectric constant in the system [3]. Using this new approach, model parameters such as the binary interaction parameters between the H_3O^+-ion and the other reactants were successfully parametrized (e.g. using Gibbs energy of solvation at infinite dilution).
Different reaction conditions, such as temperature, reactant molar ratios, additive amount, catalyst concentrations and different catalysts (e.g., HCl or Polyoxometalates) were screened using this approach and validated using experimental data. ePC-SAFT was able to describe the equilibrium and kinetics for many different reaction conditions and allowed for a reduction in experimental effort by eliminating conditions and additives that had an unfavourable effect on the reaction parameters according to the screening process. In addition, some esterification reactions form a second liquid phase over the cause of the reaction. This effect was also taken into consideration by coupling reaction equilibrium and phase equilibrium calculations. Choline chloride and acetonitrile were identified as beneficial components for the reaction equilibrium of the investigated esterification reactions.

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POSTERS

Abstracts

Bubble point pressure measurements and predictions for dimethyl ether – chloroform – ethanol and propane – chloroform – ethanol at 313.15 K

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A solvent mixture, chloroform – ethanol, has been sometimes employed for extraction of lipids from biomaterials. In this study, the authors proposed the solvent mixture to add a new performance, rapid vaporization without remaining solvent, by pressurizing with dimethyl ether or propane. Then, the bubble point pressures were measured for dimethyl ether – chloroform – ethanol and propane – chloroform – ethanol, where the mole ratio of chloroform: ethanol was set to be 1:1, by use of a static apparatus at 313.15 K. The measurements were also carried out for dimethyl ether – chloroform, dimethyl ether – ethanol at (283.15-313.15) K, and propane -chloroform at 313.15 K. **Fig. 1** shows the typical experimental results for dimethyl ether – chloroform, dimethyl ether – ethanol and dimethyl ether – chloroform – ethanol at 313.15 K. As shown in **Fig.1**, the bubble point pressures of the binary, dimethyl ether – chloroform, were lower than those of ideal solution. The other binaries showed the bubble point pressures higher than those of ideal solution. The results suggested that a strong interaction will be existing between dimethyl ether and chloroform. For dimethyl ether – chloroform – ethanol, the pressures were higher than those for dimethyl ether – chloroform, and lower than those for dimethyl ether – ethanol. The similar results were also observed for propane – chloroform – ethanol. Together with the literature data for chloroform - ethanol and propane -ethanol, the bubble point pressures were correlated with the NRTL equation for the constituent binaries. The ternary VLE were also predicted only by using for the binary parameters of the NRTL equation. The predictions showed good reproducibility for dimethyl ether – chloroform – ethanol and propane – chloroform – ethanol only by using the binary parameters. **Fig. 1** compares the calculations and the experimental bubble point pressures. The reproducibility was almost the same as those for the binaries.

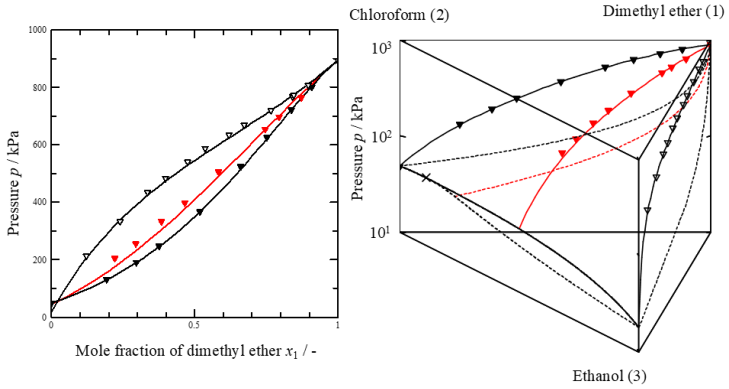

Figure 1. VLE for dimethyl ether (1) – chloroform (2) – ethanol (3) at 313.15 K; (▼) : dimethyl ether (1) – chloroform (2); (▼) : dimethyl ether (1) – chloroform (2) – ethanol (3) [x_2:x_3=1:1];(▽) : dimethyl ether (1) – ethanol (3), bubble point; (, ------): NRTL eq., correlated; (,------): NRTL eq., predicted.

Surface Tension of n-Alkane Mixtures: Model Comparison and Performance Analysis

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The prediction of surface tension in binary mixtures of n-alkanes is of great relevance for industrial applications such as fuel refining, solvent extraction, and lubricant production. However, experimental determination for all compositions and temperatures is unfeasible. This study evaluates the performance of 13 literature models [1], including both empirical and physico-chemical ones, containing from one to three adjustable coefficients, in order to identify the most suitable approach for these systems.

A dataset of 466 points (328 mixture data and 138 pure component data) covering 69 isotherms for 17 binary mixtures was compiled. Two scenarios were investigated: Case A, where experimental pure fluid data were employed, and Case B, where these values were replaced by the correlations proposed by Mulero et al. [2]. Model performance was assessed using statistical deviation indicators and the Corrected Akaike Information Criterion (AICc) [3, 4]. In Case A, all the models demonstrated excellent accuracy, with the Winterfeld–Scriven–Davis (WSD) and Eberhart (EBE) one-coefficient formulations showing the lowest mean absolute percentage deviations, below 0.40%, while two-coefficient models such as the Redlich–Kister (RK2) and Connors–Wright (CW) further improved precision to 0.22%. In Case B, replacing experimental data with correlated values led to a slight increase in deviations, but accuracy remained excellent, with the WSD model reaching a mean absolute percentage deviation of 0.65% and the RK2 and CW models showing 0.57% and 0.56%, respectively, still among the models with the lowest deviations. However, the AICc analysis revealed that the WSD model, which requires only one coefficient, offers the best compromise between precision and simplicity, confirming that additional coefficients do not significantly improve predictive power and may lead to overfitting.

Overall, the results demonstrate that the correlation proposed by Mulero et al. [2] for pure components provides a reliable alternative when experimental data are unavailable, with deviations remaining consistently below 1%. Among the models evaluated, the WSD formulation emerges as the most robust and parsimonious option for predicting the surface tension of binary n-alkane mixtures under subcritical conditions.

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Fives ProSim, a Range of Process Engineering Software Dedicated to Industrials and Model Developers

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Fives ProSim [1] offers a set of chemical engineering simulation software for different applications: steady-state process, batch reactors, batch distillation, water and energy saving in industrial processes, … All these solutions required a powerful calculation server for thermophysical properties and phase equilibria calculations: Simulis Thermodynamics.

With 35 years of experience, Fives ProSim has developed partnerships with industrial customers from a variety of fields: chemicals and petrochemicals, oil and gas production, refining, energy and many other areas, such as alcohols, air separation, carbon capture and storage, biofuels, pharmaceuticals, ingredients, flavours and fragrance, pulp and paper, food industry, metallurgy...

The diversity of all these fields, as well as new applications and the quest for ever greater precision, drive Fives ProSim to constantly expand its library of thermodynamic models and the databases of parameters suitable for these models. To this end, Fives ProSim maintains strong interactions with research teams around the world who develop thermodynamic models and parameters.

In return, model developers use Fives ProSim tools to benchmark models, easily test their equations on experimental data, or apply them to simulate industrial processes.

From the industrial side, Simulis Thermodynamics users have access to support that helps them choose and configure thermodynamic models for their application. This support interaction makes it possible to quantify demands for certain types of models, but also to identify any gaps and shortcomings that still exist. This virtuous circle between industrials, software vendor and research teams is the main purpose of this poster.

By analyzing feedback and requests from industrials, we will show the growing interest for electrolyte models and the importance of predictive models and equation of state with complex mixing rules.

We will also show how Fives ProSim is attempting to respond to these requests through collaborations with thermodynamic models' publishers:

- With the IFPEN team, eNRTL and electrolyte models' parameters databases are constantly developed [2]
- With the Université de Pau et Pays de l'Adour, complex mixing rules to represent gas in solution are improved [3]
- With the DDBST, new thermodynamic models based on Machine Learning and new parameters for predictive models are added [4]
- For novel industrial applications, a new thermodynamic model dedicated to mixtures containing spin isomers of hydrogen was added to represent their fluid phase equilibria and transport properties [1].

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Impact of nanostructuring on the chemical and phase equilibria of switchable hydrophobicity solvents

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Switchable Hydrophobicity Solvents (SHSs) are liquid mixtures that can transition between a biphasic and a hydrophilic monophasic state in response to a chemical reaction [1]. Their dual ability to display either hydrophilic or hydrophobic properties makes SHSs particularly promising for the extraction of organic molecules. Recently, short- and medium-chain carboxylic acids (CAs) have been proposed as the organic components of SHSs [2]. The addition of an inorganic base to a CA + water biphasic liquid mixture triggers its switch to a monophasic state, due to the formation of hydrophilic carboxylates. The switching ability of CA-based SHSs thus depends on the simultaneous chemical and phase equilibria (CPE) in the quaternary CA + carboxylate + inorganic base + water system. Research on the CPE in quaternary systems remains limited, with only a few studies addressing the complex interplay between reaction and liquid-liquid phase equilibrium [3]. Moreover, although short- and medium-chain carboxylates are known to aggregate in water in the presence of hydrophobic components [4], the impact of nanostructuring on the CPE of CA-based SHSs has not yet been investigated.

In this work, the interplay of CPE and nanostructuring in SHSs was investigated to elucidate the factors influencing their switching ability. The quaternary phase diagram of novel SHSs composed of two representative CAs—2-propylpentanoic acid and 2-ethylhexanoic acid—their conjugate sodium carboxylates, NaOH, and water was determined at 298.15 K and 1 bar. Nanoscopic domains in monophasic compositions near the binodal surface were identified and characterized by Small-Angle X-ray Scattering. Molecular dynamics simulations further clarified the molecular interactions driving nanoscopic aggregation. The results demonstrate that nanoscopic structuring, driven by CA and carboxylate aggregation, significantly affects the switching ability of SHSs undergoing simultaneous CPE, providing a foundation for the design of innovative separation processes.

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A Novel Method for Multiphase Equilibrium Calculations for CO_2-Water-Hydrocarbon Mixtures

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This work addresses the development of new robust and efficient multiphase flash methods dedicated to compositional reservoir simulators, with focus on CO_2-water-hydrocarbon mixtures. The conventional approach for multiphase equilibrium consists of a sequence of phase stability and flash calculations. At each level of the stepwise process, stability testing is performed starting from several initial guesses. Therefore, reducing the number of stability calls and using judiciously the information from stability to initialize a phase split are key points in developing an efficient stability-flash algorithm. Moreover, the presence of water makes the stability test and split calculations more challenging. To properly handle the difficulties encountered in multiphase flash for CO_2-water-hydrocarbon mixtures, while enhancing the computational efficiency, two new initialization strategies for multiphase flash calculations dedicated to mixtures containing water are proposed. The first one (improved stepwise initialization) follows the conventional procedure, but uses some additional initial guesses. In the second one (improved multiple initialization), a three-phase split is initiated if at least three minima of the tangent plane distance (TPD) function are detected by stability analysis of feed composition. Both proposed methods are using all information from phase stability testing at each stage. Unlike in previous formulations, compositions at all minima of the TPD function, including positive and trivial TPDs are used to generate initial equilibrium constants. These two algorithms are formulated to handle the case in which water is present, by taking advantage of the particularities of physics and of the mathematical structure of the problem. The proposed methods are tested and compared with the conventional procedures for several benchmark mixtures from the literature, containing hydrocarbon components, CO_2 and water. Phase diagrams are constructed in the P-Z plane, focusing on the number of stationary points of the TPD functions found in each step of the multiphase stability-flash algorithm and on how they must be efficiently used in initialization. Additionally, some limitations and potential issues when water is present are carefully addressed. For all the test mixtures, in the proposed stability-flash strategy, the number of calls of the stability and flash routines and the number of iterations in flash calculations are significantly reduced as compared to previous approaches, recommending the new approach as a useful tool in compositional simulation.

Thermodynamic Modelling of Carbon Dioxide, Water and Sodium Chloride Systems at Moderate Pressures

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The study of phase equilibria in systems with electrolytes is of great relevance for processes in the chemical industry and environmental studies, as the presence of electrolytes can significantly alter boiling points, mutual solubility, and relative volatility [1]. Such effects are crucial in separation processes such as distillation, extraction, and crystallization, in corrosion prevention where the speciation of ionic species must be known. Although the theoretical basis for equilibrium was established by Gibbs, the practical resolution of multiphase, multicomponent systems with dissociated electrolytes and chemical reactions are very complex and the subject of ongoing research, highlighting the need for accurate and broadly applicable thermodynamic models [2]. The aim of this work was to develop a thermodynamic model capable of predicting the behaviour of the carbon dioxide, water and salts mixture in the range of temperatures from 25 to 120 °C, pressure from up to 20 bar, and sodium chloride concentrations up to 300 g/L. The methodology involves four main steps: identification of relevant phenomena within the studied range of temperature and pressure, including vapor-liquid equilibrium, liquid-liquid equilibrium, vapor-liquid-liquid equilibrium, chemical reactions, and hydrate formation; compilation of experimental data from the literature for carbon dioxide, water and sodium chloride systems under relevant pressure and temperature conditions; development of a thermodynamic model combining the Peng-Robinson equation of state for the vapor phase with the extended UNIQUAC model for electrolytic liquid phases [3]; and integration of phase equilibria with chemical speciation through equilibrium constants for carbon dioxide hydration and dissociation reactions. This framework enables consistent calculation of fugacity and activity coefficients, Henry's constants, bubble point pressures, and ionic equilibria for the studied conditions. The approach is designed to reproduce experimental solubility trends of carbon dioxide and ionic species in high saline media and moderate pressures, as well as to provide a robust predictive tool for assessing phase behaviour, speciation, and pH conditions in carbon dioxide, water and salts systems.

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Characterisation and Modelling of Liquid-Liquid Equilibria for Novel Ternary Systems Containing Water and Ethyl Acetate

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Liquid Biphasic Systems (LBSs) are a simple, biocompatible and easily scalable liquid-liquid extraction technique which has recently gained attention due to its eco-friendly nature compared to traditional methods [1]. With promising applications in residue valorisation [2], water purification [3], and pharmaceutical recovery [4], further research is vital to enhance the understanding of these systems and promote their implementation at an industrial scale.

In this work, the liquid-liquid equilibria (LLE) were determined for two new LBSs composed of three green solvents: {ethyl acetate (1) + propan-1-ol or ethyl lactate (2) + water (3)}. In these systems, while the second component was miscible with both water and ethyl acetate, these two components were mostly immiscible, enabling the formation of two distinct liquid phases. The cloud-point method was employed to determine the solubility curve for each system, and 6 tie-lines were subsequently obtained using third-degree polynomial correlations of liquid density (ρ) and refractive index (n_{D}). The tie-line lengths (TLL) ranged from 41 to 77 % in mass for the system containing propan-1-ol, and from 47 to 103 % for the one based on ethyl lactate. The experimental tie-line data were successfully correlated using the Othmer-Tobias and Bancroft-Hubard models, with both yielding coefficients of determination (R^2) higher than 0.985. Moreover, the obtained LLE data were effectively described using the UNIversal QUAsi-Chemical (UNIQUAC) and UNIQUAC Functional-group Activity Coefficients (UNIFAC) models, with a novel group contribution methodology being also applied. These models displayed standard deviations (σ) lower than 10^{-3} (in mass fraction basis) for both systems. Overall, this work provides valuable data for greener LBSs, supporting their potential application in sustainable liquid-liquid extraction processes.

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Polymer-based Aqueous Two-Phase Systems as a Sustainable Separation Strategy for the Textile Industry: Dye partitioning

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As global initiatives move toward a more sustainable and eco-friendly future, there is a growing need for separation and extraction methods that are both efficient and environmentally benign. Aqueous two-phase systems (ATPSs) have gained attention as an innovative liquid-liquid extraction approach with minimal ecological footprint, commonly using a salting-out agent to induce phase separation between otherwise miscible substances [1,2]. Characterised by a high-water content, these systems also offer lower toxicity when employed with polymers such as poly(ethylene glycol) (PEG) and polyvinylpyrrolidone (PVP) or with greener solvents such as ethyl lactate and ethyl acetate [3].

These characteristics make ATPSs suitable for the extraction of dyes, reducing water pollution from the textile industry and promoting a more circular economy [4]. Moreover, their removal through conventional treatment methods is considered expensive and inefficient [5,6], while ATPSs are known for their scalability and for being cost-effective.

In this work, the liquid-liquid equilibria (solubility curves and tie-line compositions) of new Aqueous Two-Phase Systems (ATPSs) were determined at 298.15 K and 0.1 MPa, envisioning the removal of textile dyes from polluted water streams. Solubility curves, obtained by the "cloud-point" titration methodology, were described by empirical correlations, while tie-line compositions were determined using third-degree polynomials of liquid density (ρ) and electrical conductivity (κ). Then, the UNIversal QUAsi-Chemical (UNIQUAC) model was coupled with a Pitzer-Debye-Hückel (PDH) term and was successfully applied in the description of tie-line composition. Finally, partition studies were conducted for common textile dyes using the novel ATPSs, obtaining promising performance indicators (extraction efficiencies and partition coefficients).

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Aqueous Two-Phase Systems based on Greener Solvents: Phase Equilibria, Thermodynamic Modelling and Amoxicillin Removal

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As the world directs efforts to a more sustainable and greener future, the demand for more efficient and less harmful separation and extraction processes has increased substantially. Aqueous two-phase systems (ATPSs) emerged as an innovative liquid-liquid extraction technique with low environmental impact, typically relying on the use of a salting-out agent to separate two otherwise miscible components. Characterised by a high-water content, these systems offer enhanced biocompatibility and lower toxicity when employed with greener solvents, making them suitable for the extraction of active pharmaceutical ingredients (APIs), such as amoxicillin [1] or salicylic acid [2], from polluted water streams.

Due to its strong antibiotic activity, amoxicillin is widely applied in the treatment of bacterial infections, significantly contaminating hospital and urban effluents [3]. Moreover, its removal through conventional treatment methods, such as advanced oxidation processes (AOPs), is considered expensive and inefficient [4].

In this work, the liquid-liquid equilibria (solubility curves and tie-line compositions) of new Aqueous Two-Phase Systems (ATPSs) based on greener solvents were determined at 298.15 K and 0.1 MPa, envisioning the removal of amoxicillin from polluted water streams. Solubility curves, obtained by the "cloud-point" titration methodology, were described by empirical correlations, while tie-line compositions were determined using third-degree polynomials of liquid density (ρ) and electrical conductivity (κ). Then, the electrolyte non-random two-liquid (eNRTL) model [5], that couples with a Pitzer-Debye-Hückel (PDH) term [6] to the NRTL theory [7], was successfully applied in the description of tie-line composition. Finally, partition studies were conducted for amoxicillin using the novel ATPSs, obtaining promising performance indicators (extraction efficiencies and partition coefficients).

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Solubility of bioactive compounds contained in spent coffee ground: computational screening and experimental data

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Coffee is one of the most consumed beverages worldwide. Related to its consumption an unavoidable waste is created, the spent coffee ground. This residue is generated either during the industrial production of soluble coffee or by the coffee extraction at coffee shops and households [1]. The composition of this residue allows for different routes of valorisation, ranging from thermochemical to biotechnological routes [2]. One of them is connected to the significant number of bioactive compounds present in the residue that could be extracted by a solid-liquid extraction [3] and further purified. This pathway is regarded as one of the most promising technologies to valorise this waste due to the high market price of the extracts in the cosmetic industry. However, the use of conventional fossil-based solvents is associated with high (or significant) environmental impacts, which can be minimized by switching to greener compounds such as bio-based solvents. In order to shed some light on the interaction between the different bio-solvents and the solutes of interest, a solid-liquid solubility study is presented herein using both computational and experimental techniques.

Thus, this work is focused on determining the solubility of three compounds found in spent coffee grounds (caffeine, caffeic acid and chlorogenic acid) in different biosolvents (water, ethanol, 2-propanol, γ-valerolactone, ethyl acetate, ethyl lactate, 2-methyl-tetrahydrofuran, dimethyl isosorbide, dimethyl carbonate, cyclopentyl methyl ether and limonene). First, the quantum-chemical method COnductor-like Screening MOdel for Real Solvents (COSMO-RS) was used to analyze the thermodynamic behavior in terms of excess enthalpies and intermolecular interactions between the solutes and the solvents. The Hansen solubility parameter method was also used as a predictive tool to anticipate the behaviour of the systems under study. Finally, the results were experimentally validated at 303.15 K using the isothermal shake-flask method followed by HPLC analyses.
The results show promising consistency between experimental measurements and computational calculations for the tested solvents, identifying the most promising compounds from a thermodynamic point view. In particular, ethyl lactate and γ-valerolactone are the solvents with the highest solvation capacity of caffeine, while 2-methyl-tetrahydrofuran, ethanol, and dimethyl isosorbide present the best solvation capacity of caffeic acid.

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Density Gradient Theory for interfacial tension: Cubic EoS and Flory-Huggins approaches

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Interfacial tension is a fundamental thermodynamic quantity reflecting the free energy cost of forming an interface between coexisting phases, yet its reliable determination in experiment can be challenging. In this work, an *ab initio* model combining the Density Gradient Theory (DGT) with an equation of state (EoS) is employed to evaluate the interfacial tension for one and two component systems [1]. DGT relies on the definition of the Helmholtz free energy of the system and its free energy density, which is formulated here using a modified version of the classic van der Waals EoS, the van der Waals-711 model [2]. This modification introduces a third parameter that accounts for the temperature and acentric factor, making it more comparable to modern cubic EoS such as Peng-Robinson. Within the Cahn-Hilliard framework (for numerical stability), integration of the interfacial Helmholtz free energy yields the equilibrium density profile and, from it, the corresponding interfacial tension. The model with van der Waals-711 modification provides results close to experimental data in difference from a classical van der Waals equation. We investigate how the vdW-711 modification comperes with more complex equations of state, like Peng-Robbinson or Soave-Redlich-Kwong.

The methodology on one-component alkane and cycloalkane systems was established, so that we now focus on binary systems. In particular, the approach is extended to polymer-solvent mixtures, where interfacial tension is a key parameter for processes such as liquid-liquid polymer fractionation [3] used as part of solvent-based recycling. Similarly, the Helmholtz free energy density is formulated using Flory-Huggins theory, and the interfacial tension is obtained from volume-fraction profiles rather than density profiles [4]. The initial results for the cyclohexane-polystyrene system show promising agreement with the experimental data. Additional polymer-solvent systems relevant for solvent-based polymer recycling, as well as comparison of van der Waals-711 with modern EoS, will be investigated.

