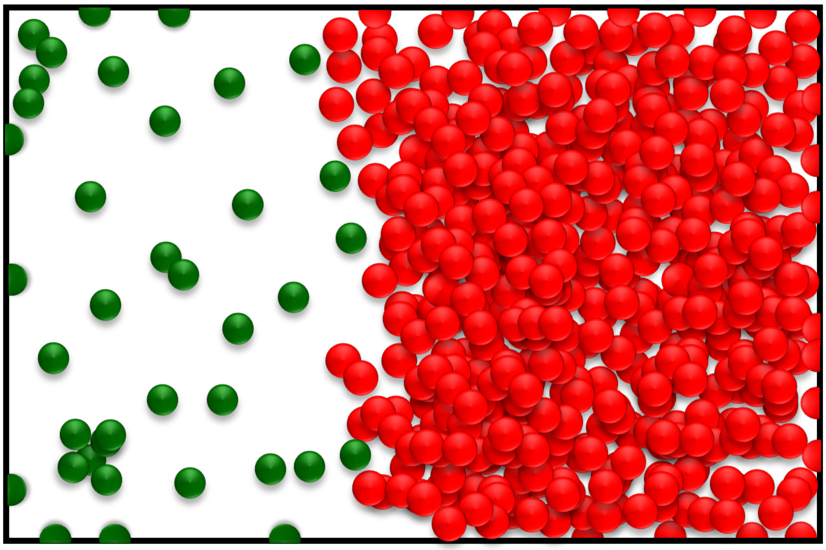

EQUIFASE 2024

9th - 12th of September 2024
Évora | Portugal

Book of Abstracts

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EQUIFASE 2024
Program

		9th September (Monday)
11.00	15.00	**Registration**
15.00	15.10	**Opening Session**
15.10	15.20	
15.20	15.30	
15.30	15.40	**IL1 - Walter Chapman** *Towards Linking Engineering Workflows: Phase Behavior, Self-Assembly, and Fluctuations from Thermodynamic Perturbation Theory and Molecular Simulation*
15.40	15.50	
15.50	16.00	
16.00	16.10	
16.10	16.20	**O1.1 - Velisa Vesovic** Predicting the Viscosity of Liquid Mixtures
16.20	16.30	
16.30	16.40	**O1.2 - Gustavo Chaparro** Multiphase parametrization of quasi-spherical Mie particles
16.40	16.50	
16.50	17.00	**O1.3 - Andrés Mejía** Reliable prediction of VLE in mixtures using the SAFT VR Mie EoS
17.00	17.10	
17.10	18.00	
18.00	20.00	**Welcome Reception**

EQUIFASE 2024
Program

		10th September (Tuesday)
9.00	9.10	**IL2 - Carlos Vega** *Simulations of water and electrolyte solutions: where are we?*
9.10	9.20	
9.20	9.30	
9.30	9.40	
9.40	9.50	**O2.1 - German Perez-Sanchez** Interactions between phospholipid membranes and drug nanocarriers through CG sims.
9.50	10.00	
10.00	10.10	**O2.2 - Leslie V. Woodcock** Physical-constant Fluid EoSs Using Boyle and Rigidity-Symmetry Lines: Water-Steam Example
10.10	10.20	
10.20	10.30	**O2.3 - Mariana Hoyer Moreira** Characterizing K+-Based Conductive Hydrogels through Exp. and Comput. Analysis
10.30	10.40	
10.40	11.10	**coffee break**
11.10	11.20	**IL3 - Frederico W. Tavares** *Thermodynamics of Confined Fluids via EoS, DFT, and Molecular Simulation*
11.20	11.30	
11.30	11.40	
11.40	11.50	
11.50	12.00	**O3.1 - Felipe Mourão Coelho** Dielectric Constant Tensor of Electrolyte Solutions Confined by Quartz Crystals via MD
12.00	12.10	
12.10	12.20	**O3.2 - David A. Kofke** Virial Equation of State Using Volume-Dependent Coefficient
12.20	12.30	
12.30	12.40	**O3.3 - Luís Franco** H and S of Mixing of Hydrocarbon Mixtures: Insights from Molecular Simulations
12.40	12.50	
12.50	14.30	**Lunch**
14.30	14.40	**IL4 - José Palomar** *Carbon Capture and Conversion Thermodynamics: How to Promote Process Efficiency*
14.40	14.50	
14.50	15.00	
15.00	15.10	
15.10	15.20	**O4.1 - Arthur B. Weidmann** Nucleation and growth of mixed CO2 and C3H8 hydrates through MD simulations
15.20	15.30	
15.30	15.40	**O4.2 - Rafael de P. Soares** Addressing Hydrogen Bond Cooperativity in Modern Quasi-Chemical Methods
15.40	15.50	
15.50	16.00	**O4.3 - Martín Cismondi Duarte** yaeos: Yet Another Equation of State Library
16.00	16.10	
16.10	16.20	**coffee break**
16.20	16.30	
16.30	16.40	
16.40	18.00	**Poster Session**

EQUIFASE 2024
Program

		11th September (Wednesday)
9.00	9.10	**IL5 - Clare McCabe** *Understanding the Self-Assembly of Skin Lipids from Molecular Dynamics Simulations: A Multiscale Perspective*
9.10	9.20	
9.20	9.30	
9.30	9.40	
9.40	9.50	**O5.1 - Eugénia A. Macedo** The impact of the nonrandomness factor on biomolecule partitioning in green ATPS
9.50	10.00	
10.00	10.10	**O5.2 - Jorge F. B. Pereira** New insights into the molecular interactions governing PEG/PPG ATPS formation
10.10	10.20	
10.20	10.30	**O5.3 - Oscar Rodríguez** PEG/sodium citrate ATPS: phase diagrams & fish protein partitioning
10.30	10.40	
10.40	11.10	**coffee break**
11.10	11.20	**IL6 - Carlos M. Silva** *Advancements in Supercritical Fluid Extraction: Research-Based Strategies for Effective Scale-Up and Design*
11.20	11.30	
11.30	11.40	
11.40	11.50	
11.50	12.00	**O6.1 - Murilo L. Alcantara** Thermodynamic Insights into Thiocyanate-Enhanced ATPS for Redox Flow Batteries
12.00	12.10	
12.10	12.20	**O6.2 - Mariana Pereira** FPE modelling to enhance downstream processes in the pharmaceutical industry
12.20	12.30	
12.30	12.40	**O6.3 - Antonio Marcilla** On the