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Phase Equilibria, eNRTL Modelling and Quantum-Informed Force-Fields: Aqueous Biphasic Systems based on Sodium Formate

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Aqueous Biphasic Systems (ABSs) constitute a versatile and sustainable platform for separation and purification processes [1,2], but their thermodynamic characterisation remains a challenge due to the complex interplay between ionic, hydrogen-bonding, and dispersion interactions. In this work, an integrated experimental and theoretical study of the ABSs {ethyl lactate or propan-1-ol (1) + sodium formate (2) + water (3)} is presented at 298.15 K and 0.1 MPa, with the objective of coupling macroscopic thermodynamic modelling with molecular-level insights obtained from quantum mechanical calculations.

Experimental liquid-liquid equilibria (LLE) data were obtained using the "cloud-point" titration method and correlated by empirical equations. Tie-line compositions were estimated from polynomial correlations of density and refractive index and modelled using the electrolyte Non-Random Two-Liquid (eNRTL) model [3]. In eNRTL, three parameterisation strategies for the nonrandomness factor (α_{ij}) were examined: (i) fixed α values (0.2 or 0.3) for all species; (ii) α_{ij} values estimated via Density Functional Theory (DFT) for solvent-solvent interactions; and (iii) hybrid approaches maintaining $\alpha = 0.2$ for salts. The eNRTL model reproduced the experimental LLE data with low deviations, confirming that the use of physically informed parameters can reduce empirical fitting without compromising accuracy.

The distinctive aspect of this work is the force-field parameterisation based on quantum mechanical interaction energies, establishing a direct link between DFT-derived molecular information and macroscopic thermodynamic modelling. Optimised molecular geometries and interaction energies were computed for the system constituents and correlated with classical potential energy models. Among the tested potentials, the Mie potential [4] provided the most accurate description, effectively capturing both repulsive and dispersive effects. These results highlight the balance between computational simplicity and representational accuracy required for transferable, physically meaningful force-fields. Moreover, by integrating quantum-informed molecular parameters into the eNRTL modelling framework, this study demonstrates a multiscale approach that enhances the predictive capability of thermodynamic models for complex Aqueous Biphasic Systems.

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Determination of Henry's law coefficients of CO_2 in Cyrene

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In recent years, increasing attention has been devoted to the use of innovative solvents for CO_2 removal processes. Among the newly proposed green solvents, Dihydrolevoglucosenone (commercially known as Cyrene) has emerged as a promising candidate [1]. Cyrene is a biodegradable, non-mutagenic and non-toxic solvent derived from biomass.

To assess the suitability of Cyrene for CO_2 removal from gas mixtures such as natural gas and syngas, it is essential to determine its absorption performance through process simulations using software such as Aspen Plus®. Since CO_2 removal from such gas streams typically occurs under operating conditions above its critical temperature [2], the knowledge of the Henry's law constant of CO_2 in Cyrene is necessary for performing a reliable modelling.

Therefore, the aim of this work is to determine the values of the coefficients used to calculate this thermodynamic parameter for the CO_2–Cyrene system for its employment in Aspen Plus®. To the authors' knowledge, no data on the Henry's law constant of CO_2 in Cyrene have been previously reported. The regression has been carried out using experimental solubility data obtained in the Process Thermodynamics laboratory (PT lab) of Politecnico di Milano at 313.15, 323.15, 333.15, and 353.15 K and at pressures up to 2.5 MPa [3]. To preserve the physical meaning of Henry's law, instead of simply regressing the parameters of the already available expression in the process simulator, the theoretical definition of the Henry's law as the slope at the origin of the curve describing the variation of the CO_2 mole fraction in the liquid phase with respect to its fugacity has been considered. Then, the Henry's law constants determined at the four investigated temperatures have been subsequently correlated using a second-order polynomial equation, yielding the coefficients of the equation employed by Aspen Plus® to calculate the temperature dependence of such constant.

This work has been carried out in the context of the PRIN 2022 project "GREEN-based water-lean SOLvent for CO_2 capture" (GREENSOL), funded by the European Union – NextGenerationEU, CUP D53D23003100001 – and we acknowledge financial support under the National Recovery and Resilience Plan (NRRP), Mission 4, Component C2, Call for tender No. 104 published on 2.2.2022 by the Italian Ministry of University and Research (MUR).

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Modeling the complete PEG/Citrate Aqueous Two-Phase System Phase Diagram

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Aqueous Two-Phase Systems (ATPS) are ternary systems typically formulated with two polymers or a polymer and a salt, that split into two partially miscible liquid phases where the solvent is water in both liquid phases. Most of the papers on Liquid-Liquid Equilibria (LLE) of ATPS typically report a few tie-lines and do not provide the complete LLE phase envelope and other equilibrium regions with solid phases. Modeling of the phase equilibria can be done using different approaches, from Gibbs energy activity coefficient models that account for electrolytes and/or polymers [1] to equations of state such as PC-SAFT [2]. In order to provide a model that truly represents the system behavior, it is important to have experimental data from the whole LLE phase envelope and the other regions of phase equilibria, together with the use of the Gibbs common tangent equilibrium condition [3,4]. In this work, we present the complete phase diagram of PEG/sodium citrate ATPS, including all phase equilibria regions (Liquid-Liquid, Solid-Liquid, Solid-Liquid-Liquid, etc) and the modeling using the classic NRTL equation [5]. In order to account for the large differences in molecular weight between PEG and other chemicals, auxiliary compositions are used. Long range interactions (Pitzer-Debye-Hückel models) are not considered, but even so NRTL is able to simultaneously correlate all the equilibrium regions with a single set of parameters. By using temperature-dependent interaction parameters the model can even represent simultaneously phase diagrams at different temperatures, with overall standard deviations <2 %wt.

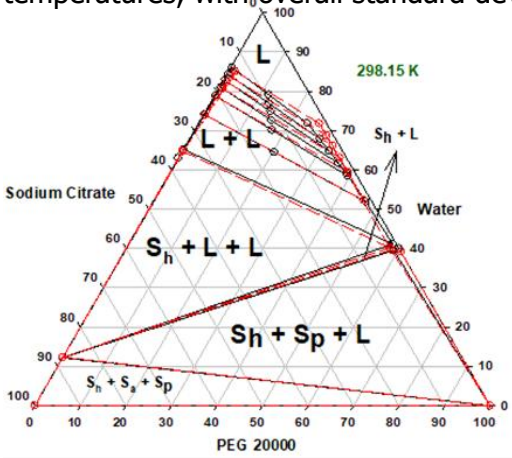

Figure 1. Complete phase diagrams (w/w units) at 298.2 K for PEG 20000/sodium citrate

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Determination and Prediction of Excess Molar Enthalpies at High Pressure of the Binary Systems Carbon Dioxide + Bio-based Solvent

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Recently, it is well known that occurred large exothermic behavior (heats of mixing, excess molar enthalpies, H^E), when carbon dioxide (CO_2) and organic solvents mixed at near critical point of CO_2. The exothermic effects can be used in a new heat supply system[1]. In addition, CO_2-expanded liquid (CXL) is a mixed solvent consisting of compressed CO_2 gas dissolved in a conventional organic solvent, which requires milder process pressures and less energy than neat supercritical CO_2. CXL have been used in various applications such as particle formation, polymer processing, and extraction of bioactive compounds[2,3]. In order to design of environmentally responsive system, it is necessary to change solvents such as volatile organic compounds to bio-based solvent from biomass resources. Therefore, H^E data is one of the physical property of CO_2 mixture to apply for a new heat supply system or CXL.

The purpose of this work is to obtain the experimental H^E data of the binary systems CO_2 + bio-based solvent at temperatures of 298.15, 303.15 K and pressures of 5.0, 6.0, 6.5 MPa using a flow-type isothermal microcalorimeter. g-butyrolactone (GBL) and diethyl oxalate were selected as bio-based solvents in this study. Figure 1 shows the experimental H^E data of the binary system CO_2 + GBL at 298.15 K and 5.0, 6.0, 6.5 MPa. The experimental H^E data were correlated by the modified Redlich-Kister (mRK) equation[4] and the Peng-Robinson equation of state (PR-EOS) with the van der Waals one fluid (vdW1) mixing rule or modified Huron-Vidal first order (MHV1) model[5]. Binary parameters in these mixing rules with PR-EOS was regressed to be independent of temperature and pressure, except for the condition of 298.15 K and 6.5 MPa, at which a different behavior was observed compared with the other pressures. Besides, prediction of the H^E data for this mixture was performed using PR-EOS with the vdW1 mixing rule or MHV1 model, with parameters obtained from the vapor-liquid equilibrium data.

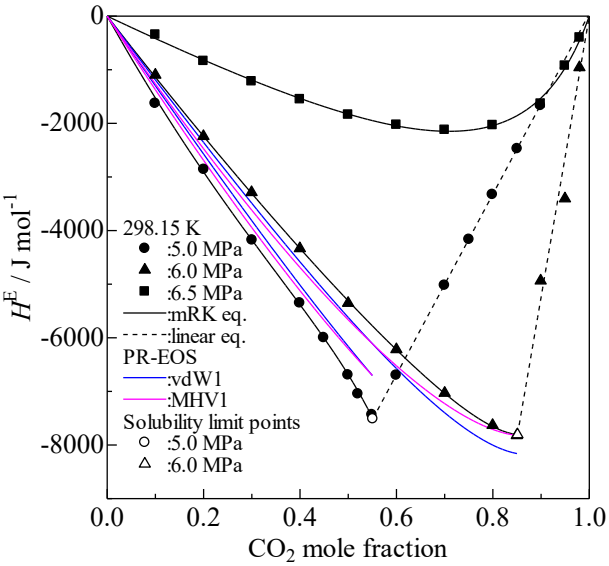

Figure 1. Experimental H^E data of the binary system CO_2 + GBL.

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Surface Tension for 27 alkenes. Selection of Data and Correlation with the Temperature.

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Surface tension values for 27 alkenes at different temperatures have been compiled from databases, books, and literature papers. The considered fluids include 1-alkenes, dialkenes, cycloalkenes, methyl-alkenes and 2-, 3-, and 4-alkenes according to the DIPPR notation [1]. The data were screened, and a final set of 1000 data points was selected, ranging from 25 to 68 for each fluid. The Guggenheim–Katayama analytical expression was used to correlate the selected values with temperature. Two or four adjustable coefficients were used for each fluid, except for 1-octene, which required six coefficients [2].

The proposed correlations provide mean absolute deviations less than or equal to 0.4 mN/m and mean absolute percentage deviations below 2.2%. Moreover, percentage deviations for each data point were less than 8.2% whereas the maximum absolute deviation was found to be 1.54 mN/m. In general, the highest deviations are due to discrepancies between the data reported by different authors and not to the poor performance of the correlation model.

The correlations presented herein are sufficiently accurate to serve as a reliable reference in both theoretical research and practical applications. They are also suitable for integration into computational platforms such as REFPROP and CoolProp. In addition, the comprehensive dataset compiled in this work could be incorporated into updated versions of established thermophysical property databases, including DIPPR [1] and DETHERM [3].

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Screening of Aqueous Two-Phase Systems for Fish Protein Recovery

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The residues generated in the fish processing industry provide many opportunities for the recovery of added value chemicals that can help to improve the economics of the industry, at the same time that improves its circularity. Indeed, the wastewaters (cooking, washing, etc) are a known source of valuable proteins (typically in the range 500-20000 ppm) that can be used as food additives, supplements in animal feed, biopharma, etc [1]. Aqueous Two-Phase Systems (ATPS) are typically formulated combining aqueous solutions of two polymers or a polymer and a salt, that split into two immiscible liquid phases upon mixing. Since the solvent on both phases is water, ATPS have found a great application as liquid extraction media for biotechnology.

In this work, the partitioning of fish proteins in PEG/salt ATPS has been investigated as a way for the concentration and/or recovery of fish proteins from fish industry wastewaters. Fishmeal has been used as source of fish protein to simulate wastewater. Polymer used was polyethylene glycol (PEG) in all cases, since it is the most used polymer in ATPS formulation. A large screening of salts was carried out in order to evaluate their effect on protein partitioning, including sulfate, phosphates, carbonates, nitrates and citrates anions and sodium, potassium and ammonium cations. Partition coefficients of proteins between the ATPS equilibrium phases were measured experimentally at protein infinite dilution (true thermodynamic partition coefficient).

The BCA method was used to quantify the protein content in each phase. Our results show that best partitioning is obtained in sulfate and carbonate anions and potassium cation. Best ATPS were selected to further evaluate the protein recovery and optimize other operation parameters such as pH and ionic strength.

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Phase transitions of polymer networks under tension

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Volume instabilities in polymer networks have attracted the interest of researchers since the early days of polymer science because they are associated with unique thermomechanical and optical properties – e.g., auxetic behavior. Cavitation in rubbers under tensile stress was first described by Gent in the '50s [1] and has a central role in fracture problems. Separately, in the '70s a different type of instability deemed volume phase transition (VPT, or gel-gel transition) was observed in solvent-swollen gels [2], inspiring continuing research on thermo-responsive polymers. Since both phenomena originate from discontinuities in the network density, it is surprising that they have been largely treated independently. This was highlighted in recent simulation work by some of us [3], where an implicit-solvent (i.e., dry) polymer network model was shown to reproduce all the qualitative features of the VPT.
In a contribution under review in *Physical Review Letters* [4] we formalize this analogy through thermodynamic arguments, showing that cavitation and VPT are analogous phenomena if one employs standard assumptions on the free energy change due to cross-linking. In particular, the swelling equilibrium and stability criteria in the two cases are equivalent if one identifies the thermodynamic pressure of the reference, uncross-linked mixture with its osmotic pressure. Leveraging this analogy, we develop a model of soft polymer networks capable of representing both dry networks and solvent-swollen gels. We assume affine displacement of network junctions and treat chain extensibility and bond stretching exactly. The model predicts simulation data at low density without adjustable parameters, and displays all the phenomenology of cavitation and VPT.

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MOFs as Potent Ice Recrystallization Inhibitors: Mechanistic Insights from Machine Learning and Molecular Simulations

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Investigations into ice recrystallization inhibition (IRI) agents have focused on natural antifreeze proteins (AFP), antifreeze glycoproteins (AFGP), their synthetic analogues, and polymers[1,2]. Recently, metal–organic frameworks (MOFs) have been shown experimentally to exhibit IRI activity by enhancing cell viability during cryopreservation[4], but their mechanisms remain computationally unexplored. We present the first computational study of MOF based organic linkers as IRI agents. In this work, a machine learning model[3] was trained on an experimental database of AFPs and AFGPs, using mean grain size (%MGS) of ice as the target property. Organic linkers having IRI potentials were identified from the CoRE MOF 2019 database. The top four linkers were tested for stability using DFT and atomistic models were used to verify the prediction. Interestingly, the molecular dynamics simulations conducted at 240K are in line with the machine learning predictions. Our analysis revealed that higher linker concentrations enhanced the clustering of linkers to form clusters at the ice interface. This clustering correlated with an increased number of hydrogen bond formation with ice, which strongly anchored the linkers to the ice surface and suppressed further growth. The anchoring induced curvatures on the ice surface, thereby inhibiting ice growth via the Gibbs–Thomson effect and highlighting the linkers' potential IRI activity. These findings underscore the potential of MOF organic linkers as promising IRI agents[4].
Further, we performed classical MD simulations with UiO-66 MOF variants containing the identified top four linkers as structural building units (SBUs). The simulations were conducted using MOFs modeled as nanoparticles, with linkers exposed to freely interact with water, in line with our previous results. These simulations showed that the MOFs bound firmly with ice and inhibited ice growth through the Gibbs–Thomson effect. The thermal hysteresis induced by the Gibbs–Thomson effect indicated that the melting point of water decreased by approximately 10–12 K. The binding was observed to be stronger for linkers predicted from the above machine learning models, demonstrating that MOFs capable of forming strong hydrogen bonds with ice could inhibit ice growth and prevent recrystallization. This opened up a new avenue for selecting MOFs as potential IRI agents[4].

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Evaluation of Excess Surface Tensions at Normal and High Pressure for Binary and Ternary Systems Using Wilson- and ASOG-SurTension Models

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1. Introduction

Surface tension is one of the surface properties necessary for the consideration of wetness in solid-liquids separation and design of another separation processes. The many models of the correlation and prediction of surface tensions have been proposed [1]. In the models, the procedure for considering the excess properties and mixing properties using mole fraction summation is useful from a practical point of view. The authors have discussed Wilson-SurTension [2] and ASOG-SurTension [3] models using Eyring equation with Wilson, ASOG activity coefficient models.
The paper deals with the evaluation of excess surface tensions for mixtures at normal and high pressures using Wilson- and ASOG-SurTension models.

2. Evaluation of Surface Tensions for Liquid Mixtures at Normal and High-Pressure

This paper deals with evaluation of excess surface tension σ^E using mole fraction average one similar to Eyring's model [4] for kinematic viscosity.

$$\ln\sigma\mathrm{M} = \sum x_i ln\sigma_i M_i + \sigma^E \qquad (1)$$

$$\sigma^E = kg^E \qquad (2)$$

Where k=-1 will be used similar to kinematic viscosity [5,6] and thermal conductivity [6,7]. The excess Gibbs free energy will be obtained using Wilson equation and ASOG group contribution model. a) for binary and ternary systems at normal pressure using Wilson-SurTension equation [2,3] b) for binary and ternary systems at normal pressure using ASOG-SurTension method [3,4] c) for binary and ternary systems at high pressure using Wilson-SurTension equation d) for binary and ternary systems at high pressure using ASOG-SurTension method.

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Molecular Dynamics Simulations of the Dielectric Constant of R410A

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Growing climate concerns highlight the need to better characterize high-GWP hydrofluorocarbons, such as the refrigerant R410A. This work presents an evaluation of R410A dielectric behavior in both liquid and vapor phases using molecular dynamics (MD) simulations, something not previously reported in the literature. MD simulations were performed with GROMACS in NVT and NPT ensembles, applying force fields for R32 and R125 available in the literature [1]. The dielectric constant was determined from dipole moment fluctuations. Complementary experimental measurements using the capacitance method were obtained in both phases, providing benchmarks, particularly for the vapor region where data are scarce. MD results were first validated against literature data [2] for the liquid phase, showing deviations of 0.35% and 3.30% for density and dielectric constant, respectively. Additional simulations under the same conditions as our experiments reproduced the observed trends (Figure 1) with deviations below 7.85% for both phases. The results demonstrate the force field's transferability in predicting electrical properties and support the assessment of low-GWP refrigerants with similar characteristics.

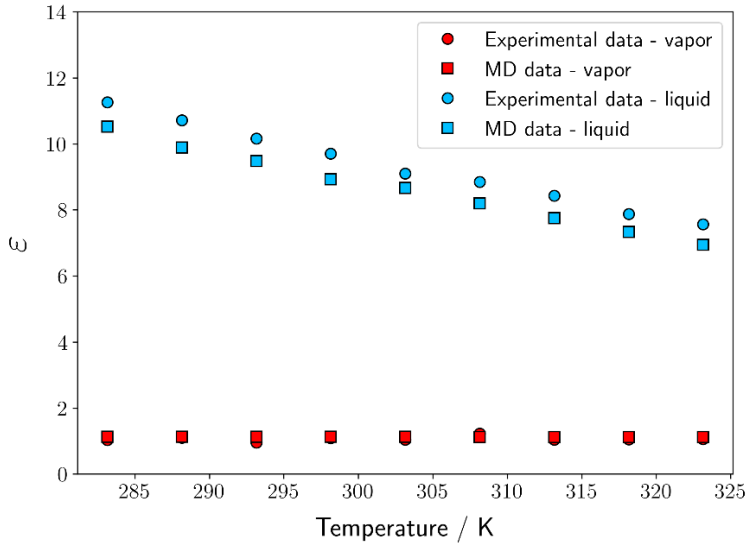

Figure 1. Dielectric constants of R410A for both phases: experimental measurements and MD predictions.

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Thermodynamic Behaviour of 2-(2-ethoxyethoxy)ethanol + 1-Alkanol Mixtures: Excess Molar Enthalpies and Molecular Interactions

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The transition toward sustainable energy requires the exploration of alternative fuel additives capable of enhancing combustion performance while reducing pollutant emissions. Oxygenated solvents, including glycol ethers and higher alcohols, have emerged as promising candidates due to their favourable physicochemical properties, miscibility with hydrocarbons, and ability to influence intermolecular interactions in liquid mixtures. Understanding the thermodynamic behaviour of such systems is essential for optimizing their use in practical applications, particularly in the formulation of cleaner fuels. In this work, the thermodynamic behaviour of 2-(2-ethoxyethoxy)ethanol + 1-heptanol and 2-(2-ethoxyethoxy)ethanol + 1-pentanol binary mixtures was studied at 298.15 K and 313.15 K under atmospheric pressure (0.1 MPa) using a quasi-isothermal flow calorimeter. The excess molar enthalpies (H_m^E) are positive throughout the composition range, confirming the endothermic character of mixing. For the mixture with 1-heptanol, higher H_m^E values were observed, reflecting the greater disruption of hydrogen-bond networks due to the longer alkyl chain and steric hindrance. The 2-(2-ethoxyethoxy)ethanol + 1-pentanol system shows a similar trend but with slightly lower enthalpic effects, consistent with shorter-chain alcohol interactions. In both cases, the maxima occur near equimolar compositions, and H_m^E increases with temperature, indicating reduced hydrogen bonding and enhanced molecular mobility. Correlation with the Redlich–Kister equation provided an excellent fit, while NRTL and UNIQUAC models accurately reproduced the experimental data. In contrast, the modified UNIFAC (Dortmund) model captured overall trends but systematically underestimated or overestimated H_m^E, highlighting its limitations in describing specific hydrogen-bonding interactions. These findings demonstrate that molecular size, polarity, and steric effects play a central role in non-ideal mixing of glycol ethers with higher alcohols and provide new insight into the design of oxygenated fuel additives with improved stability, combustion, and emission profiles.

Simulation of the N_2 hydrate-water interfacial free energy from computer simulation along the dissociation line of the N_2 hydrate

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In this work, the nitrogen (N_2) hydrate-aqueous interfacial free energy, g_{hw}, is determined along the dissociation line of the N_2 hydrate from molecular dynamics simulations. In particular, we determine g_{hw} at 250, 500, 1500, 2500, 3500, and 4500 bar and at the corresponding coexistence temperatures. g_{hw} is directly evaluated from simulation using the Mold Integration-Host methodology [1], which is an extension of the original Mold Integration method [2]. Water and N_2 molecules are described using the well-known TIP4P/Ice model [3] and a TraPPE model [4], respectively. The same model combination has also been used to describe the dissociation line of the N_2 hydrate in a wide range of pressures [5,6]. This is the first time that the N_2 hydrate-water g_{hw} is predicted along the dissociation line of the N_2 hydrate. Our results suggest that there exists a minimum of energy at the intermediate-low pressure, and the g_{hw} shows a significant change with the pressure in the range considered in this work. Once again, it is confirmed that the Mold Integration-Host technique can be used to predict directly and accurately the hydrate-water g_{hw} for hydrates with a sII crystallography structure.

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Molecular Dynamics Insights into Solvent-Biomass Interactions in Green Solvent Mixtures

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Biomass valorization critically depends on understanding how solvent mixtures interact with its major constituents (lignin and cellulose) at the molecular scale. In this study, we employed molecular dynamics (MD) simulations to investigate selected green solvent mixtures, both with and without additives, to elucidate structural and interaction mechanisms governing biomass dissolution.

Lignin and cellulose were represented using model structures: monomeric, oligomeric, and larger lignin fragments, and a crystalline cellulose segment. Solvent systems include binary and ternary mixtures with hydrogen-bond donors/acceptors, salts, and co-solvents, chosen to reflect efficient combinations identified in previous experiments. Key MD observables include radius of gyration, solvent-accessible surface area, hydrogen bond distributions, radial distribution functions, and cluster size analysis to measure the microheterogeneity.

For lignin, the simulations reveal that solvent systems must possess a mutual presence of hydrophilic and hydrophobic motifs to effectively interact with the chemically diverse functional groups of lignin. Solvents capable of forming hydrogen bonds with phenolic and aliphatic hydroxyl groups while simultaneously engaging in non-polar interactions (e.g., with aromatic or methylene segments) lead to more extended lignin conformations and enhanced solvation. Such dual-interaction capability is essential for disrupting intra-lignin associations and enabling it dissolution at the molecular level.

For cellulose, the results show that certain additives (e.g., small protic molecules or salts) can partially disrupt the surface hydrogen-bonding network of crystalline cellulose, facilitating initial swelling and partial penetration of solvent molecules. Solvent components that form stable hydrogen bonds with surface hydroxyl groups contribute to increased accessibility of cellulose functional groups and thus promoting effective solubilization.

These findings align with recent MD studies: for example, hydrogen-bonding descriptors and solute hydrophilicity have been shown to predict lignin solubility in DES + water systems [1], while in the cellulose–*N*-methyl morpholine-*N*-oxide (NMMO) system, initial hydrogen-bond disruption by hydrate water followed by self-interactions between NMMO molecules has been proposed as the dissolution mechanism [2].

Altogether, these MD results contribute to a deeper mechanistic understanding of solvent–biomass interactions and support the rational design of next-generation green solvents for efficient biomass fractionation.

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Effects of force fields on the mechanical properties of CALF-20 via molecular dynamics simulations

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CALF-20 is a metal–organic framework notable for its structural flexibility, selective CO_2 capture under post-combustion conditions, and potential for industrial-scale applications [1]. Its distinctive structure gives rise to unconventional mechanical behavior [2], a polymorphic response to humidity [3], and temperature-induced transformations [4], while maintaining remarkable structural resilience. Understanding CALF-20's behavior under operational conditions is therefore essential for the rational design of adsorptive materials. To investigate it, molecular dynamics simulations are performed using LAMMPS [5] with the Universal Force Field (UFF), UFF-Modified [2], and "HoFF" [7] force fields. The elastic constants of CALF-20 at 300 K are determined via the explicit deformation method, and effective elastic moduli are computed using the Voigt–Reuss–Hill approximation. The results indicate pronounced anisotropy, with maximum stiffness along [100] and reductions of up to 86% along [001] relative to the stiffest direction. While UFF and UFF-Modified tended to overestimate the elastic moduli, HoFF showed better agreement with DFT reference values [2], although it did not reproduce the auxetic response along [001] previously reported in DFT calculations [2].

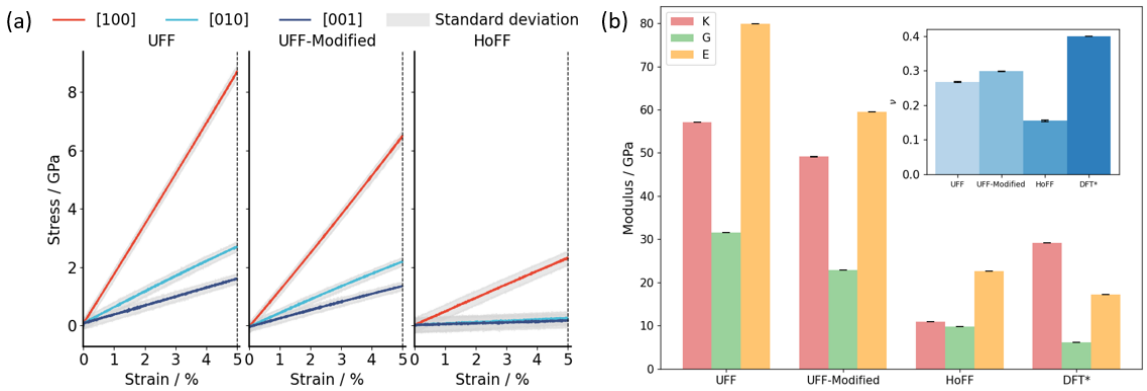

Figure 1. (a) Stress-strain curves for the three crystallographic directions; (b) VRH Elastic Modulus at 300 K *DFT results [2].

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Requirements and Limitations for Optimised Property Packages in Process Simulation – a Case Study on Aromatics Extraction

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An accurate simulation of a chemical process requires the definition of a set of physical property models (the property package) that provides all the necessary equilibrium and transport property data. The selection of the most reliable set of models is often trivial for simple mixtures of the most common species, but it can be more elaborate if we need to deal with new chemical species or mixtures that are significantly non-ideal, such as those involved in vapour-liquid-liquid equilibria (VLLE) [1]. Dealing with mixtures containing many components (such as petrochemical streams) or components that are not well-defined, such as petroleum fractions, is also a challenge, as we need to define the model parameters for such components and sometimes these parameters cannot be obtained exclusively from a small set of pure component data. This is the case of binary interaction parameters for activity models such as NRTL or UNIQUAC, which are the most used thermodynamic models for complex phase equilibria, such as VLLE.

In this work we discuss a methodology for obtaining an accurate property package to be used in process simulation. We will look at pure component data and make an analysis of the constant and temperature dependent data required for a given new chemical species. We will then discuss the appropriate selection of phase equilibria models and provide advantages and limitations for equation of state and activity coefficient models. We will also emphasize the importance of thermal property data (such as enthalpy and heat capacity) which is often sidelined with respect to phase equilibria in applied thermodynamics research. Having reliable thermal property data not only allows for the most accurate energy balance in our simulation but also helps saving on future operating expenses (OpEx) related with running a non-optimized process.

We will use the extraction of aromatics as case studies to discuss our methodology. This often involves using extractive polar solvents such as sulfolane, NMP or NFM in a liquid-liquid separator or an extractive distillation process. We will show how a given thermodynamic model can be optimised, also addressing mixtures of non-well-defined components and how to approach multicomponent mixtures. Results will be compared with available data and some conclusions about the most appropriate set of models will be presented.

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Density and surface tension modelling of binary mixtures containing a deep eutectic solvent

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In this work, the Gibbs adsorption equation (GAE) coupled with a cubic equation of state (CEoS: Soave-Redlich-Kwong or Peng-Robinson) was applied to represent the surface tension of binary solutions consisting of a polar, associating substance (*e.g.* water, ethanol and acetonitrile) and a deep eutectic solvent (*e.g.* choline chloride/urea and tetraethylammonium bromide/ethylene glycol) over the whole composition range, at atmospheric pressure, and within a temperature range varying from 10 to 35 °C. As a matter of fact, the main thermodynamic potentials (fugacity coefficients in the bulk and surface liquid phases) present in the resulting GAE-based model were estimated via the use of the CEoS which also served to model the experimental mixture density data of the aforementioned mixtures using various volume translation and refitting techniques, thus obtaining highly satisfactory results.

Deep Eutectic Solvents as Green Agents for Dye Removal and Textile Recycling

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The textile industry is a substantial part of the global economy, yet it remains one of the most polluting sectors due to its reliance on synthetic dyes and resource-intensive processing. Vast quantities of wastewater, often containing recalcitrant dyes and auxiliary chemicals, are discharged daily, while dyed fabrics present significant challenges for recycling because of the strong dye-fiber interactions that resist removal. Conventional treatment methods such as adsorption, oxidation or incineration tend to be costly, energy-demanding or polluting, and they rarely offer solutions for fiber reuse. As a result, both water resources and textile materials are lost to waste streams, perpetuating a linear model of production that is incompatible with circular economy goals.

In this context, deep eutectic solvents (DESs) emerge as promising alternatives for sustainable textile waste remediation. These solvents, obtained from inexpensive and biodegradable components, combine tunability, low toxicity and ease of preparation, allowing their properties to be tailored for specific applications. In this work, two DES systems were designed to tackle the challenge of dye removal from wastewater and fabric substrates: a hydrophobic solvent suitable for liquid-liquid extraction of colored effluents, and a hydrophilic solvent capable of disrupting dye-fiber interactions to decolorize cotton textiles. By coupling wastewater purification with fiber recovery, this approach addresses the environmental footprint of the textile industry while enabling closed-loop recycling of materials. Thus, the use of DESs represents a scalable and green pathway towards reducing pollution, conserving resources and integrating circularity into textile manufacturing.

From solubility to extraction processes: gelatine from fish skin

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Understanding the solubility of biomolecules in alternative solvents is a fundamental step in the development of efficient and sustainable extraction processes. Solubility data provide critical insights into molecular interactions, solvent compatibility, and thermodynamic behaviour, which are essential for designing suitable systems for protein recovery. In particular, the use of ionic liquids (ILs) as solvents offers a versatile platform due to their customizable physicochemical properties, low volatility, and potential for selective solvation of amino acids and proteins.
In this work, the solubilities of collagen-forming amino acids (glycine, β-alanine, L-proline, trans-4-hydroxy-L-proline, and L-arginine) in several imidazolium ILs and their mixtures with water in equal proportions were determined at temperatures ranging from 298.15 to 328.15 K and at atmospheric pressure. Fish by-products, such as skin, constitute a biological matrix rich in hydrogen bonding. Therefore, carboxylate-based ILs were selected for their strong hydrogen bond acceptor capacity, which enables them to interact effectively with the biomass. This opens up possibilities for two treatment options. The IL may facilitate the disruption of the hydrogen bonding network, promoting protein extraction. Alternatively, these ILs may penetrate the matrix and induce swelling, thereby increasing the surface area and enhancing accessibility for subsequent extraction with water.
In the first part of this work, the solubilities of the above-mentioned amino acids were determined in 1-ethyl-3-methylimidazolium acetate [1], 1-hexyl-3-methylimidazolium acetate [1], and 1-ethyl-3-methylimidazolium propionate, as well as in their aqueous solutions. An excess of amino acid was introduced into the IL or its aqueous mixtures and equilibrated at the target temperature. The solute concentration in the saturated solution was subsequently determined by densitometry, based on calibration curves established beforehand. The influence of the alkyl chain of the cation and anion on the solvation capability of ILs was analysed. Moreover, the data were correlated using the van't Hoff model, and the apparent properties of dissolution were determined.
In the second part, the extraction of gelatine from tuna skin was carried out. Two approaches were used. First, the total solubilisation of the fish by-product in the solvent (IL or aqueous solution) followed by the recovery of the gelatine by precipitation. Second, a maceration step with the solvent and subsequent extraction with warm water. Rheology was used to compare the quality of the gelatine obtained with the different solvents and extraction methods.

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Synthesis and thermophysical characterisation of binary mixtures containing bio-based ionic liquids: choline L-threoninate

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The development of bio-based ionic liquids (ILs) represents a promising route towards more sustainable chemical processes [1,2], due to their enhanced non-toxicity and biodegradability compared to conventional ionic liquids [3,4]. Therefore, in this work, the synthesis and thermophysical characterisation of choline L-threoninate ([Ch][Treo]) and its binary mixtures with ethanol or propan-1-ol were investigated.

The structure and purity (98 %) of the synthesised ionic liquid were evaluated, after purification, using proton nuclear magnetic resonance (^{1}H-NMR) and Fourier-transform infrared (FTIR) spectroscopies. Then, experimental measurements of liquid density (ρ) and refractive index (n_{D}) were carried out over 288.15-308.15 K at 0.1 MPa for the pure IL and for its binary mixtures, covering all the composition range.

As expected, liquid density decreased with temperature but increased with IL content, while the refractive index rose with IL concentration, reflecting enhanced solution polarisability. Excess molar volumes (V^{E}) were calculated to assess deviations from ideality, and several empirical models were tested to correlate these data, with the Redlich-Kister (RK) expansion providing the most accurate fit. Linearisation of the temperature-dependent coefficients reduced the number of adjustable parameters from 20 to 6, while maintaining high accuracy ($\sigma \approx 5{\cdot}10^{-8}$ m^3·mol^{-1}). Compared to aqueous mixtures [5], which are more polar, the addition of ionic liquid to ethanol or propan-1-ol causes more pronounced negative excess molar volumes, reflecting a greater effect of charged species in less polar solvents.

These findings provide essential data for predictive computational approaches, including density functional theory (DFT), and demonstrate that integrating experimental and computational approaches accelerates the characterization of bio-based ILs.

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Application of Hydrophilic and Hydrophobic Deep Eutectic Solvents for the Extraction of Caffeine and Piperine

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Deep Eutectic Solvents (DESs) are becoming significant for the extraction of bioactive compounds owing to their adjustable properties, low toxicity, and excellent dissolution capacity, providing an environmentally friendly and efficient alternative to conventional organic solvents. Their advantageous properties enable high extraction yields and simplify downstream processing, meeting the increasing need for environmentally friendly chemical processes.
This research examines the feasibility of DES as selective solvents for the solid-liquid extraction of bioactive compounds. The extraction was conducted in a laboratory batch extractor equipped with a magnetic stirrer. Various types of DESs (hydrophobic and hydrophilic) were employed for the extraction of caffeine from tea and piperine from different species of pepper. The solubility of bioactive compounds in DESs, along with their activity coefficients and activities, was assessed utilizing COSMO-RS. The data obtained were utilized for the preliminary selection of solvents. The solubility of bioactive compounds was determined using experimental methods. Extracts were examined using UV/Vis and FTIR spectroscopy. The solvent with the highest yield was chosen. The impact of the solute-to-solvent mass ratio and the size of pepper particles on piperine yield was examined. The optimal solvents for the extraction of caffeine from tea and piperine from pepper were malic acid:glucose:glycerol (1:1:1 molar ratio) containing 30% water and thymol:1-octanol (1:1), respectively. Following the extraction, caffeine and piperine were effectively recovered: caffeine by cooling crystallization, and piperine by antisolvent crystallization with water. Water was removed from DES using vacuum evaporation. These findings underscore the need of choosing suitable solvent systems to optimize the extraction efficiency of bioactive compounds. Furthermore, the techniques utilized for regeneration illustrate the viability of recovery processes and highlight the potential for sustainable practices in the extraction of valuable phytochemicals.

Phase Equilibria and Thermal Decomposition of Binary Eutectic Systems: Quaternary Ammonium Salts and Fatty Acids

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A eutectic solvent is a mixture of two or more solid components that, when mixed in a specific ratio, undergo a solid-to-liquid phase transition at a certain temperature. This temperature, known as the eutectic temperature, represents the minimum melting temperature for the mixture compared to any other possible composition of the same components, as well as the individual components themselves [1]. These mixtures expand the range of possibilities of solvents to be used for any particular application, and also offer increased options for tunability of solubilisation or polarity, among others. Although the literature on applications of eutectic solvents is vast, fundamental questions associated with their physicochemical properties remain underexplored. Many studies apply eutectic solvents in common fixed molar proportions (e.g., 1:1, 1:2, 1:3) rather than thoroughly investigating the thermal behaviour of such mixtures before use. In fact, studies reporting reliable solid-liquid equilibrium (SLE) and thermal stability data of eutectic solvents are scarce in the open literature [2,3].

This work contributes to mitigating this gap by investigating the thermal behaviour of binary mixtures composed of two popular families of eutectic-forming components: tetraalkylammonium chlorides and fatty acids. The selected salts included tetraethylammonium chloride ($[N_{2222}]Cl$) and tetrapropylammonium chloride ($[N_{3333}]Cl$), while the organic acids were octanoic, decanoic, and dodecanoic acid. Experimental SLE data of the six binary mixtures were obtained by differential scanning calorimetry (DSC), and the thermal stability of the pure components and key mixtures was investigated by thermogravimetric analysis (TGA). The DSC results indicate that the mixtures exhibit a eutectic-type behaviour, with the eutectic point temperature increasing with the alkyl chain length of the fatty acid, and with the corresponding composition being richer in the acid than in the salt. In parallel, preliminary TGA results indicate that the complete development of the solid-liquid equilibrium diagram is not possible due to limited thermal stability at the salt-rich compositional range of the investigated systems.

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Carbon Dioxide Absorption in an Equimolar Mixture of Two Acetate-Based Ionic Liquids

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In the context of global warming, CO_2 is the greenhouse gas with the highest emission levels related to industrial activities. To reduce its environmental impact, various CO_2 capture techniques have been developed, commonly by absorption using a suitable absorbent. The current benchmark technology is represented by reactive absorption using aqueous amine solutions. However, this technology presents several drawbacks, such as high energy requirements in the solvent regeneration step (largely contributed by the heating of water, which is the non-active component of the absorbent), volatile organic emissions due to amine evaporation (with the concomitant need for amine makeup in the process), and the corrosive nature of the solution. Ionic liquids are a promising non-aqueous alternative for the development of more sustainable solvent-based approaches for CO_2 capture, due to their negligible volatility, unique solvation ability, and tunability of physical properties and type of absorption thanks to judicious selection of the constitutive ions. Some ionic liquids with the acetate anion, such as 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) and tetrabutylphosphonium acetate ([$P_{4\,4\,4\,4}$][OAc]), have been shown to chemically absorb CO_2 in a 1:2 molar ratio (CO_2 to solvent) [1,2], while also presenting a moderately low toxicity and a good potential for cost-competitive production in the large scale. Nevertheless, on the one hand, the product of CO_2 chemisorption by [C_2mim][OAc] is a solid at ambient temperature, which complicates handling; and, on the other hand, [$P_{4\,4\,4\,4}$][OAc] itself is also a solid at ambient temperature, requiring operational temperatures of at least ca. 70 °C to operate as a solvent. To avoid such problems associated to the independent utilisation of each individual ionic liquid, in this work the equimolar mixture of [C_2mim][OAc] and [$P_{4\,4\,4\,4}$][OAc] (liquid at ambient temperature) has been investigated as a synergistic strategy. Thus, CO_2 absorption isotherms in this mixture have been experimentally determined at 25 °C, 40 °C, 55 °C, and 70 °C, in the pressure range up to 15 bar. The results show that, compared to the use of neat [C_2mim][OAc], the mixture exhibits increased absorption capacity over the studied pressure range at 25 °C, likely due to enabling a physisorption mechanism beyond the chemisorption upon suppression of the solid character of the corresponding chemisorption product. At higher temperatures, the isotherm for the mixture is reasonably similar to either of the isotherms for the pure ionic liquids.

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The ionic liquid 1-ethyl-3-methylimidazolium propionate as entrainer for the deterpenation of citrus essential oil by solvent extraction

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Citrus essential oils are valuable ingredients in the cosmetics and food sectors, among others. In these complex mixtures, most of their constituents can be grouped into two categories: terpenes (hydrocarbons) and terpenoids (oxygenated compounds). The latter are the main contributors to the desirable properties in the application of citrus essential oils, despite typically representing a small fraction in the mixture. In contrast, terpenes, whcih can represent up to 95% of the oil composition, show minimal contribution to the aroma and flavour, and are more prone to instability by exposition to factors such as heat, oxygen, or light. Thus, the development of efficient deterpenation processes may improve the quality of the citrus essential oils directly obtained from the corresponding natural source, while substantially reducing the volumes to be transported and handled. In trying to make the deterpenation step technically viable and economically feasible, solvent-assisted unit operations such as liquid-liquid extraction and extractive distillation have been considered. However, conventional solvents exhibit poor performance from a thermodynamic perspective. Ionic liquids constitute an appealing alternative to conventional solvents due to their unique solvation ability and their extremely low volatility, which may facilitate the necessary recovery of the solvent in the deterpenation process. Preliminary works have evidenced a good performance by ionic liquids comprising the acetate anion and a dialkylimidazolium cation [1,2]. In this work, we investigate the deterpenation of citrus essential oil by extractive distillation using as entrainer an ionic liquid with an analogue carboxylate anion, namely propionate. Particularly, the ionic liquid 1-ethyl-3-methylimidazolium propionate ([C_2mim][propionate]) was selected. The essential oil was simplified as a binary mixture of limonene (the most representative terpene) and linalool (the most representative terpenoid), and the vapour-liquid equilibrium of the ternary system limonene + linalool + [C_2mim][propionate] has been experimentally determined at an absolute pressure of 5 kPa. The vapour-liquid equilibrium data have been correlated by the classical NRTL model, enabling the implementation of a suitable description of the experimental equilibrium behaviour in the commercial process simulator Aspen Plus. The corresponding simulations have allowed to explore the influence of the number of stages and the reflux ratio of the distillation column on the level of recovery and the purity of the deterpenated essential oil, as well as an assessment of the energy needed in the overall deterpenation process, including the auxiliary flash unit for recovery and recycling of the ionic liquid.

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Rational Screening and Pre-Design of Deep Eutectic Solvents for Biomass Fractionation via COSMO-RS and soft-SAFT

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Efficient fractionation of lignocellulosic biomass into lignin-rich and cellulose–hemicellulose streams constitutes a central challenge in advanced biorefinery design [1]. Deep eutectic solvents (DESs) have attracted increasing attention as tunable and potentially sustainable media for this purpose. However, the large combinatorial design space associated with DES formulations limits purely experimental screening. In this context, predictive thermodynamic frameworks are indispensable tools for rational solvent selection and process-oriented evaluation.

In this contribution, we develop an integrated computational strategy combining COSMO-RS with molecular thermodynamic modeling based on the soft-SAFT equation of state to assist in the pre-design of DESs for biomass fractionation [2]. COSMO-RS is first employed to compute activity coefficients of representative lignin- and carbohydrate-derived compounds in various DES environments, from which partition coefficients are derived as quantitative indicators of solvent selectivity. To address the structural complexity of lignin and hemicellulose derivatives while maintaining computational tractability, surrogate molecular models are constructed to represent their dominant functional groups. This approach enables systematic screening across chemical families and supports high-throughput evaluation of DES systems composed of choline chloride combined with different hydrogen bond donors (HBDs), including urea, betaine, and selected carboxylic acids. The screening identifies DES formulations exhibiting preferential affinity for lignin-type species while limiting the solubilization of cellulose and hemicellulose analogues.

The most promising candidates are subsequently analyzed using soft-SAFT, which provides a physically consistent representation of hydrogen bonding, polarity, and dispersive interactions within DES mixtures. The proposed integrated workflow accelerates solvent selection, reduces the experimental burden, and establishes a rational foundation for downstream validation and process-scale design.

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Modelling of Light-Driven CO_2 Capture Using the ePC-SAFT Equation of State

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Capturing carbon dioxide (CO_2) emissions is essential for meeting climate change goals. Current technologies capture CO_2 using amine-based solvents. Although effective, this technology is energy-intensive, especially in releasing the CO_2 and in reusing the solvent. Recently, an alternative process to capture based on photoacid molecules has been proposed [1]. Photoacids react with CO_2 to form bicarbonate. The reaction is photosensitive, allowing CO2 to be captured and released by changing light conditions. Hence, photoacid solutions provide an energy-efficient method for capturing greenhouse gases. However, the process is limited by the low solubility of photoacids in water. As a result, large amounts of solvent are required compared to amine-based systems.

This study investigates optimal conditions for capturing CO_2 using photoacid-based solutions. We assess the role of organic cosolvents in enhancing the photoacid solubility. The CO_2 capture process involves simultaneous phase equilibria and several acid-base reactions. The mixture behaviour is modelled using the ePC-SAFT equation of state [2] coupled with a permittivity model based on perturbation theory [3]. The modified RAND algorithm [4] is used to compute chemical and phase equilibria. This algorithm can handle chemical reactions, as well as multiple coexisting phases, including solid precipitation. This framework enables the systematic screening of solvents to enhance CO_2 capture with photoacids.

Our results show that organic cosolvents enhance the solubility of the photoacid (PHA). The ePC-SAFT's solubility predictions are in modest agreement with the experimental data but still provide valuable insights to optimize the solvent formulation in an absorber/desorber capture plant [1]. Future work aims to engineer optimal solvent formulations to decrease the operational cost of this technology and make it competitive against standard CO_2 capture processes.

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Flue gas and desalination from seawater with cyclopentane hydrates: thermodynamic experiments and modelling, kinetic influence

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Hydrate-based technologies for carbon capture and seawater desalination have recently attracted growing interest. While several studies focus on CO_2 sequestration or water purification independently, the combined thermodynamic behaviour of both processes remains underexplored.
In this work, hydrate equilibrium was experimentally investigated in the 20–65 bar range using a CO_2/N_2 mixture (15/85 mol%). Cyclopentane (CP) was employed as a thermodynamic promoter, reducing equilibrium pressure and shifting the stability zone to milder conditions. Its low water miscibility also facilitates recovery after dissociation. The obtained equilibrium data were compared with reference systems without additives and with seawater (see figure 1), confirming the strong stabilising effect of cyclopentane. The impact of salinity on water activity was assessed, showing that 3.5 wt% NaCl significantly decreases hydrate stability
Besides, a thermodynamic modelling was performed to investigate deeper phase equilibrium in details. First, fluid fugacities of the vapor-liquid cyclopentane phase have been modelled with PPR78 equation of states (EoS). Binaries were used to evaluate this choice with good agreement. Then, PPR78 EoS has been used in combination with the standard van der Walls and Platteeuw approach for clathrates hydrates.
Then, kinetic experiments monitored pressure and temperature evolution under two cooling rates. Although the cooling rate had little impact on the final hydrate state, the presence of NaCl markedly slowed down crystallisation. Hydrate conversion was further estimated using established correlations.
Finally, the main results showed that: the introduction of 3.5% by weight of NaCl into the system significantly slowed down the crystallisation process; the cooling rate had no significant effect on the final state of the system after crystallisation; PPR78 was used with apparent success for the CO_2-N_2-CP vapour-liquid system.

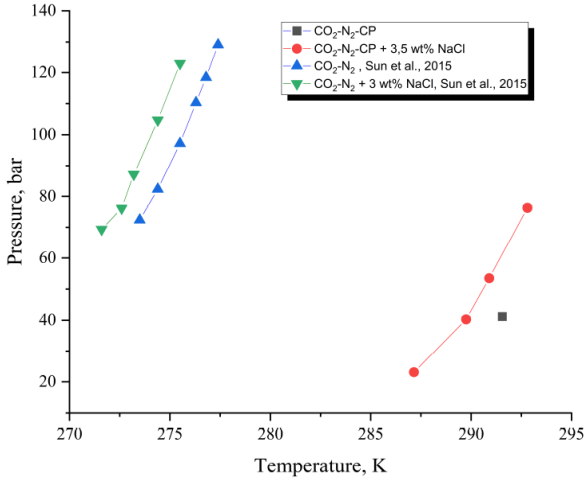

Figure 1. Thermodynamic data associated with the dissociation of mixed CO2-N2-CP hydrates.

Predicting Chemical Speciation Using SAFT-γ Mie: Extension to CO_2-Loaded Aqueous Multi-Amines and Blended Amine Solutions

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In amine-based carbon capture, the selection of efficient amine absorbents relies on predictive molecular models that can accurately describe key thermophysical properties and chemical speciation. The SAFT-γ Mie equation of state has previously been employed to describe both phase equilibria and chemical speciation in aqueous solutions of monoamines, such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). To model chemical speciation, reactions are represented as physical association between specific interaction sites on the molecular segments. This implicit chemical approach is not reliant on chemical equilibrium constants, which makes the framework more easily generalizable. In this study, we extend the SAFT-γ Mie speciation framework to diamines and other multi-amine compounds in CO_2-loaded aqueous amine systems. The developed approach generalizes to molecules with multiple amine sites (e.g. primary, secondary, and tertiary), which are considerably more challenging due to the presence of additional ionic species. The approach is evaluated for multiple systems including piperazine (PZ), 3-methylaminopropylamine (MAPA), with model predictions validated against experimental data through comparisons of CO_2 solubility and speciation fractions over a range of loadings, showing good agreement. The results highlight the importance of accurately determining equilibrium speciation, as it directly influences transport properties such as viscosity prediction.

Thermodynamic Modelling and Property Prediction of CO_2 Mixtures for Ship-Based Transport in CCUS

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The shipping of carbon dioxide (CO_2) is increasingly recognized as an important element in international efforts to mitigate climate change through Carbon Capture, Utilization, and Storage (CCUS). Liquefied CO_2 (LCO_2) carriers represent a flexible link between capture sites and long-term storage or utilization facilities, enabling the safe and reliable movement of CO_2 over long distances and at different scales.

Up to now, CO_2 shipping has mainly supported food-grade and high-purity markets, where the product is transported at medium pressure (around 15 bar at –28 °C) using relatively small ships. While scaling up typically reduces costs, the high cargo pressure of medium-pressure LCO_2 limits the tank size, restricting potential cost savings from larger vessels. For CCUS, however, there is a clear need for low-pressure transport solutions that can accommodate larger tanks and larger vessels, allowing much greater volumes of CO_2 to be shipped economically [1].

Captured CO_2 streams differ from food-grade CO_2 in terms of impurities presence. Actually, the former usually contain impurities such as water, nitrogen, oxygen, methane, hydrogen, carbon monoxide, argon, etc, which may affect the liquefaction and transport processes, introducing risks of corrosion, phase separation, and reduced efficiency [2]. With respect to phase behavior, non-condensable impurities (N_2, O_2, H_2, Ar, CO, CH_4) have a strong influence on vapor pressure under low-pressure conditions near the CO_2 triple point—precisely the conditions that are of most interest for large-scale transport. Condensable impurities such as water, on the other hand, can promote phase separation. For this reason, a clear understanding of impurity effects is essential for defining purity specifications in CO_2 shipping.

The aim of this work has been to develop a predictive tool for phase equilibrium calculations in CO_2 mixtures under transport conditions, and to show how impurities influence key properties such as vapor pressure and density. To achieve this, the Peng–Robinson Equation of State [3] was employed, modified with new interaction parameters and a volume translation to improve accuracy. In parallel, empirical correlations were derived for practical use, providing simple but reliable estimates of vapor pressure, density, heat capacity, speed of sound, and viscosity as functions of temperature, pressure, and composition.

First, an overview of the existing CO_2 transport specifications and impurity ranges is given. Then, the thermodynamic model is described in detail, including its ability to reproduce vapor–liquid equilibria (VLE), vapor–liquid–solid equilibria (VLSE), triple-point conditions, and liquid–liquid equilibria (LLE) related to water. Finally, the development of the empirical models is presented, together with their application as a practical tool for engineers working with CO_2 transport.

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Techno-Economic Boundaries and Material Design of Aprotic Heterocyclic Anion-Based Ionic Liquids for Diluted CO_2 Capture

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Capturing CO_2 from diluted gas streams presents a significant technical and economic challenge for industrial decarbonization. This study explores the potential of Aprotic Heterocyclic Anion-based Ionic Liquids (AHA-ILs) as versatile solvents for CO_2 abatement across a wide range of inlet concentrations. Utilizing a multi-scale approach, over 200 AHA-ILs were designed and screened using DFT/COSMO methodology to predict fundamental material properties, including reaction equilibrium constants and physical solubility (Henry's constants), when paired with the $[P_{66614}]^+$. Top-performing candidates were integrated into rigorous Aspen Plus process simulations to evaluate an absorption-regeneration scheme utilizing temperature and pressure swing configurations. The study spanned a spectrum of CO_2 partial pressures, from post-combustion levels (0.13 bar) down to the thermodynamic limits of Direct Air Capture (DAC). Key findings demonstrate that the enthalpy of reaction is the primary driver of cyclic capacity, directly dictating the ionic liquid flow rates required to achieve a 90% CO_2 removal efficiency. These flow requirements serve as the critical link between molecular design and macro-scale economics, heavily influencing both variable operating costs (OPEX) and capital investment (CAPEX). Economic analysis reveals a total annualized cost of approximately 35\$/tCO_2 at 0.13 bar. However, as the CO_2 source becomes more diluted, the number of viable AHA-ILs diminishes. A practical operability limit for traditional packed columns was identified at 0.01 bar, yielding a minimum cost of 84\$/tCO_2 (Figure 1). Below this threshold, exponential cost increases, rising utility-related emissions, and physical constraints such as column flooding render conventional packed-bed technology unfeasible. These results highlight a critical "technological wall," suggesting that while AHA-ILs possess the chemical affinity required for extreme dilution, realizing their full potential necessitates a transition to alternative contactor technologies.

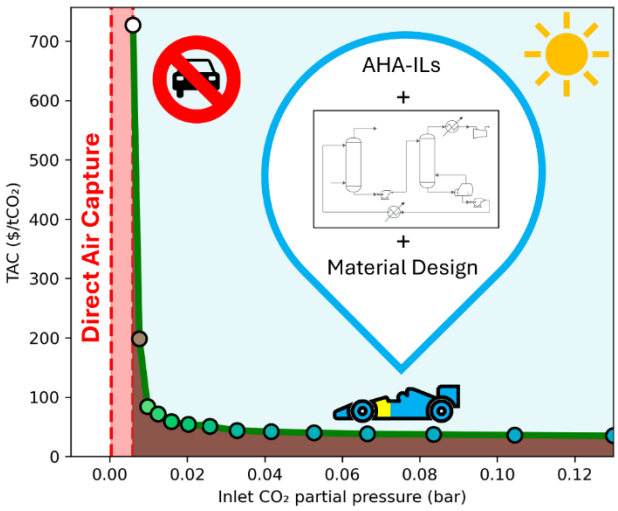

Figure 1. Total Annualized Cost per ton of CO_2 captured as a function of partial pressure

Improvement of an Equation of State for Non-spherical Molecules Based on Statistical Mechanics

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Lopes and Franco [1, 2] proposed an equation of state for non-spherical particles, based on Gil-Villegas' SAFT-VR with the square well potential [3]. In this formulation, the Helmholtz free energy terms for monomer and chain interactions were replaced by a single reference contribution, modelled as the free energy of a non-spherical system. The modification showed that considering excluded-volume contributions due to rotations and translations of the non-spherical molecular geometry in the reference term improves the predictive capacity of the equation, surpassing the version with the spherical attractive term. The attractive interactions between particles, however, were kept according to the SAFT-VR formulation, based on a second-order Thermodynamic Perturbation Theory (TPT) for spherical particles.

In this work, models were developed for the first- and second-order perturbation coefficients for ellipsoidal particles to overcome the spherical limitation of the attractive term in the Lopes and Franco Equation. First, a new model for the first-order perturbation coefficient was derived for a non-spherical potential. The chosen potential is characterized by the contact distance between the non-spherical particles and is constant within its fixed limit, so that the attractive region is a contour of the original particle, located within a fixed distance from its surface. In addition, the repulsive region was treated via hard-core interactions. This potential was denominated as a non-spherical square well potential.

Then, a model was proposed for the first-order perturbation coefficient of the new anisotropic potential. The formulation, however, required an expression for the average radial distribution function. Hence, Monte Carlo simulations in the canonical ensemble (NVT) were performed to determine the first-order perturbation coefficients with the new non-spherical square well potential. This same strategy had already been adopted in SAFT-VR. Gay-Berne's Hard Gaussian Overlap (HGO) model [4] was used to compute the contact distances between the ellipsoids of revolution. The model developed for the first-order perturbation coefficient showed excellent agreement with the data obtained in the simulations. After that, a model for the second-order perturbation coefficient was also developed.

The terms were incorporated into the Lopes-Franco equation, and the parameters of the equation were fitted for 14 components, based on vapor-liquid equilibrium data available in the literature. Despite a significant gain in physical meaning, the modified equation of state performed worse in predicting phase equilibrium than the original equation for particles with ellipsoidal geometry.

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Extension of openCOSMO-RS-Phi to Binary Mixtures: Towards a Predictive Equation of State for Real Systems

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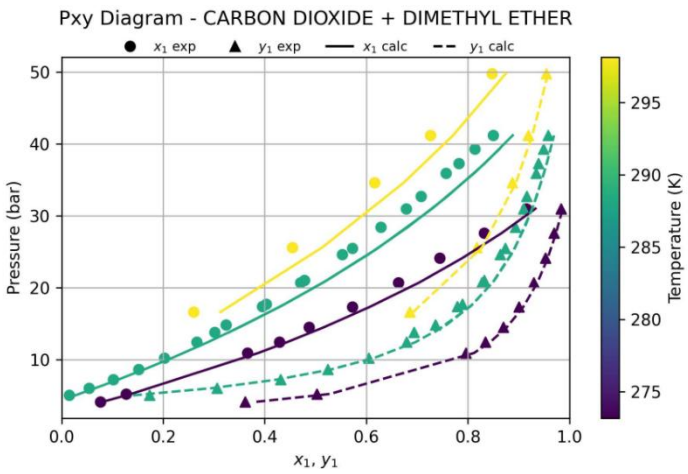

Equations of state (EOS) are indispensable in predicting thermodynamic behavior, yet most conventional approaches rely on mixing rules or fitted binary interaction parameters. The recently developed openCOSMO-RS-Phi framework offers a fundamentally different alternative. By combining the activity coefficient model from openCOSMO-RS[1] with the pseudo-mixture free-volume concept of COSMO-SAC-Phi[2], this model successfully represents pure substances as mixtures of real molecules and a pseudo-component capturing free volume. Building on this foundation, we extend the framework from pure substances to binary mixtures without introducing additional adjustable parameters or compromising predictive power. Each component is paired with its own pseudo-component, ensuring consistency between pure and mixed systems. The only required input data are molecular surface charge distributions, pure-component vapor pressures, and liquid densities. Predictive accuracy was systematically tested against the thermodynamic database of Jaubert et al.[3], enabling direct comparison with recent PC-SAFT benchmarks. The results demonstrate that openCOSMO-RS-Phi maintains strong predictive capability for binary systems, establishing a robust platform for future developments focused on electrolyte modeling. This work emphasizes the importance of open, reproducible, and predictive EOS frameworks for advancing chemical engineering thermodynamics.

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Speed of Sound Measurements in Nitrogen, Argon, and Xenon at Cryogenic Temperatures Between 80 K and 220 K

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Accurate speed-of-sound datasets are essential for the development of equations of state and validation of molecular simulation results. The speed of sound in the liquid regions of nitrogen, argon, and xenon has so far not accurately been measured. We therefore performed comprehensive and accurate measurements of the speed of sound in nitrogen, argon, and xenon at cryogenic temperatures using the pulse-echo technique. Our measurements cover the temperature ranges from 80 K to 200 K for nitrogen, from 90 K to 220 K for argon, and from 170 K to 220 K for xenon with pressures up to 100 MPa, where the accessible pressure range near the triple-point temperature is restricted by the melting pressure curve. To reach these temperature ranges, we employed a thermostat cooled with liquid nitrogen. The expanded (k = 2) measurement uncertainties are 3.1 mK in temperature, 0.005 % in pressure, and 0.01 % in speed of sound. Comparisons with the current reference equations of state and data of other authors from the literature confirm the high accuracy of our measurements.

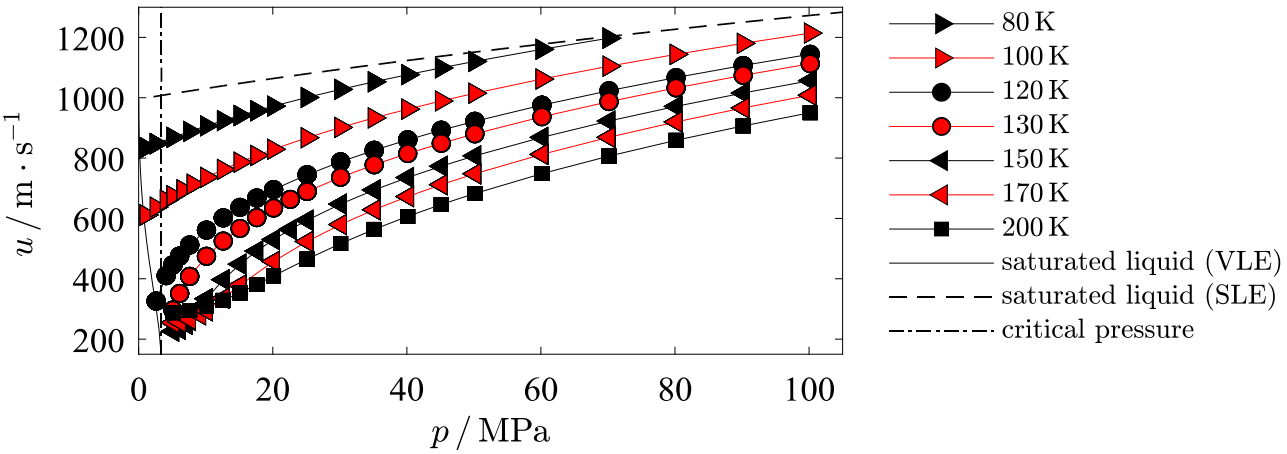

Figure 1. Experimental speeds of sound in nitrogen as a function of pressure.

Evaluation and Extension of the GC-PPC-SAFT Model on binary mixtures

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The design of innovative, efficient, and sustainable processes in chemical and pharmaceutical industries relies heavily on accurate thermophysical data. While experimental data remains the gold standard, it is often unavailable for specific conditions, compositions or new fluids. Bridging these gaps necessitates predictive thermodynamic models, such as equations of state (EoS). Among existing EoS approaches, the Polar Perturbed-Chain Statistical Associating Fluid Theory (PPC-SAFT) [1,2,3] stands out for its ability to describe complex systems, including associating and polar compounds, without the need for binary interaction parameters [4]. However, the tedious parameterization of PPC-SAFT, limits its broader adoption in industrial applications [5].
In this study, we evaluate an existing group contribution method, GC-PPC-SAFT [6], for predicting PPC-SAFT parameters using a comprehensive reference database of binary mixtures experimental VLE, LLE, enthalpy, heat capacity, azeotropes and critical points developed by Jaubert et al. [7]. The evaluation assesses the GC-PPC-SAFT model's capability to predict properties of mixtures, employing a scoring methodology proposed by Piña-Martinez et al. [8]. The mixtures are categorized into nine association classes regarding the pure components capability to accept or to give a labile hydrogen [7]. In this database, halogenated molecules are present in every mixture of a hydrogen donor and a non-associating molecule, and mixtures of a hydrogen donor and a hydrogen acceptor. However, it was identified that halogenated molecules could not be taken into account by GC-PPC-SAFT. To address this gap, we propose new parameters to support chlorinated molecules, which considerably extend the model applicability and enhance the model's overall scoring and predictive accuracy. This study not only underscores the importance of comprehensive evaluation using a reference database but also broadens the scope of GC-PPC-SAFT and sets a benchmark for the development of advanced predictive PPC-SAFT parameterization methods.

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High-Pressure Phase Equilibria for Carbon Dioxide + Diisopropyl ether: Experimental Measurements and Modelling

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Understanding the high-pressure phase behaviour of carbon dioxide mixtures with organic compounds is critical for applications in chemical processing, extraction, and carbon dioxide (CO_2)-based technologies. In this work, we present new experimental investigations of the phase equilibrium of CO_2 + diisopropyl ether (DIPE) system at elevated pressures and various temperatures. Using a high-precision high-pressure installation, we measured vapor–liquid equilibrium (VLE) and density data over a broad range of compositions and pressures, and temperatures up to 398.15 K. The critical curve for the CO_2 + diisopropyl ether (DIPE) binary system was also measured.
The experimental data were modelled with cubic equations of state using different approaches such as with temperature-dependent parameters. The combined experimental and modelling approach allows accurate representation of the system's thermodynamic behaviour, providing insights into molecular interactions between CO_2 and DIPE and their impact on phase boundaries.
This study underscores the importance of integrated experimental and modelling efforts in elucidating high-pressure phase behaviour of CO_2-containing systems and highlights methodological considerations for extending these approaches to other CO_2–organic solvent mixtures.

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Benchmarking of thermodynamic derivative properties by various thermodynamic models for a wide range of polar mixtures

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Thermodynamic models are integral to chemical process design, relying on accurate predictions of the thermodynamic properties of chemical species and their mixtures. Yet, selecting the most suitable model for a given system remains a persistent challenge. Despite the development of numerous model variants, including SAFT-type families as well as their polar extensions, their predictive performance varies significantly across systems, particularly for binary mixtures. While incorporating dipolar terms is beneficial, the magnitude and direction of the improvement depend strongly on the molecular polarity and the sensitivity of the specific thermodynamic property to dipole interactions. To support systematic benchmarking, we have compiled an extendable SQLite database containing vapor-liquid equilibrium (VLE) and thermodynamic derivative properties for a wide range of binary mixtures inspired by the work of Jaubert *et al.* [1]. In this study, we conducted extensive parameterizations for all mixtures in our database, both with and without the inclusion of binary interaction parameters (k_{ij}), to assess the influence of this parameter on predictive accuracy. The optimized parameter sets are integrated into our database to facilitate future model refinement and validation across diverse thermodynamic systems.

Acknowledgment
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Incorporating Ion-Size Effects into the eSAFT-VR Mie Equation of State for Electrolyte Solutions

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Electrolyte solutions play a crucial role in energy, environmental, and industrial processes. This work based on eSAFT-VR Mie extends and refines the model to compare the predictive performance and properties across various salts and thermodynamic conditions, focusing on mean and individual ionic activity coefficients (MIAC, IIAC) and density. Previous study evaluated how different treatments of ion size and association influenced model consistency. Comparisons between the models of different researchers [1, 2] reveal that using a temperature-dependent effective segment diameter (*d*) instead of a fixed σ, and ion-pairing effects enhances the description of electrostatic effect between cations and anions, especially in concentrated and multivalent systems.
In this work, the eSAFT-VR Mie framework is further extended and optimized to improve the description of mean and individual ionic activity coefficients (MIAC, IIAC) and density across a wide range of salts and conditions. The updated parameter matrix [3,4] integrates temperature-dependent segment diameters and refined combining-rule parameters, enabling consistent treatment of electrostatic and dispersion interactions. The model successfully reproduces experimental MIAC and density trends and captures the asymmetric behavior between cations and anions in multivalent systems. Significant improvements are obtained for strongly associated electrolytes such as $MgSO_4$ and $CaCl_2$, where deviations in MIAC are substantially reduced. In particular, the optimized parameters achieve MIAC deviations of approximately 2 % for NaCl, 8.8 % for LiCl, 5.4 % for $MgCl_2$, and 6.6 % for $CaCl_2$, while maintaining density predictions within a few percent. These results confirm the enhanced accuracy and transferability of the extended eSAFT-VR Mie model.

Acknowledgements
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Applications of Large Language Models in Thermodynamics

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Large Language Models (LLMs) have made significant progress in reasoning and can now generate human-like responses, even in specialized domains. This will transform both scientific research and engineering practice. In our contribution, we will present recent findings on using LLMs for solving thermodynamic problems. We consider two questions:
1) How good are LLMs at solving textbook-style problems from thermodynamics?
Different widely used LLMs were tested on problems of varying complexity [1]. The results demonstrate the breath-taking pace at which the problem-solving capabilities of LLMs have evolved since 2024. We tested OpenAI's latest reasoning models on our Thermodynamics I exam: o3 in spring 2025 and later GPT-5 Thinking in September 2025 [2]. The problems and the way the answers were evaluated were precisely the same as in the student's exam, enabling a fair direct comparison: o3 and GPT-5 Thinking came out first, better than the best student who scored grade A. This signals that machines now excel in complex tasks, usually taken as proof of human intellectual capabilities.
2) Can LLMs reliably collect fluid property data from the literature?
Fluid property data are essential for solving many engineering problems. Their retrieval from the literature is therefore a basic task that has to be carried out routinely. It is a step-wise procedure starting with the identification of relevant sources, the interpretation of the information in the source, the extraction of the relevant data, its validation and the collection of the data from different sources in a data bank. Using data on vapor-liquid equilibria of binary systems as a test case, we show that reasoning LLMs can efficiently support this process, but that we presently need humans in the loop. Based on the findings, we will discuss implications for future development of thermodynamics and, more generally, engineering.

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Structure-Based Machine Learning for Predicting Speed of Sound in Deep Eutectic Solvents

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Deep eutectic solvents (DESs) are increasingly recognized as sustainable substitutes for conventional solvents because of their environmental benefits and tunable physicochemical properties. Nevertheless, the prediction of their thermophysical and acoustic behavior, particularly the speed of sound, remains a significant challenge, mainly due to the complex nature of their molecular interactions. In this study, a hybrid machine learning framework is proposed that explicitly incorporates structural information through group contribution (GC) and atomic contribution (AC) descriptors to improve predictive accuracy and interpretability. A comprehensive databank of 1031 experimental measurements collected from 97 distinct DES systems at atmospheric pressure and over a wide temperature range was assembled and employed for model development. By combining these molecular-level descriptors with machine learning algorithms, robust models were established that capture the underlying structure–property relationships beyond bulk experimental parameters. The developed framework exhibited excellent predictive performance, with average absolute relative deviations (AARD%) consistently below 1%, demonstrating both reliability and generalizability. Furthermore, the interpretability of the models highlights the contribution of specific functional groups and atomic environments of hydrogen-bond donors and acceptors to the observed acoustic properties. These insights not only validate the predictive approach but also provide a mechanistic understanding of DES behavior at the molecular level. Overall, this work illustrates how uniting GC/AC-based chemical intuition with data-driven modeling enables accurate and transparent prediction of solvent properties. The proposed methodology represents a valuable tool for the rational design and selection of DESs in thermodynamics, green chemistry, and industrial applications.

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HNCB-AI: Integral Equation Theory Meets Machine Learning

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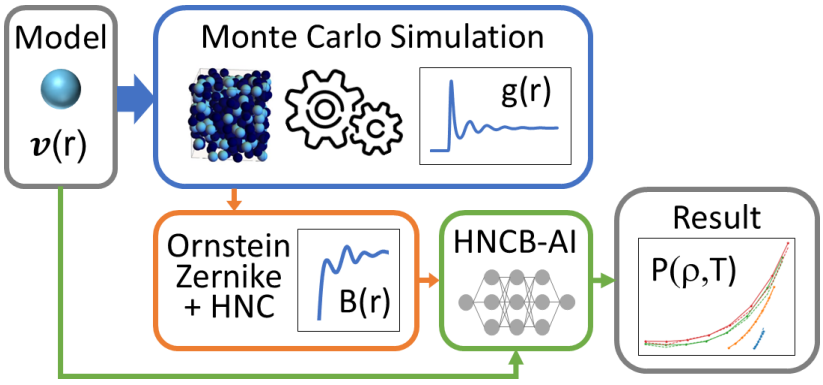
Properties of classical molecular systems can be calculated with integral equation theories based on the Ornstein-Zernike (OZ) equation and a complementing closure relation. One such closure relation is the hyper netted chain (HNC) approximation, which neglects the so-called bridge function. We present a new way to use machine learning to train a deep operator network to predict the bridge function, based on the radial distribution function as input [1].
Bridge functions for the Lennard-Jones fluid are calculated from Monte Carlo simulations in a wide range of densities and temperatures. These results are used to train the deep operator network. This network is employed to improve the HNC closure by the prediction for the bridge function, and the resulting set of equations is solved iteratively. Scheme 1 shows the elements of this novel closure, referred to as HNCB-AI.
For assessment, we compare the radial distribution function and the pressure, calculated by the viral expression, with Monte Carlo results and standard HNC. It is evident that incorporating the neural network- based bridge function in the closure relation leads to substantially improved predictions.
Universality of our method is demonstrated by comparing results for the Mie fluid and the hard sphere fluid, calculated with HNCB-AI trained only on Lennard-Jones data, with exact Mie and hard sphere results, showing overall good agreement.



Scheme 1. Elements of the novel HNCB-AI closure.

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A Bayesian methodology for the sequential updating of parameters in group contribution equations of state

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Group contribution (GC) equations of state (EOS) make thermodynamic models predictive and capable of predicting thermophysical properties in the absence of experimental data. Two methods are currently employed in the parameterization of GC EOSs: sequential and end-to-end parameterization. The sequential approach involves fitting parameters consisting of specific groups sequentially, either keeping the previously regressed group parameters unchanged or by updating the relevant previously regressed parameters. The end-to-end parameterization is a once-off regression where all data is used to parameterize the GC EOS for all groups present in the training set. The computational cost of such an approach has been historically infeasible, but even in the age of GPU powered high-performance computing, database paywalls still make such approaches prohibitive to most researchers.

Within the SAFT-γ Mie EOS [1], sequential parameterization without updating is used to fit group parameters [2]. Sequential parameterization without updating only requires data for compounds consisting of new groups, where parameters are only fit for the new groups. This approach biases the predictions to be more accurate for chemical species firstly regressed at the expense of chemical species later introduced. The UNIFAC consortium on the other hand uses sequential parameterization with updating [3]. This approach updates all relevant group parameters when new data is introduced, by requiring some of the previously used data in the objective function. This maintains good predictions across all chemical species, irrespective of the order in which they were introduced, but requires that previous data, and hence property predictions for the previously used data, be considered again. Due to these EOSs typically being parameterized on phase equilibria data, the iterative flash computations that characterise the equilibrium calculations are required at each iteration during optimization. This has made sequential parameterization with updating less attractive, due to additional computational expense.

We propose a Bayesian methodology for sequential parameterization, which circumvents this problem by encoding all previous data into the posterior distribution. The approach also challenges the accuracy of end-to-end parameterisation without requiring access to expensive databases and allowing data to be considered as it is available. This approach ensures that the appropriate weighting is given to previous datasets whilst only requiring the consideration of new data and providing estimates of uncertainty.

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Machine Learning-Empowered Group-Contribution Methods

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Accurate predictions of thermophysical properties of mixtures are crucial for process design and optimization in chemical engineering. Group-contribution models of the excess Gibbs energy (G^E), such as UNIFAC, which estimate mixture properties based on pair-interaction parameters between structural groups, are well-established in both academic and industrial practice. However, despite their success, these models still have substantial limitations, mainly due to incomplete parameter tables, which result, in turn, from missing experimental data and the challenging parameter fitting procedure. As a consequence, the scope of UNIFAC is still, even after decades of development and refinement, highly restricted [1,2].

In this work, we address this shortcoming by combining matrix completion methods (MCMs) from machine learning (ML), widely used in recommender systems, with physical group-contribution methods, resulting in powerful hybrid models [3]. Specifically, we train and utilize MCMs for predicting the pair-interaction parameters of various versions of UNIFAC, including both publicly available and commercially licensed ones within the UNIFAC Consortium (TUC) [4], thereby filling all gaps in their parameter tables [5,6]. The developed models were trained end-to-end on hundreds of thousands of experimental data points for phase equilibria from the Dortmund Data Bank. The resulting hybrid models not only have a significantly larger scope than the original models but also exhibit substantially higher prediction accuracies.

We demonstrate the performance of the developed models by predicting activity coefficients and phase equilibria across a wide range of binary and multi-component mixtures, showcasing an unprecedented combination of the physical model's robust extrapolation capabilities and the predictive power of the MCM for previously unreported parameters. Furthermore, we systematically analyze the key factors influencing the performance of the hybrid and original models, e.g., regarding the quality of individual pair-interaction parameters, which hint at paths for further refining the novel models.

The novel hybrid models can be readily transferred to process simulators and industrial workflows, as only the parameter tables in established implementations need to be changed. Furthermore, the presented hybridization strategy is not limited to group-contribution G^E models. Instead, it will serve as a role model for advancing models that rely on pair-interaction parameters in general, thereby paving the way for a new generation of prediction methods for thermophysical properties.

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From Molecular Structures to Property Prediction – Efficient Generation of Sigma Profiles as a Machine Learning Feature

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The charge distribution of molecules determines their intermolecular interactions. One-dimensional representations of the surface charge distribution, referred to as sigma profiles, are used as molecular descriptors in models such as COSMO-RS, COSMO-SAC and QSPR to predict the properties of fluids on a macroscopic scale. More recently, sigma profiles have also been explored as feature vectors for machine learning [1, 2]. A key advantage of sigma profiles is that they can be derived from quantum mechanical (QM) calculations while remaining physically interpretable.
This study examines the impact of various parameters in the underlying QM calculations on the predictive accuracy of simple machine learning (ML) models for thermophysical properties. Specifically, this study analyses the impact of sigma profile post-processing, the choice of QM method and the quality of the molecular geometries. The results show that the most precise (and computationally expensive) QM methods are not necessary to generate sigma profiles suitable for machine learning (ML) applications. These findings suggest that a comprehensive sigma profile database could be constructed with comparatively moderate computational effort, providing a valuable foundation for ML-assisted thermodynamic predictions.

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Toward AI-Accelerated Prediction of Gas Adsorption in Metal–Organic Frameworks via Macrostate Probability Distributions

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Metal–organic frameworks (MOFs) are promising porous materials for gas adsorption and storage due to their tunable structures and high surface areas. As hundreds of thousands of MOFs have been reported in the literature, identifying high performing MOFs for the given application, such as gas storage and separation, is important. Traditional methods like grand canonical Monte Carlo (GCMC) simulations provide accurate prediction of adsorption loading in MOFs but are computationally expensive especially when applied to large-scale MOF screening. Recently, macrostate probability distributions (MPDs) from flat-histogram Monte Carlo simulations have been proposed as an efficient method to obtain adsorption loading [1][2]. Nevertheless, generating MPDs for thousands of MOF structures remains computationally demanding, potentially limiting their use in large-scale screening.

We hereby propose a transformer-based approach that maps MOF structural and physicochemical descriptors with MPDs. Instead of predicting a single adsorption loading, the model predicts a full probability map describing how likely each adsorption state is at a reference condition. By enforcing physical constraints such as normalization and thermodynamic consistency, the model predicts physically consistent MPDs, which can then be used to compute adsorption isotherms via post-processing calculations, enabling rapid, physics-informed screening of MOFs. MPDs generated from a large-scale NVT + Widom swap simulations were used to train the transformer, and the trained model is used to predict MPDs to rapidly generate adsorption isotherms for CO_2, CH_4, and N_2 via post-processed extrapolation.

This study demonstrates a transformer-based approach can efficiently generate adsorption isotherms from predicted MPDs, paving the way for AI-accelerated molecular simulation and scalable discovery of new porous materials for adsorption-based separation applications.

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A Data-driven Approach to Evaluating the Applicability of Ideal Adsorbed Solution Theory (IAST) based on Site-Heterogeneity in Metal-Organic Frameworks

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Ideal Adsorbed Solution Theory (IAST) is a vital tool for predicting mixture adsorption from single-component isotherms. However, its accuracy hinges on key assumptions, most notably uniform adsorption site accessibility, which are often violated in heterogeneous nanoporous materials such as metal-organic frameworks (MOFs). While IAST failures from strong intermolecular interactions (e.g., in polar mixtures such as water/ethanol) are often anticipated, failures caused by adsorbent heterogeneity are more difficult to detect a priori. As high-throughput, multiscale computational screening becomes a common approach to identify promising materials under realistic mixture conditions, an efficient computational method is needed to identify materials where IAST will fail before running these simulations.

To address this, we systematically evaluated a diverse set of over 8,000 metal-organic frameworks (MOFs). We employed high-throughput grand canonical Monte Carlo (GCMC) simulations to generate single-component CO_2 and CH_4 adsorption isotherms and performed energy distribution analyses for each MOF for each adsorbate. By classifying materials based on the energy distribution features (e.g., number of peaks), we developed a robust metric for adsorption site heterogeneity. We then established a quantitative correlation between this heterogeneity metric and the IAST prediction error for CO_2/CH_4 mixtures. Our results show that IAST accuracy progressively decreases as site heterogeneity increases. This work provides a computationally inexpensive screening metric to define the practical limits of IAST's applicability.

Interfacial Thermodynamics of Ether-Based Fuel Blends: A Predictive Machine Learning Approach

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Oxygenated ethers are widely used as fuel additives due to their high-octane numbers and their ability to reduce particulate emissions. When blended with alkanes and alcohols, these compounds form multicomponent mixtures whose interfacial tension (IFT) directly influences spray atomization and combustion efficiency. However, experimental IFT data remain limited, particularly for ternary fuel formulations of practical relevance. In this work, we develop a machine-learning framework to predict the interfacial tension of ether-based fuel systems, including pure compounds, binary mixtures, and fully predictive ternary mixtures composed of ethers + alkanes + alcohols. The model is trained using experimental data for selected pure fluids and binary systems, while ternary mixtures are evaluated under strict predictive conditions, without prior exposure during training. Molecular structure and thermodynamic state variables are encoded through hybrid structural and compositional descriptors, including Morgan fingerprints to represent molecular topology, RDKit-derived physicochemical parameters, and relevant thermodynamic variables such as temperature and composition. Multiple learning algorithms are assessed. Special attention is given to the data-splitting strategy, where compounds and mixtures are classified by components and assigned to train, validation, and test sets, following a K-fold validation. This component-based split ensures a realistic evaluation of predictive capability and prevents data leakage between related systems.

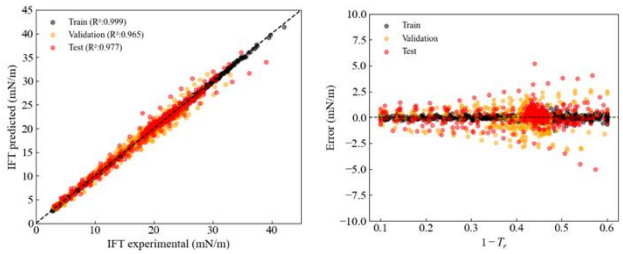

Figure 1. Predicted vs. experimental surface tension for ethers using Catboost regression.

The resulting models demonstrate strong generalization performance and accurately capture composition-dependent interfacial behaviour in unseen ternary blends. Importantly, the framework enables reliable prediction of interfacial tension in oxygenated mixtures under fully predictive conditions. This approach provides a computationally efficient tool for screening multicomponent oxygenated fuel formulations and supports the accelerated design of environmentally compatible fuel systems.

Acknowledgements
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Functionalized Porous Materials for the Selective Adsorption of Pharmaceutical Pollutants from wastewater

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The persistence of pharmaceutical pollutants in aquatic environments poses an increasing threat to ecosystems and public health due to their bioactive nature and resistance to conventional wastewater treatment processes. To address this challenge, this study investigates the design and development of advanced functionalized porous materials for the selective adsorption of pharmaceutical contaminants (Valsartan, Diclofenac, and Iopramide) from wastewater, with a particular focus to biomass-derived carbon adsorbents functionalized with ionic liquids and deep eutectic solvents, engineered to enhance adsorption capacity, selectivity, and reusability. Laboratory-scale experiments will assess the materials' performance through adsorption isotherms and kinetic studies. The optimization of parameters such as pH and temperature is carried out to maximize efficiency, regeneration and reuse to further evaluate the long-term sustainability and economic feasibility of the proposed materials. By contributing with innovative, high-performance, and environmentally friendly adsorbents, this work aims to advance wastewater treatment technologies and support the transition toward zero-pollution objectives in line with European sustainability goals.

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Removal of PFAS from wastewater using novel functional adsorbents

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The widespread detection of per- and polyfluoroalkyl substances (PFAS) in wastewater has raised serious environmental and public health concerns, primarily due to their extreme persistence, toxicological effects, and bioaccumulative behaviour [1]. Conventional treatment approaches have consistently failed to achieve satisfactory removal of these emerging contaminants, underlining a pressing need for innovative strategies that can deliver both efficiency and sustainability [2].
The study aims to address this gap by developing advanced adsorbents specifically tailored for the removal of PFAS from wastewater. The main focus of the study is design and functionalization of novel carbon-based materials, more specifically Polymers of Intrinsic Porosity, with particular attention to PIM1 and modified PIM1. The final goal is to enhance adsorption capacity, selectivity towards target pollutants, and regeneration efficiency beyond what is currently achievable with existing adsorbents.
To achieve this, the project will conduct systematic laboratory investigations encompassing adsorption kinetics, equilibrium capacity, and breakthrough performance. The regeneration potential of the developed adsorbents will also be rigorously assessed to establish their economic viability and long-term environmental benefits.
By combining high removal efficiency with sustainability considerations, this research seeks to deliver next-generation adsorbents that are cost-effective, scalable, and environmentally friendly. The outcomes are expected to contribute significantly to advanced wastewater treatment technologies and to align with broader zero-pollution and circular economy goals.

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Innovative Solutions for Selective Capture of Industrial Emissions and Circular Economy Integration

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Air pollution remains a critical global challenge, with contaminants of emerging concern (CECs), such as industrial chemicals and by-products, posing serious risks to human health and ecosystems. In particular, industrial sectors like foundries emit significant amounts of non-metal volatile organic compounds (especially amines), demanding advanced mitigation strategies. Innovative solutions are being developed to selectively capture and reclaim amines from foundry emissions, aligning with stricter regulatory frameworks that set ambitious emission reduction targets. A novel dual-purpose technology integrating adsorption and membrane processes has demonstrated the ability to significantly abate amine emissions while enabling resource recovery, improving both environmental performance and process economics. With a treatment capacity of 240 Nm^3/day and proven replicability across the foundry sector and beyond, this approach enhances gas treatment efficiency, lowers production costs, and supports circular economy objectives. By combining materials innovation, process integration, and regulatory alignment, these technologies hold the potential to achieve over 90% reduction in targeted pollutants, advance industrial sustainability, and protect both public health and the environment.

Biomass-Derived Activated Carbon as a Sustainable Adsorbent for PFAS and Pharmaceutical Removal from Water

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The increasing presence of contaminants of emerging concern (CECs), e.g. per- and polyfluoroalkyl substances (PFAS) and pharmaceuticals, in environmental waters has raised significant concerns due to their persistence and potential toxicity. Conventional water treatment technologies are often inefficient in removal of these persistent contaminants which underscores the necessity for novel approaches.

Activated carbons (AC) have emerged as a promising adsorbent for the removal of CECs, due to their high surface area, adsorption capacity and ease of implementation[1]. However, the sustainability of AC production and its cost-effectiveness remain key challenges, especially when considering the environmental impact of its sourcing. The present study focuses on the characterisation of the adsorption capacity of AC derived from biomass waste as part of a circular economy approach. Different waste biomass is used in the production of activated carbon, and its ability to adsorb per- and polyfluoroalkyl substances (PFAS) and pharmaceutical contaminants from aqueous solutions is evaluated. A range of parameters, including adsorption kinetics, equilibrium, and capacity, are evaluated under varied conditions to ascertain the efficacy of AC in eliminating these pollutants. The findings indicate a substantial capacity for the elimination of PFAS and pharmaceuticals from environmental water sources. This approach offers a sustainable method for waste valorisation through the principles of the circular economy, as well as providing an effective solution for tackling water contamination by persistent pollutants. The promising adsorption capacity of biomass-based AC offers a pathway for more sustainable, cost-effective water treatment strategies.

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Green Solvent-Based Regeneration of Biomass-Derived Activated Carbons for Contaminant Removal

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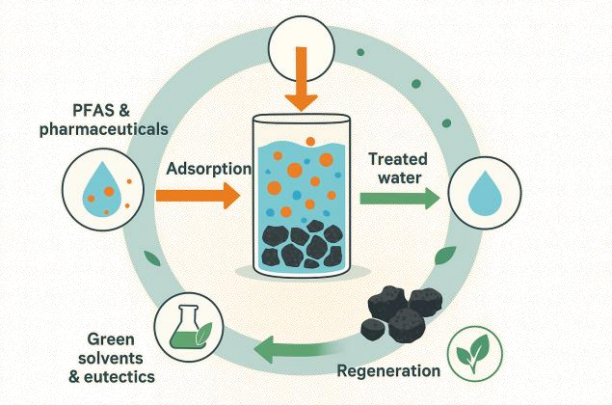
The durability of contaminants of emerging concern (CECs), including per- and polyfluoroalkyl substances (PFAS) and pharmaceuticals, within environmental water matrices, such as surface water and groundwater, poses considerable challenges to both the environment and public health. It is important to note that, due to their resistance to conventional treatment methods, these CECs have the potential to accumulate overtime, thereby posing long-term toxicity risks. This study focuses on the regeneration of activated carbons using greener solvents, such as ionic liquids and eutectic systems, as a sustainable alternative to conventional ethanol and methanol solvents [1]. The effectiveness of these environmentally friendly solvents in restoring the adsorptive capacity of activated carbon for removing perfluoroalkyl substances (PFAS) and pharmaceutical contaminants will be evaluated. This study proposes a novel approach to address the pressing issue of water contamination by persistent pollutants, with a focus on the integration of environmentally sustainable regeneration methods.



Scheme 1. The scheme shows how biomass-based activated carbons can clean water from PFAS and pharmaceuticals. First, the pollutants are trapped in the carbon (**adsorption**), leaving clean water. Then, the used carbon is recovered with **green solvents and eutectic mixtures**, making it ready to be reused.

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Extraction of per- and poly-fluoroalkyl substances (PFAS) and pharmaceuticals from wastewater effluents using activated carbon

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Per- and polyfluoroalkyl substances (PFAS) are highly persistent chemicals whose toxicity and bioaccumulative properties render them particularly hazardous, with elevated concentrations posing substantial risks to both human health and the environment [1]. In addition, pharmaceutical micropollutants represent an emerging environmental concern due to their continuous release and persistence in aquatic and terrestrial ecosystems [2]. These contaminants contribute to long-term adverse effects on human health and ecological integrity.
Activated carbons (AC) derived from biomass waste are efficient and versatile adsorbent materials for the removal of a wide range of contaminants. To evaluate their performance in fixed-bed column systems and assess their potential for industrial-scale applications, an AC synthesized from biomass waste was tested against three perfluoroalkyl acids (PFOA, PFBS, and PFPeA) and three pharmaceutical compounds (diclofenac (DCF), valsartan (VAL), and iopromide (IOP)). The adsorption behaviour and breakthrough curves of these systems were systematically determined. Based on these results, the processes were scaled up to pilot-scale columns using real wastewater. This study provides valuable insights into the removal of priority contaminants of emerging concern, which pose significant risks to both public health and the environment.

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Classical Density Functional Theory for Efficient Inverse Design of Adsorption Applications

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Microporous materials, such as zeolites and metal-organic frameworks (MOFs), have emerged as a promising class of materials for adsorption applications, including gas storage and separation. Given their vast design space, identifying the optimal adsorbent for a specific application often relies on high throughput screening, which is limited to already known adsorbents. Inverse design enables not only the identification of the optimal adsorbent, but also the exploration of undiscovered regions of the design space. In this work, we propose an inverse design workflow that integrates classical density functional theory (DFT) for adsorption property prediction and diffusion models (a deep generative model) for structure generation during optimization [1,2] (cf. Figure 1). Unlike most inverse design workflows, which applies machine learning models for adsorption prediction, we employ classical DFT directly at each iteration of the optimization, eliminating the need of model training. Classical density functional theory has been shown to predict adsorption properties of small apolar molecules such as CH_4, C_2H_6, C_3H_8, and H_2, in very good agreement with grand canonical Monte Carlo simulations (GCMC), while requiring up to four orders of magnitude less computational time [3]. When combined with process modelling, such an approach can be extended to include adsorption process parameters (such as recovery and purity).

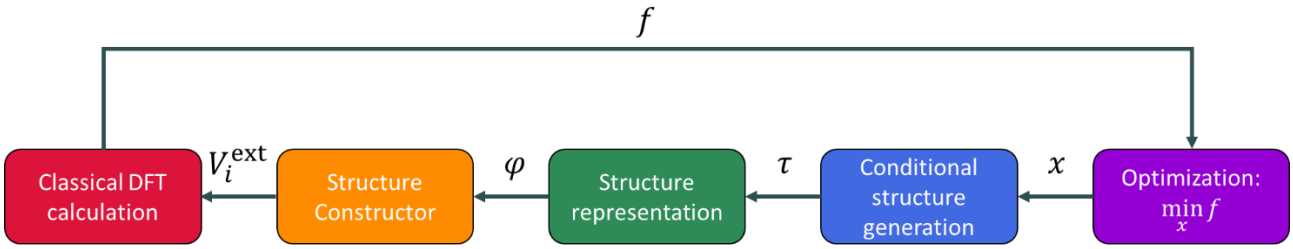

Figure 1. Iterative approach for structure optimization. Classical DFT delivers adsorption properties used to calculate f(e.g., selectivity or working capacity). In every iteration, f is optimized w.r.t. the gradient $\partial f/\partial x$, where x is a structure property (e.g., largest cavity diameter or helium void fraction). In conditional generation, x is specified as an input for the diffusion models, which generate structures most probably under that condition. The model output, denoted τ (e.g., probability grids or signed distance function), requires post-processing or structure constructor codes to obtain crystallographic information file (CIF). The CIF file grants access to the external potential, V_i^{ext}, which describes the effects of adsorbent atoms on the adsorbate fluid in classical DFT calculations.

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Sustainable Recovery of Oleuropein from Olive Leaves using Ultrasound-Assisted Extraction and Natural Eutectic Solvents

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Olive leaves, a significant source of agri-food waste, can be valorized as feedstock in biorefineries due to their high polyphenol content. These compounds, known for their potent antioxidant activity, have become high-added-value ingredients used in the food, medical, cosmetic, and pharmaceutical industries [1]. The major polyphenol found in olive leaves is oleuropein, a compound with numerous reported biological and pharmacological activities, mainly attributed to its antioxidant properties [2]. This study aims to valorize olive leaves through efficient solid-liquid extraction of oleuropein using green solvents and advanced extraction technologies. For this purpose, natural eutectic solvents (NAES) and ultrasound-assisted extraction (USAE) were employed. NAES are a class of green solvents formed by mixing naturally occurring hydrogen bond donors and acceptors. They offer tunable physicochemical properties such as low melting points, low volatility, nonflammability, low vapor pressure, and chemical and thermal stability. In addition, they exhibit high biodegradability, low toxicity, easy preparation, and low cost, making them a more sustainable alternative to conventional solvents [3–4]. On the other hand, USAE is an efficient and economically viable technique for polyphenol recovery, enabling the extraction of thermolabile compounds that would otherwise degrade at higher temperatures. Compared to conventional methods, USAE significantly reduces both extraction time and temperature, enhancing process efficiency [5].
Specifically, three natural eutectic solvents—formed by combining 1) choline chloride, 2) betaine, or 3) proline with 1,2-butanediol and incorporating water or ethanol as cosolvents to reduce viscosity and enhance extraction—were used in this work for the recovery of oleuropein through conventional and ultrasound-assisted methods. Oleuropein extraction efficiency was measured using high-performance liquid chromatography, and the antioxidant activity of the extracts was also assessed over time to determine their stability. Results showed that ultrasound-assisted extraction using the proline:1,2-butanediol solvent with ethanol at 25–75% composition yielded the best performance, reaching 37.00 mg of oleuropein per gram of dry sample (g/ds), with a notable reduction in both time and energy consumption compared to conventional extraction, while maintaining significant antioxidant activity and stability.

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NADES-Assisted Isolation of Polyphenols from Peanut Shells for Cosmeceutical Use

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This study addresses the extraction of polyphenolic compounds from peanut shells using natural deep eutectic solvents (NADES) and the application of the resulting extract in a cosmetic formulation. The aim was to optimize the extraction process and assess the stability of the final cream.

Peanut shells were ground and characterized using the BET method, which revealed a mesoporous structure that significantly enhanced extraction efficiency. In the preliminary study, eight different NADES were prepared and physically characterized. The total polyphenol concentration in the extract was determined by the standard Folin-Ciocalteu method and UV/Vis spectrophotometry. The NADES containing malic acid, glucose, glycerol and water in a molar ratio of 1:1:1:5 was selected for further extraction due to its highest polyphenol yield. Comparison showed that NADES is effective in extracting phenolic compounds, comparable to a conventional solvent (70 vol.% ethanol:water), and its use may be suitable for the cosmetic industry.

Batch extraction optimization was performed using response surface methodology (RSM) in the Design-Expert software. The model inputs were temperature, water content in the solvent, and phase ratio (mass of solid phase/volume of NADES). The optimal extraction time was determined to be 3 hours. The linear model was most suitable for predicting polyphenol concentration. The model predicted that optimal extraction conditions were achieved at 45 °C, a water mass ratio of 7.5, and a phase ratio of 1/20 g/cm³, with a predicted polyphenol concentration of 22.76 mg/dm³ (experimentally measured: 20.37 mg/dm³).

The extract with the highest phenolic compound concentration was incorporated into a base moisturizing cream at mass fractions of 5%, 8%, 10%, and 15%. The stability of all prepared creams was monitored for four months. The creams remained stable – white, firm, and uniform, without visible separation of the extract – confirming the feasibility of using the extract in cosmetic formulations.

The results confirm that NADES can be successfully used for the extraction of phenolic compounds from peanut shell by-products, and the resulting extract is stable in the base cream.

Purification of Biodiesel-Derived Biolubricants Using Liquefied Gases: Experimental and Thermodynamic Modelling

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Biolubricants synthesized via double transesterification of vegetable oils represent a sustainable alternative to mineral-based lubricants, offering high biodegradability, low toxicity, and reduced environmental impact. Their use contributes to safer working conditions, extended machinery lifespan, and lower operational costs due to improved lubricity and thermal stability. From an economic and industrial perspective, biolubricants enable partial raw material recycling, reduce energy consumption, and simplify production logistics by using commercially available biodiesel, primarily composed of fatty acid methyl esters (FAMEs), as a readily accessible intermediate in biolubricant synthesis [1–3].

This work explores the fractionation of raw biolubricants using liquefied gas mixtures of CO_2 and C_3H_8, aiming to selectively extract residual biodiesel (FAMEs) and enhance product quality. Phase behaviour was investigated in biolubricant–CO_2–C_3H_8 systems to define feasible operating conditions for the fractionation process. A high-pressure equilibrium cell was used to observe liquid–liquid–vapor (LLVE) to liquid–vapor (LVE) transitions, allowing the identification of regions suitable for component separation. Additionally, solubility and selectivity were evaluated in a high-pressure extraction column under varying temperature (25–50 °C), pressure (48–85 bar), and solvent composition (from pure CO_2 to 80/20 wt.% C_3H_8/CO_2). Mixtures containing up to 40 wt.% propane showed enhanced solubility for fatty oil components (62 g/kg solvent) and preferential extraction of residual FAMEs, with concentrations between 67 to 82 wt.% in the extract.

Thermodynamic modelling was also performed using the Redlich–Kwong–Peng–Robinson (RKPR) equation of state [4]. Binary and ternary systems involving biolubricant, CO_2, and C_3H_8 were modelled to predict phase behaviour and validate experimental solubility trends. The RKPR model successfully reproduced the liquid–liquid–vapor transitions and provided insight into the operating window for efficient separation.

This integrated experimental-modelling approach demonstrates the feasibility of using liquefied gases for biolubricant purification and highlights the predictive capabilities of RKPR modelling for process design and optimization.

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Ionic Liquids in Separation of Sulfur Compounds from LPG

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The mathematical LSSVM (Least Squares Support Vector Machine) model [1], based on the group contribution method and linear solvation energy relationship (LSER) descriptors, was used to calculate the selectivity coefficients of ionic liquids for the separation of sulfur compounds from LPG (Liquefied Petroleum Gas). The selectivities were derived from theoretically determined infinite dilution activity coefficients. Selectivity coefficients as a function of temperature for alkane/mercaptan systems (including propane, butane, and ethanethiol, propanethiol, butanethiol, and H_2S) were determined for approximately 10,000 ionic liquids, covering both hypothetical structures and those described in the literature. The influence of functional groups in the cation, the alkyl chain length of the cation substituent, and the overall cation and anion structure on selectivity was examined.
The obtained results were verified experimentally for selected ionic liquids. Selectivities were calculated from experimental infinite dilution activity coefficients. To investigate the influence of functional groups on selectivity, three ionic liquids with a common dicyanamide $[DCA]^-$ anion were selected: 1-ethyl-3-methyl-3*H*-imidazol-1-ium dicyanamide, 3-(2-hydroxyethyl)-1-methyl-3*H*-imidazol-1-ium dicyanamide, and 3-allyl-1-methyl-3*H*-imidazol-1-ium dicyanamide. Additionally, two further ionic liquids were studied: 1,3-dimethyl-3*H*-imidazol-1-ium dimethyl phosphate and tris(2-hydroxyethyl)methylammonium methyl sulfate. In general, the experimental results were higher than those obtained from calculations, particularly for ionic liquids containing hydroxyl substituents.

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Ionic liquids as selective solvents for the separation of 1,3-butadiene from C4 hydrocarbon mixtures

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1,3-Butadiene is an important petrochemical feedstock used primarily in the production of synthetic rubber and other industrial chemicals. It is mainly obtained as a by-product of naphtha steam cracking, which produces complex C4 hydrocarbon mixtures containing n-butene, iso-butene, n-butane, iso-butane, and 1,3-butadiene. The separation of these compounds is challenging due to their similar physicochemical properties, including close boiling points and comparable molecular sizes. Currently, extractive distillation is the predominant industrial method used to recover 1,3-butadiene from C4 fractions [1].

This work continues our studies on the application of ionic liquids as alternative solvents for the separation of butadiene from C4 hydrocarbon mixtures. In particular, imidazolium-based ionic liquids with different anions and a phosphonium ionic liquid were investigated. Activity coefficients at infinite dilution for 1,3-butadiene, 1-butene, n-butane, and isobutene were determined using inverse gas chromatography (IGC). Additionally, the effect of adding silver bis(trifluoromethanesulfonyl)imide to 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide was examined.

The obtained data allowed the calculation of selectivity and capacity parameters for the separation of n-butane/1,3-butadiene, 1-butene/1,3-butadiene, and isobutene/1,3-butadiene systems. Among the investigated solvents, ionic liquids containing tetrafluoroborate and thiocyanate anions exhibited the highest selectivity toward 1,3-butadiene, whereas ionic liquids with tricyanomethanide anions and longer alkyl chains in the imidazolium cation showed higher capacity values. The cobalt-containing ionic liquid bis(1-ethyl-3-methylimidazolium) tetrathiocyanatocobaltate exhibited relatively high capacity but lower selectivity compared to other systems. The addition of silver bis(trifluoromethanesulfonyl)imide increased both capacity and selectivity, with a particularly strong improvement observed for the selectivity of the 1,3-butadiene/n-butane system.

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Temperature Effects on Thermophysical Properties and Non-Ideal Behaviour of the 2-Phenoxyethanol + 1-Heptanol Mixture

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The search for sustainable and efficient oxygenated fuel additives requires a comprehensive understanding of the thermophysical behaviour of liquid mixtures, particularly those involving glycol ethers and higher alcohols. Such systems are of great interest because their molecular interactions strongly influence properties such as density, compressibility, and refractive index, which are directly linked to stability, miscibility, and combustion efficiency. In this work, the system 2-phenoxyethanol + 1-heptanol was investigated at 293.15 K and 323.15 K under atmospheric pressure. Experimental measurements of density (ρ), speed of sound (u), and refractive index (n_D) were performed across the full composition range, and the corresponding excess molar volume (V^E), isentropic compressibility (k_s), and refractive index deviation (Δn_d) were derived. The experimental density, (ρ), data were modelled using the Perturbed Chain – Statistical Associating Fluid Theory (PC-SAFT) equation of state, and a good agreement was obtained between the experimental and calculated values. The results reveal that V^E and Δn_D are negative at both temperatures, with minima near equimolar compositions, indicating efficient molecular packing and strong specific interactions between the hydroxyl group of 1-heptanol and the ether/phenyl functionalities of 2-phenoxyethanol. The k_s values, derived from acoustic measurements, exhibit clear minima at intermediate mole fractions, confirming the formation of compact molecular arrangements. Increasing the temperature at both 293.15 K and 323.15 K reduces the magnitude of negative deviations, consistent with the weakening of hydrogen bonding and π–hydrogen interactions as thermal motion increases and dispersive forces become more dominant. The composition dependence of all excess properties was successfully correlated using Redlich–Kister expansions, yielding excellent agreement with experimental values. These findings highlight the role of aromatic functionalities in modifying non-ideal behavior in ether–alcohol mixtures and provide molecular-level insights into the potential of 2-phenoxyethanol + 1-heptanol as a promising combination for sustainable oxygenated fuel additives.

Utilizing an Experimental and Modeling Approach for Mass Transfer of Small Molecules in Polyolefins

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The monomer mass transfer behavior during the polymerization reaction is an essential information for engineers to control reaction conditions and the properties of the final polymer. Nevertheless, understanding the diffusion of gaseous monomers remains a challenging problem due to the complex morphology of polyolefins. In this contribution, we present several differential pressure decay methods for investigating mass transfer and sorption equilibria in semicrystalline polymers, which are validated by the Raman spectroscopy and the magnetic suspension balance.
The objective of our research is to investigate the diffusion and sorption of low-hydrocarbon gases in semicrystalline polyolefins. Polyolefins consist of two phases: crystalline (rigid) and amorphous. The research [1] showed that the amorphous phase can be further divided into the free amorphous phase (mobile) and the constrained amorphous phase (semi-rigid). Penetrant molecules have to pass through the regions of different permeability and thus there is a significant effect of the polymer sample composition. Recent work [2] showed that penetrant molecules (ethylene and propylene) reduce crystal content in polymer, thus complicating even more the theoretical diffusion description. To employ a theoretical model for diffusion, e.g., Free Volume Theory [3], with all effects including changing paths for penetrants, a comprehensive experimental study is needed first. In this contribution, we are comparing diffusion coefficients for different hydrocarbon penetrants (C2-C6) in polymer matrix for a series of PE and PP particles of various sizes and densities, and their sorption and desorption dynamics. Different particle sizes of the same polyolefin nascent sample can result in different mass-transfer behavior. It is a consequence of polymer compact zones present in the particles, and their distribution is changing during the polymerization in industrial reactors.

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On the Flash Point of Monoterpene Mixtures: Experimental and Modeling Studies

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The flash point (FP) is a critical property for assessing fire and explosion (F&E) risks of flammable liquid mixtures [1]. While well-studied for fuels, reliable FP data for complex mixtures such as essential oils and their major constituents (terpenes and terpenoids) are scarce. This work addresses this gap by presenting experimental FP data for four key monoterpenoids (*p*-cymene, linalool, carvacrol, and eugenol) and their binary and ternary mixtures, which are key components of essential oils obtained from cinnamon, basil, and oregano species. Experimental FP measurements were performed using the ASTM D6450 closed-cup procedure. To complement the experimental data, the FP of the mixtures was modeled with the well-established COSMO-RS [2] and Liaw model [3]; for the latter, both an ideal solution and the UNIFAC model [4] were used to describe the liquid phase fugacity.
For the pure components, the results show a strong linear correlation between the FP and the normal boiling point (NBP), leading to the development of a very straightforward linear correlation for rapid, first-estimate FP values of monoterpenoids. For the mixtures, positive deviations from the ideal behavior were observed for systems containing *p*-cymene, while the opposite trend was found for the oxygenated mixtures containing eugenol. The modeling results show that COSMO-RS offers the best FP description for all the studied systems, achieving a global average relative deviation (ARD) of 0.2%. The Liaw-UNIFAC model (ARD = 0.7%) globally outperformed the ideal approach (ARD = 0.9%), showing particular strength for the systems containing the hydrocarbon *p*-cymene. This work offers novel FP data and provides valuable insights into modeling the complex FP behavior of terpene mixtures.

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Quantitative Evaluation of Precursor Desorption Characteristics for Optimizing Purge Performance in Vent Header

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In the semiconductor industry, efficient neutralization of large-diameter vent headers has emerged as a critical safety challenge, particularly during infrastructure retrofitting and dismantling processes. This is primarily due to the absence of vacuum-assisted purging and significant cross-sectional mismatches between lateral lines and a vent header, which create stagnant zones. Consequently, condensed hazardous precursors, such as TEOS and OMCTS, often persist on the internal surfaces, necessitating a robust physical purging strategy.[1] Therefore, this study investigates the synergistic effects of temperature and purge pressure to establish an operational window for optimized desorption. An experimental setup was developed, integrating gas chromatography to precisely quantify desorption rates. Also, precursor-surface interactions were evaluated via contact angle and surface topography measurements on pipe material. A parametric study was conducted across a range of temperatures (30-100 °C) and pressures (30-80 psi) to determine the optimal condition for neutralization of vent header. The parametric studies on TEOS demonstrated a significant reduction in desorption completion time (DCT) by 88.3% at 100 °C compared to 30 °C, in which a saturation plateau was observed at 70 °C. Regarding purge pressure effects, increasing the pressure up to 60 psi resulted in a drastic 99.7% reduction of DCT, however, a subsequent performance decline occurred at 80 psi. This counter-intuitive result shows a heat transfer-limited regime, where excessive N_2 velocity suppresses convective heat transfer from the heated pipe walls to purge flow and precursor residues. Furthermore, while TEOS was effectively removed over 95%, OMCTS exhibited a desorption ceiling of 85%, which is attributed to differences of intrinsic precursor properties. This study figures out an optimal purge condition—70 °C and 60 psi—for neutralization of vent system and provides practical guidelines for enhancing environmental safety during infrastructure decommissioning. Ultimately, the results suggest the necessity of developing physicochemical desorption methods to overcome current physical constraints.

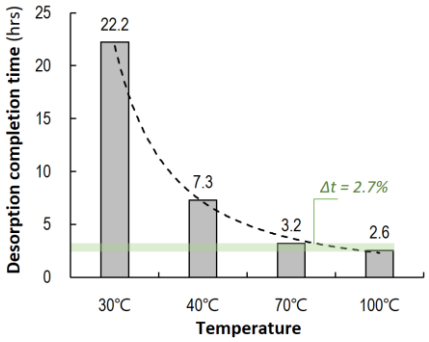

Figure 1. Changes of desorption completion time (TEOS) with an increase of temperature

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Towards the Selective Separation of p-Coumaric Acid: Experimental Solubility in Pure Organic Solvents and Binary Mixtures

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p-Coumaric acid is a natural polyphenol widely recognized for its bioactive properties, including antioxidant, antimicrobial, anti-inflammatory, and potential anticancer effects. This compound is especially abundant in grape pomace, a major by-product of winemaking, which makes this residue an attractive and sustainable source for its recovery [1]. Due to its diverse biological activities, *p*-coumaric acid has promising applications in pharmaceutical formulations, functional foods, nutraceuticals, and cosmetic products [2]. However, the efficient valorization of this polyphenol requires accurate knowledge of its solubility behavior in green solvents to design selective extraction and purification processes.

In this work, the solubility of *p*-coumaric acid was systematically studied in six pure solvents (methanol, ethanol, 1-propanol, 1-butanol, methyl ethyl ketone—MEK, and methyl isobutyl ketone—MiBK) as well as in binary mixtures composed of these solvents, which were chosen based on their polarity and green character. Experimental measurements were performed using the gravimetric method combined with Ultraviolet-Visible Spectroscopy for solubility determination. The results show that solubility of *p*-coumaric acid in alcohols decreases progressively with the increase in the carbon chain length, while in ketones it displays markedly lower solubility. In binary mixtures, solubility maxima were observed in all systems composed of solvents with different functional groups (alcohol + ketone), while the presence of the same ones limited this synergistic effect.

The results of this study will serve as a fundamental basis for future applications aimed at the selective extraction of *p*-coumaric acid from complex natural matrices. The experimental data reported here not only contribute to the solubility database of this phenolic acid but also support the development of green and efficient extraction processes for its integration into pharmaceutical, food, and cosmetic industries.

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Process Engineering and Thermodynamics Challenges in Plastics Circularity: Closing the Loop with Industrial Recycling Technologies

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Plastics circularity is a prerequisite to ensure life-cycle sustainability of polymeric materials along "make", "use" and "recycle" phases. At industrial scale, recycling methods from mechanical to chemical recycling are in principle well known [1] but need to be matched to waste streams and go beyond "easy" plastics as found in e.g. rigid packaging applications. The task for industry and process engineering is to develop robust, economically and operationally feasible processes.
This round-table will reflect on recent industrial experiences with advanced recycling technologies and discusses issues of scale-up and engineering topics. Drawing on examples across depolymerization-based routes, recurring challenges related to feedstock variability, process integration, energy management, and product quality control can be discussed, which ultimately define whether a technology can close material loops in practice: Rather than thermodynamics, kinetics, or reactor concepts in isolation, their interplay with design choices, separation strategies and boundary conditions and value chains define their potential.
The session is intended to foster an informed exchange on how process engineering, system thinking, and industrial learning can accelerate the transition from promising concepts to truly circular plastics systems.

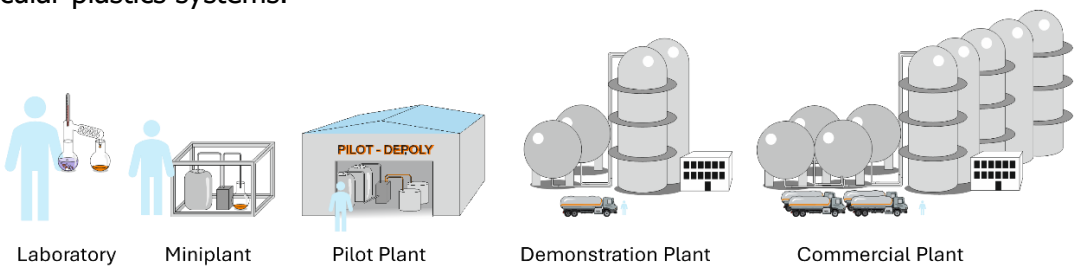

Figure 1. Scale-up and process development for recycling: Specific chemical engineering challenges. Figure reproduced from Ref. [2] under CC-BY Creative Commons License.

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Thermochemical perspective on a Transient World (a personal view from an industrial practitioner)

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We are living in times of strong focus on sustainability and energy transition. The products and services we want as consumers must be produced in more sustainable less energy demanding processes, making use of renewable feedstock, and emitting less waste and reducing the carbon footprint.
There is a multitude of options to improve our footprint on planet earth. But which of the options is most preferred from a sustainable perspective? Thermodynamics is the science relating energy and matter, and as such it is instrumental in process & product design, in the end defining the sustainability profile of the targeted process and product.
Here the author would like to present a personal view on sustainability from a thermochemical perspective. Which routes appear more logical to pursue based on thermochemistry? Can thermochemistry provide an early-stage indication of the impact on sustainability and techno-economics? With this high-level view, the author aims to provide a, hopefully thought provoking, perspective on the role of applied thermodynamics, and therewith perhaps also of its community, in the grand challenges that we are facing.

Keywords: Sustainability, Energy and Materials Transition, Applied Thermochemistry

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Superstructure Optimization of Hybrid Membrane–Distillation Systems for Thermodynamically Efficient Hydrocarbon Separation

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Separation of light hydrocarbons such as ethylene/ethane is among the most energy-demanding processes in petrochemical sector, where usually it is carried out by very large cryogenic distillation. Making these processes more efficient is very important for advancing sustainable energy approaches and also circular economy. In this study, a superstructure-based optimization framework that combines advanced membrane materials together with distillation was presented to identify the optimal cost- and energy-efficient hybrid configurations for complex hydrocarbon mixtures. In addition to light hydrocarbons, other mixtures, including benzene-toluene and natural gas sweeting were investigated. The superstructure embeds all feasible possibilities at once for integrating a membrane unit with distillation column, including pre-feed treatment, side-stream withdrawal, top or bottom polishing, parallel feed splitting, as well as post-treatment. The optimization task is written as a Mixed-Integer Nonlinear Programming (MINLP) type model. Here, binary variables decide which configuration is selected active, while continuous decision variables—number of stages (N), reflux ratio (R), and total membrane area (A)—fix the design and operating point. Distillation was modelled using the Fenske–Underwood–Gilliland approach, and the membrane was modelled using Fick's law. In addition, comprehensive cost and techno-economic analyses were applied rigorously and in detail across all configurations to ensure credible cost and energy comparisons. A main novelty of this work is the integrating of advanced membrane material, especially Carbon Molecular Sieve (CMS) and ZIF-based (Zeolitic Imidazolate Framework) membranes, which show superior selectivity and robustness in close-boiling hydrocarbon separation. By adding realistic data for these advanced materials, the framework captures their potential to strongly decrease energy demand and also equipment size when compared against polymeric membranes and distillation alone designs. For checking robustness, the model validation was not only done with literature case studies and Aspen HYSYS simulations, but also by changing feed compositions, unit size, and utilities costs systematically. These sensitivity analyses confirmed that the optimizer consistently identified reliable and economically favourable configurations across a broad operating window, reinforcing confidence in its general applicability. The optimized hybrid systems obtained energy savings of up to 51% and a decrease in total annual costs of around 26% compared to conventional distillation models. Importantly, the optimization uncovered intuitive strategies illustrating the benefit of investigating a complete superstructure as compared to depending solely on heuristics, showing why exploring the whole superstructure is more advantage than just following heuristics. This work shows that combination of advanced membranes with superstructure optimization framework can unlock large improvements in energy efficiency, economic outcome and sustainability for these difficult separations. By providing design rules and validated performance maps under diverse conditions, the study contributes to sustainable energy and support the vision of circular economy through cleaner and resource-efficient hydrocarbon production.

Prediction of the chemical and phase equilibria of switchable hydrophobicity solvents using openCOSMO-RS

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Switchable hydrophobicity solvents (SHSs) are liquid mixtures composed of an organic and an aqueous phase, whose liquid–liquid equilibrium (LLE) can be controlled by a reversible chemical reaction. The ability to reversibly "switch" between monophasic and biphasic states makes SHSs attractive for integrated extraction–purification processes. In practice, the organic phase of the SHS is used to extract hydrophobic compounds, and switching the SHS to its monophasic aqueous state drives their separation by making them insoluble [1]. From an engineering perspective, predicting the LLE of SHSs is important for the rational design of extraction processes. At the same time, SHSs provide a valuable benchmark system for the development of thermodynamic models. The LLE of SHSs involves an acid-base reaction, which introduces ionic species into the mixture. Accurate reproduction of SHS LLE therefore requires a model capable of simultaneously computing chemical and phase equilibrium (CPE), while also accounting for long-range (LR) interactions induced by ionic species.

In this work, the open-source implementation of COSMO-RS (Conductor-like Screening Model for Real Solvents), openCOSMO-RS, is applied to compute the CPE of SHSs. For this purpose, an algorithm for solving the CPE [2] is implemented in the openCOSMO-RS framework. LR interactions are treated with the extended-modified Pitzer–Debye–Hückel model [3]. Optimized geometries of the compounds are obtained using the CRENSO workflow [4], employing ORCA 6.1 for the DFT calculations. The model performance is first evaluated against experimental CPE data of systems available in the literature [1,5]. The predictive capability of openCOSMO-RS is then assessed using experimental LLE data of carboxylic acid-based SHSs measured by our group. Finally, a critical assessment examines the ability of pairwise segment interaction models to describe the phase equilibrium of systems in which amphiphilic molecules in aqueous environments give rise to pronounced hydrophobic association effects.

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Solubility Enhancement of Zwitterions in Water in the Presence of Hydrotrope-like Molecules: The Case of Levofloxacin

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Improving the aqueous solubility of active pharmaceutical ingredients (APIs) remains a central challenge in drug formulation. Among the various strategies explored, hydrotropy has emerged as a powerful approach. Hydrotropes are small amphiphilic molecules that can enhance the solubility of poorly soluble compounds in water by the formation of aggregates other than micelles.
Fluoroquinolones, a relevant class of antibiotics, manifest poor water solubility. Due to their zwitterionic character, their solubility is classically tuned by pH variations. It has been shown that their solubility in water can also be improved by the addition of molecules that are commonly employed as hydrotropes [1]. However, because of the charge separation in zwitterions, it is uncertain whether the mechanisms typically observed in hydrotropic solubilization are still valid.
In this work, levofloxacin (LVX), one of the most used fluoroquinolones, is chosen as a model zwitterionic solute. A set of three solubilizers (nicotinamide, urea and caffeine), commonly used hydrotropes, are tested as solubility enhancers. Two complementary approaches are employed. First, the solubility of LVX in water and water-solubilizer mixtures are determined at 298.15 K. The results are analyzed using the multiplicative solubility isotherm approach developed by Shimizu et al. [2], which allows the determination of fitted interaction parameters that are correlated to Kirkwood–Buff integrals (KBIs), thereby providing thermodynamic insight into solute–solubilizer interactions. Second, small-angle X-ray scattering (SAXS) experiments are used to identify the presence of nanoscopic domains resulting from solubilizer aggregation and investigate their role in enhancing the water solubility of zwitterionic molecules.
The results of the study will fill an existing gap in current research, providing new insight into the solubility enhancement of zwitterionic drugs in water and extending the understanding of how molecules commonly used as hydrotropes interact with clinically relevant zwitterionic compounds such as levofloxacin.

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Mitigating high GWP F-Gas Emissions Through Activated Carbon Capture and Separation Technologies

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Fluorinated gases (F-gases) are synthetic greenhouse gases widely applied across industrial sectors, such as air conditioning, refrigeration and electrical insulation. Despite their usefulness, these gases are potent greenhouse agents, with global warming potentials reaching up to 23,000 times that of carbon dioxide. Developing efficient recovery and reuse technologies for F-gases is therefore crucial—both to mitigate climate impacts and to take advantage of their economic value.
Among the most promising approaches for F-gas capture and separation is the use of porous solid adsorbents such as activated carbons (ACs), metal–organic frameworks (MOFs), and zeolites. These materials prevent atmospheric release and enable gas reclamation. While MOFs generally offer high adsorption capacities, ACs remain the most widely used in industry thanks to their large pore volumes, high surface area, diverse surface groups, low cost, and commercial accessibility.
Building on the authors' previous studies, BPL activated carbon was selected to investigate strategies for reducing the environmental footprint of the most widely used F-gases in air-conditioning and refrigeration—specifically difluoromethane (R-32), 1,1,1,2-tetrafluoroethane (R-134a), pentafluoroethane (R-125), and 1,1,1-trifluoroethane (R-143a). Adsorption equilibria of these gases were measured at 283.15, 303.15, and 323.15 K, alongside studies of adsorption kinetics for the pure components. Breakthrough experiments were also carried out to examine dynamic behaviour and to validate a mathematical model for process design through simulation. The findings highlight the strong potential of BPL-activated carbon as an effective and practical solution for F-gas capture, combining environmental benefits with industrial feasibility.

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Role of thermodynamics in battery recycling and critical raw material recovery

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Batteries have played a central role in recent years, and their increasing importance have highlighted the fragility of the underlaying supply chains (especially, but not only, in Europe). Most of the critical raw materials needed for their production are mined, extracted and processed in a few regions across the globe, and the corresponding manufacturing processes are also concentrated in limited locations. In this context the ability to recycle batteries, by recovering the most important elements, as well as the possibility of mining some of these critical raw materials (and others that are employed in other sectors and businesses) from alternative sources become crucial. This applies to several materials such as lithium, nickel, cobalt, manganese, and magnesium. While technological innovation in recycling and resource extraction is advancing rapidly, thermodynamics remains the fundamental framework that ultimately determines what is feasible, efficient, and sustainable. We will therefore explore the role of thermodynamics as the governing discipline behind battery recycling and critical raw material recovery. From high-temperature pyrometallurgical processes to solution-based hydrometallurgical routes [1, 2] and emerging direct recycling strategies, each pathway reflects a different manipulation of Gibbs free energy, chemical potentials, entropy generation, and phase equilibria. Thermodynamics explains why lithium is difficult to recover in smelting operations, why selective dissolution in hydrometallurgy depends on redox and pH control, and why preserving crystal structure in direct recycling minimizes exergy destruction. The same principles clarify the challenges of extracting dilute elements from seawater, where entropy penalties dominate separation work [3, 4]. Ultimately, a thermodynamic perspective enables more rational process design, improved resource efficiency, and clearer prioritization between recycling and primary extraction routes.

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Microfluidics and Fluorinated Ionic Liquid-based Aqueous Biphasic Systems as One-Step Miniaturized Platform for Purification of Lysozyme and Serum Albumin

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Sustainability challenges have driven advances in alternative solvents and separation techniques, with the use of ionic liquids (ILs) in biologics purification emerging as a rapidly growing field.
ILs have emerged as one of the most attractive solutes for aqueous biphasic systems (ABS), with outstanding performance in the extraction of targeted biologics.[1] Recently, we proposed a benign cholimium-based ILs route for ABS,[2] disclosed novel ABS composed of fluorinated ILs (FILs)[3-6] and demonstrated that FILs reduce the impact of the addition of water upon the IL's H-bond acceptance ability.[7] Herein, bioprivileged ILs were implemented to develop more versatile and amenable to be tuned ABS. To understand their potential as extractive platforms of biologics, the ternary phase diagrams, the polarity parameters of the coexisting phases, and the partition coefficients, stability and activity of the targeted biologics were determined. Finally, to highlight the interactions between model biologics and the ABS-phase components and better understand the interactions ruling the partition, intrinsic fluorescence, nano-differential scanning calorimetry, circular dichroism and microscale thermophoresis measurements were attained.[4-6] One of the promising results attained was the simultaneous purification of IFN-a 2b and albumin in a single-step with a high purification factor and yield.[5] Additionally, the standard batch (macroscale ABS) was compared with flow-through processes (microfluidic setups) for the purification of lysozyme and albumin in a single-step.[6] The successful integration of microfluidics with FIL-based ABS as one-step miniaturized platform for continuous purification of lysozyme and albumin was attained based on a specific setup (3 syringe pumps, microchip and downstream collection cell) allowing, (1) feed of the aqueous solutions of an ABS solutes', rather than the top- and bottom-phases of a single biphasic point, enabling operation across multiple biphasic points, (2) longer operation times (up to 13-hour); despite the low Reynolds numbers, interface oscillations and air bubbles for longer operation times hinder phase collection at the microchip outlet, (3) controlled collection through direct interface observation in the downstream collection micro-cell (easier automation).

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Evaluation of PFAS Pollution Hotspots and Mitigation Measures for Surface Water in Protected Areas

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Per- and polyfluoroalkyl substances (PFAS) represent an emerging class of contaminants of global concern due to their persistence, mobility, and potential impacts on ecosystems and human health [1]. The Council and the European Parliament recently reached a provisional agreement to update list of priority pollutants in surface and ground water including several per- and polyfluoroalkyl substances (PFAS), strengthening monitoring and control requirements [2]. The ALERT-PFAS project was designed to address these challenges by developing innovative monitoring frameworks, sharing scientific knowledge, and promoting effective management strategies across the SUDOE natural areas. By focusing on surface waters, the project aims to better understand the extent of PFAS pollution and to provide actionable solutions that can be replicated in transnational contexts around the globe.

A key component of the project is the establishment of a harmonized monitoring network to identify and characterize PFAS hotspots. Through the design of coordinated sampling campaigns, ALERT-PFAS ensures that comparable data can be gathered across different regions, thus enabling more robust evaluations of PFAS presence and distribution.

The outcomes of the most recent sampling campaign carried out in the SUDOE area will be shown. This work has allowed to unveil critical PFAS hotspots within diverse aquatic environments, highlighting spatial patterns and providing evidence of contamination levels that warrant immediate attention. These findings not only improve the understanding of PFAS behaviour in natural systems but also reinforce the urgent need for coordinated interventions.

Finally, the transnational strategy currently being developed by the ALERT-PFAS project will be presented. This strategy builds upon the evidence gathered and proposes a common roadmap to mitigate PFAS risks in natural areas. It combines technical recommendations, governance mechanisms, and cooperative frameworks designed to support decision-makers at regional, national, and European levels. By aligning scientific research with policy and management needs, the project contributes to protecting ecosystems, ensuring water quality, and safeguarding public health across borders.

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How to Implement Ion Pairing in Electrolyte Equations of State

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The incorporation of ion pairing is a critical step for extending the predictive power of electrolyte Equations of State (e-EoS), yet its implementation is often inconsistent across the literature [1]. This work presents a systematic framework to guide the integration of ion pairing, clarifying the thermodynamic consequences of key methodological choices. We address the fundamental distinction between physical association (where ions cluster via coulombic forces) and chemical association (where new ion-pair species are formed), demonstrating how each approach uniquely modifies the Helmholtz free energy of the system.

Using a model combining the Debye-Hückel [2] and Scaled-Born [3] terms, we analyse aqueous $MgSO_4$ and NaBr solutions to explore critical implementation steps: (1) the selection of a thermodynamic association constant (e.g., Bjerrum, Fuoss, Ebeling); (2) the thermodynamic consequences of choosing the physical and chemical approaches; and (3) the significant impact of defining the ion-pair non-ideality, including its solvation and dipole interactions. Our results show that these choices can lead to major quantitative and even qualitative differences in predicted Mean Ionic Activity Coefficients (MIAC). For instance, treating the ion pair as a non-ideal species by including its solvation energy fundamentally alters the shape of the MIAC curve. We provide a clear, stepwise guide for researchers to implement ion pairing in a thermodynamically consistent manner, ensuring that model predictions are thermodynamically robust.

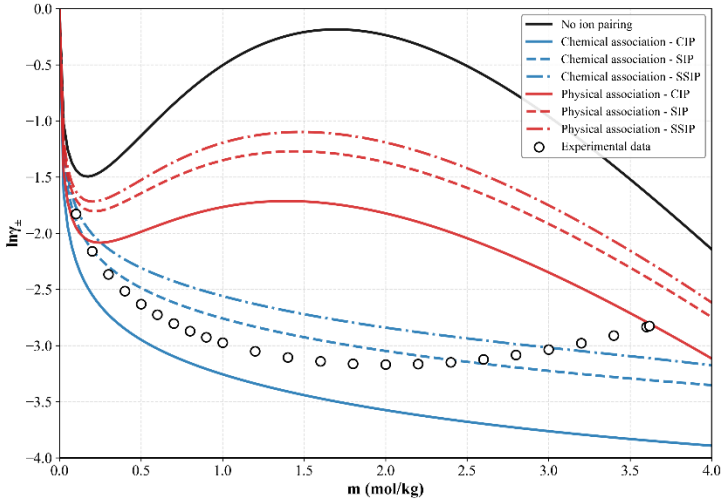

Figure 1. Ion pairing implementation into the Debye-Hückel + Born equation considering both the chemical and physical association with different ion pair configuration geometries: Contact Ion Pair (CIP), solvent-shared ion pair (SIP), solvent-separated ion pairs (SSIP).

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Interfacial immobilization and Marangoni flow dynamics in contaminated water droplets

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Droplet evaporation plays a fundamental role in both scientific research and technological applications, including inkjet printing, biomolecular patterning, digital microfluidics, and microlens fabrication. During evaporation, temperature and concentration gradients arise along the liquid–vapour interface, generating surface tension gradients that drive interfacial flows known as Marangoni flows [1–3]. Thermocapillary flow originates from temperature gradients, whereas solutal Marangoni flow is induced by concentration gradients of dissolved species such as surfactants or salts. While such flows are readily observed in volatile liquids like ethanol and methanol, their presence in pure water remains controversial. Even trace levels of airborne contaminants or unintended surfactants can significantly alter interfacial mobility and suppress internal circulation.

Previous numerical work suggested that weak Marangoni flow in evaporating water droplets results from surfactant contamination, which diminishes interfacial shear and fails to counteract the coffee-stain effect. In contrast, other experimental studies reported observable Marangoni convection in nominally pure water, attributing flow suppression to mechanisms other than surfactants. To resolve these discrepancies, we investigate the lifetime and retardation of Marangoni flow during water droplet evaporation through combined experiments and numerical simulations.

Flow visualization was conducted for droplets evaporating on PTFE-coated substrates to characterize internal circulation. A numerical model incorporating surfactant adsorption–desorption kinetics at the liquid–vapour interface was developed to elucidate the transition from a mobile (slip-like) to an immobilized (no-slip) interface. The onset of interfacial immobilization and the associated timescale of flow suppression were quantified as functions of bulk and interfacial surfactant concentrations and kinetic coefficients. The results provide a mechanistic framework for predicting the duration of thermocapillary flow and its sensitivity to trace contaminants. These insights are relevant to coating technologies, heat and mass transfer processes, droplet manipulation, and microscale pumping systems.

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Thermodynamic and kinetic studies of hydrolytic enzymes immobilized onto 3D-printed PLA-based scaffolds

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Immobilization of enzymes offers several advantages, such as the feasibility of enzyme recovery and reuse, as well as enhanced storage, thermal, and operational stability. Three-dimensional (3D) printing, or additive manufacturing, enables the production of immobilization carriers that are easily isolated from the reaction medium and possess large specific surface areas, thereby improving mass transfer. Polylactic acid (PLA), a biodegradable, biocompatible, and non-toxic polymer, serves as an excellent material for such carriers.

In the present study, 3D-printed PLA scaffolds were used to investigate the immobilization of two hydrolytic enzymes: β-glucosidase, an enzyme of high biotechnological interest, and chymosin, which is used industrially for milk coagulation. The immobilization process significantly enhanced the thermal stability of both enzymes. For instance, immobilized chymosin exhibited higher activity in the hydrolysis of milk κ-casein than free chymosin at elevated temperatures.

Thermodynamic analyses clearly demonstrated that immobilization increased the structural stability and rigidity of the enzymes. The heat inactivation rates of both hydrolases were evaluated for the free and immobilized forms over the temperature range of 40–70 °C. The activation energy (Ed) for thermal denaturation of immobilized chymosin increased approximately twofold (15.9 kJ mol^{-1}) compared to the free enzyme (8.10 kJ mol^{-1}), indicating that the immobilized enzyme required more energy to undergo denaturation, thus reflecting a substantial improvement in thermal stability.

The ΔH° values declined steadily with increasing temperature, revealing that a lower amount of energy was required to denature the enzymes at higher temperatures. Moreover, the ΔH° values of the immobilized enzymes were significantly higher than those of the native enzymes, indicating that immobilization results in greater thermostability. The ΔG° values of both free and immobilized enzymes increased with temperature; however, the ΔG° values of the immobilized enzymes were consistently higher than those of their free counterparts, suggesting that immobilization onto PLA scaffolds protects the enzyme structures from denaturation. Finally, the ΔS° values, which refer to the amount of energy per degree required for the transition from the native to the denatured state, were slightly increased after immobilization compared to the free enzymes.

In conclusion, although immobilization leads to some loss of enzymatic activity, the resulting immobilized biocatalysts exhibited enhanced thermal stability. These findings indicate that immobilization onto PLA scaffolds can effectively limit enzyme thermal denaturation at elevated temperatures.

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Adsorption of Low Global Warming Potential Hydrofluorocarbon and Hydrofluoroolefin in Commercial Activated Carbons

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Fluorinated gases (F-gases), including hydrofluorocarbons (HFCs), hydrofluoroolefins (HFOs), perfluorocarbons (PFCs), sulfur hexafluoride (SF_6), and nitrogen trifluoride (NF_3), have an important role in refrigeration, HVAC, fire retardants, foam blowing agents, propellants and electrical applications.[1] However, despite having negligible ozone depletion potentials (ODPs), F-gases are still concerning greenhouse gases with extremely high global warming potentials (GWPs), up to several orders of magnitude higher than that of the reference CO_2 (GWP = 1).[2] In the EU their emissions have increased up to 60% since 1990. EU regulation targets to cut the emissions of F-gases by 2/3 up 2030, compared to the levels of 2014.[3]
Therefore, it is important to develop technologies to efficiently capture these gases during equipment maintenance or in waste management. Many refrigerants with market value are being destroyed because they cannot be feasibly reclaimed for reuse. There are numerous reasons why reclamation may not be possible, including lack of appropriate technology or contamination (e.g., all the collected refrigerants in the waste managers facilities are mixed in cylinders for incineration, and very complex mixtures are generated). The development of technologies for efficient reclamation of F-gases is relevant, not only to reduce GHG emissions to the atmosphere, but also because their market value. A main example is the R-32, from the EU phase-down of R-410A (one of the most used HFC refrigerants blends; R-32/R-125, 50/50 wt.%), driving the switch from R-410A to R-32 (neat or blends with lower GWP).[4] Additionally, new HFC/HFO refrigerant blends,[5] containing HFOs – unsaturated hydrofluorocarbons that exhibit very low GWP –, are being formulated and incorporated into the refrigerant market as environmentally friendly alternatives (e.g., R449A (R-32/R-125/R-1234yf/R-134a, 24.3/24.7/25.3/25.7 wt.%), R454A (R-32/R-1234yf, 35/65 wt.%), R454B (R-32/R-1234yf, 68.9/31.1 wt.%), R455A (CO_2/R-32/R-1234yf, 3.0/21.5/75.5 wt.%), and R513A (R-1234yf/R-134a, 56.0/44.0 wt.%)).
This work aims at reducing the environmental impact of the most used F-gases in refrigeration and HVAC equipment: difluoromethane (R-32), pentafluoroethane (R-125), 1,1,1,2-tetrafluoroethane (R-134a), and 2,3,3,3-tetrafluoropropene (R-1234yf). Four activated carbons (ACs),[2] two non-commercial ACs – referred here to as AC1 and AC2 were developed and produced by Sutcliffe Speakman Carbons Ltd (Bristol, UK). AC1 is a granular coconut shell carbon and AC2 is an extruded carbon coal based (2 mm diameter pellets) –, Ecosorb AC, in form of pellets (4 mm diameter), was supplied by Jacobi, and BAC bead-shaped AC (0.70 mm average diameter) was supplied by Kureha, were characterized and studied for the adsorption of these F-gases, and their capacity for separation processes was assessed.

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Eyring's Rate Theory and Its Connection to Entropy Scaling: Predicting Properties of Hydrocarbons, Alcohols, and Water

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Eyring's absolute rate theory relates fluid flow with the activation energy necessary for a molecule to go from one equilibrium position to another. Developed nearly a century ago, it remains a powerful approach for understanding transport processes in liquids. This work [1] presents a revision of Eyring's theory by replacing the vaporization-based parts of the theory with a residual approach that conceptualizes transport as local (re)movement of molecules within the system rather than removal from it. In this new approach, the energy barrier corresponds to the difference between a molecule with and without intermolecular interactions, effectively treating it as the residual property related to an ideal gas reference state.
Furthermore, we explore the physical connections between Eyring's absolute rate theory and Rosenfeld excess entropy scaling, revealing that both approaches describe complementary aspects of the same transport phenomena. It is tempting to link both theories. The activation parameters in Eyring's theory, particularly the energy of activation, are shown to relate to the residual entropy used in entropy scaling.
This provides a pathway to establish entropy scaling on a more rigorous physical foundation while offering deeper insights into the molecular mechanisms governing viscous flow. In comparison to experimental data, the revised theory demonstrated significant predictive power for viscosity across a wide range of thermodynamic conditions and species, including associating liquids. Moreover, parameters are transferable to other properties, such as self-diffusion.

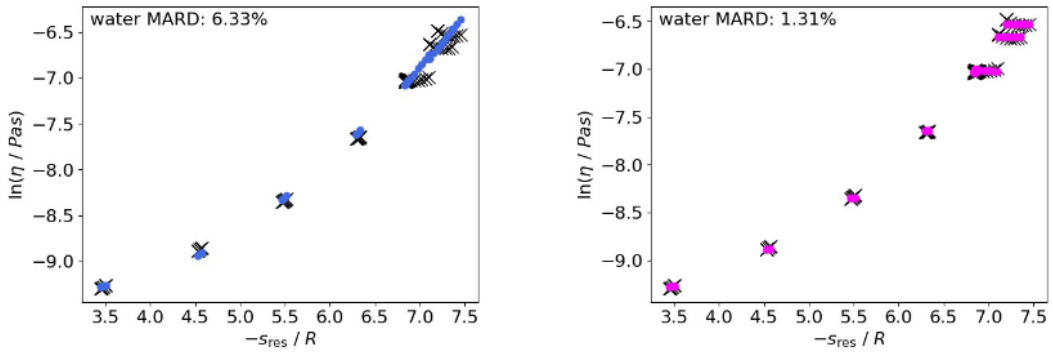

Figure 1. Viscosity predictions for water. The EES1 model (magenta, right) shows significantly improved agreement between model and experiment compared to the entropy scaling model (blue, left).

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Viscosity modelling of water-alkanol mixtures via the use of entropy scaling

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Water–alkanol mixtures often exhibit complex extrema behavior, namely, maxima or/and minima in their viscosity–composition functions due to the formation or disruption of the resulting hydrogen bonding structure. Short-chain alkanols (*e.g.*, methanol, ethanol) can enhance the water network at low to moderate compositions, thus leading to viscosity maxima, while increasing alkanol content—especially for longer chains (*e.g.* 2-propanol, *tert*-butanol)—disrupts this structure and may give rise to both maxima and minima. In these work, this highly non-ideal viscosity behavior was well captured by the entropy scaling approach for some representative water-alkanol mixtures: water+methanol, water+ethanol, water+1-propanol. water+2-propanol and water+tert-butanol over the whole composition range and within a temperature range of 283-348 K at a pressures from atmospheric up to 1,178 bar. In doing so, a combined van der Waals-Redlich-Kister mixing rule was introduced to the mixture coefficient affecting the first-order entropy-scaling contribution only requiring two binary interaction parameters to represent the whole η-T-x surface at low pressure with excellent accuracy. Furthermore, the predictive capabilities of the present modeling approach were also verified in the representation of liquid viscosities at high pressures (up to 1,178 bar) using the same model parameters previously obtained at atmospheric pressure. As a matter of fact, the required residual entropy data for the mixture were estimated via the use of the Peng-Robinson-Stryjek-Vera cubic equation of state with Wong-Sandler mixing rules, an approach that has proved to capture rather well the complex phase behavior of the aforementioned mixtures.

Assessing the Predictive Accuracy of the SAFT-γ Mie and COSMO-SAC Models for the Thermodynamic Properties Pharmaceutical Systems

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Reliable prediction of thermophysical properties is essential across the pharmaceutical lifecycle, from early discovery to process development and large-scale manufacturing. However, experimental determination of such properties, while accurate, is often expensive, labour-intensive, and sometimes infeasible. Recent advances in predictive thermodynamic models, particularly COSMO-based approaches and the SAFT-γ Mie group-contribution equation of state, have significantly enhanced our ability to predict and accurately describe the thermodynamic properties of complex mixtures. Nevertheless, their performance for pharmaceutical systems has not yet been systematically assessed. In this study, we benchmark twelve predictive models, including SAFT-γ Mie [1] and several COSMO-SAC models [2-4] (seven and four levels of theory for the 2002 [2, 5] and 2010 [3,5] variants, respectively), against a broad literature dataset covering eight active pharmaceutical ingredients (APIs). The experimental dataset contains 1692 solubility measurements in pure solvents, 1223 solubility measurements in mixed solvents, and eight octanol–water partition coefficients. Among the models, SAFT-γ Mie consistently delivers the most reliable predictions for solid–liquid solubility in both single- and mixed-solvent systems (R^2 = 0.80 and 0.76, respectively, compared to 0.62 and 0.55 for the best-performing COSMO variant). COSMO-SAC 2010 variants showed moderate accuracy for solubility but were the most accurate in predicting partition coefficients, while COSMO-SAC 2002 variants generally showed poorer performance, aside from isolated cases where certain levels of theory performed well. These findings, together with the distinct development procedures of each model (i.e., SAFT-γ Mie requires group parameters characterized with fluid data, which may not be available for all groups, whereas COSMO-based models use universal parameters and thus do not require parameter estimation for each compound or substructure) suggest that SAFT-γ Mie is well suited for process development tasks requiring accuracy within a narrow chemical space, whereas COSMO-SAC 2010 is more appropriate for large-scale screening where broad coverage is needed, such as in early screening where accuracy may be less critical. This work represents the first systematic comparison of SAFT-γ Mie and COSMO-SAC models for APIs and highlights the potential of hybrid strategies that combine the complementary strengths of both approaches.

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A Model for Multicomponent Sorption Thermodynamics and Mass Transport in Elastomeric Materials Under Large Deformation Accounting for Strong Specific Interactions

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Multicomponent penetrant mass transport and sorption thermodynamics in elastomeric materials exhibiting large deformations is a challenging task for modelling sorption/desorption kinetics in gels. In the current literature available continuum mechanics models adopt mean field approaches assuming mixing volume additivity (e.g. Flory-Huggins theory). Conversely more sophisticated EoS, such as PC-SAFT, able to account for specific interactions as well non-ideal mixing volume, only address the isotropic stress case. We propose here a model that accounts for the non-isotropic stress case in presence of strong specific interactions and volume non additivity. In fact, based upon the factorization of the chemical and mechanical contribution to the partition function proposed by Chester et.al. [1], we adopted for the chemical term the associative modular version of PC-SAFT [2]. This allows also to account for the volumetric concentration set in the constitutive class, thus removing the ideal volume mixing restriction. Finally, by exploiting. entropic inequality, mass and energy balances, frame invariance and material isotropy restrictions, self-consistent closure constitutive equations for the diffusive mass fluxes and stress tensor were determined in the isothermal case. The model was validated by interpreting the peculiar sorption behavior of water in Nipam (figure 1a), obtaining also the model parameters. Then, water-Nipam swelling kinetics as well stress and concentration kinetics profiles in confined geometries were predicted (figure 1b).

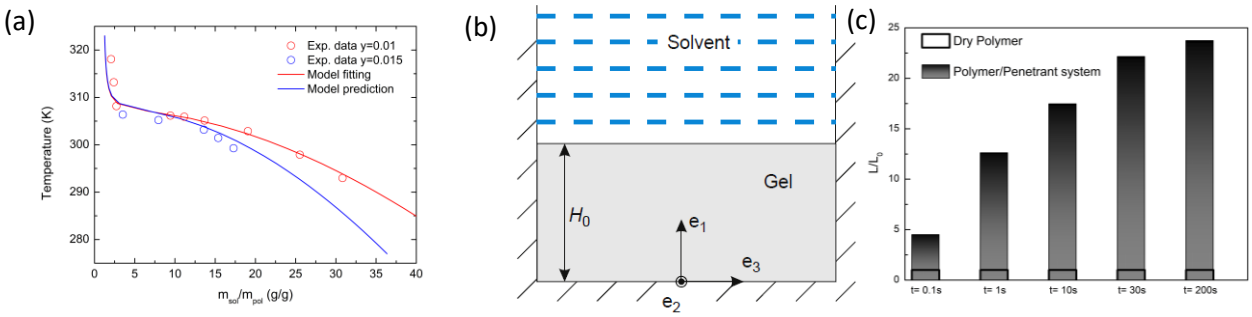

Figure 1. (a). Model regression of water/Nipam solubility data (y crosslink degree). (b) Model predictions of isothermal axial kinetic elongation of a Nipam-water mixture in the case of a cilindric confined geometry.

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Understanding the Polyethylene Crystallinity Decrease Due to Sorption of Diluents

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The sorption equilibrium of diluents in polyethylene (PE) is essential for understanding its properties. For instance, in PE slurry polymerization reactors, the concentration of absorbed ethylene monomer in the growing PE particles directly influences the polymerization reaction rate. PE is a semi-crystalline polymer; however, due to inherent constraints—polymer chain connectivity, chain ends, non-uniform chain length distribution, and the presence of comonomer units, is the complete crystallization thermodynamically unattainable. This results in the coexistence of distinct crystalline and amorphous domains. Consequently, the crystallinity at 25 °C serves as an important characteristic property that distinguishes different PE grades. While the temperature dependency of equilibrium crystallinity is well described both experimentally and theoretically [2], there is, to the best of our knowledge, a lack of experimental studies on how low molecular weight diluents influence crystallinity. Building on our recent study [1], we determined crystallinity as a function of gaseous diluent pressure using the Solid Fat Content (SFC) method based on Time-Domain Nuclear Magnetic Resonance (TD-NMR). We observed that crystallinity is not constant during the sorption process but decreases with diluent sorption in the amorphous phase. The magnitude of this change depends on both pressure and the type of diluent. Our work aims to rationalize these experimental observations by applying thermodynamic equilibrium concepts to the crystalline and amorphous phases. We extend the temperature-dependent PE crystallinity model developed by P. Paricaud [3], which is based on Flory's theory of copolymer crystallization and requires only the crystallinity/density at 25 °C as input. While Flory's theory was originally derived considering diluents in the amorphous phase, the diluents were omitted at some stage of the derivation for the sake of simplicity. Our key modification recognizes that the crystallinity decreases due to the lowered free energy of the amorphous phase due to the added diluent. The free energy of the polymer-rich amorphous phase can be evaluated using thermodynamic models for fluids. In Flory's original work, the Flory-Huggins term was proposed for the liquid phase. We predict the crystallinity decrease upon sorption of ethylene, but-1-ene, hex-1-ene, and nitrogen. Our modification allows independent selection of the thermodynamic model for the amorphous phase. Therefore, we test the applicability of three approaches: the Flory-Huggins model, the perturbed chain statistical associating fluid theory (PC-SAFT) equation of state and a conductor-like screening model for real solvents (its implementation known as COSMO-SAC). The predictions generally follow the qualitative trends; however, the best agreement is achieved with the PC-SAFT equation of state, as this model also provides essential volumetric (density) information. Our next step is to evaluate the influence of this partial melting on ethylene solubilities using our thermodynamic model with the PC-SAFT equation of state for the liquid phase, temperature-dependent crystallinity and the assumption of a pure crystalline phase.

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Short-Range Order in Binary Lennard–Jones Mixtures: An Integral Equation Theory Approach

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Short-range order (SRO) governs key properties of alloys such as strength, phase stability, and glass-forming ability by defining local atomic arrangements as ordering, segregating, or random. This study applies integral equation theory (IET) to binary Lennard-Jones mixtures to systematically quantify SRO across a range of densities, temperatures, and interaction parameters. We evaluate multiple IET closure approximations against molecular dynamics simulations to identify the most accurate framework. Using the validated model, we compute Warren–Cowley SRO parameters and construct SRO phase diagrams that delineate ordering, segregation, and glass-forming regimes. Despite the idealized nature of the Lennard–Jones potential, this approach provides fundamental insights into how interatomic interactions drive local atomic preferences, bridging theoretical predictions with experimentally observed alloy behaviour.

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Modeling of Curved and Planar Interfacial Boundaries in Nonionic Fluid Mixtures by Multilayer Quasichemical Approach

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Knowledge structural details and thermodynamic properties of interfacial boundaries in nonuniform systems, such as a drop of water in oil-rich phase, an aggregate in surfactant solution or planar interface between two equilibrium phases, is very important in many fields of research and engineering applications. Most theoretical approaches proposed for such systems do not take into account correlations between interacting functional groups of molecules, though correlations play an important role in associating fluids. For nonuniform fluids that contain chainlike and associating species, the most advanced model is iSAFT [1]; however, application of this approach is rather involved computationally. Today computer simulations are still the major instrument for predicting local structure of interfaces in nonuniform fluids.

A particularly detailed information about the local structure of interfacial boundaries may also be obtained with the aid of the Multilayer Quasichemical Model (MQuM) [2-4] that takes into account specific interactions in mixtures containing chainlike and associating species. MQuM describes directional correlations between interacting species within the Guggenheim quasichemical approximation and employs the original Smirnova's approach [5] of cutting the chainlike molecules into infinitely attracting monomeric structural units, much in spirit of SAFT. This approach also takes into account branching of molecular chains. For considering complex multicomponent fluids we extend MQuM for the systems containing monomeric units that differ in size.

In this work, we illustrate the predictions of MQuM for fluids that can contain alkanes, water, alcohols, complex ethers, etc. We consider spherical droplets, planar interfaces between liquid phases, and micellar aggregates in solution, and predict interfacial tension, profiles of normal and lateral pressure, and profiles of concentration and orientation of functional groups of the molecules. We also predict profiles of orientation of hydrogen bonds and chemical bonds of chainlike molecules within the interfaces and micelles. Special attention is paid to the description of the effect of branching of molecular chains on the interfacial properties.

Acknowledgements

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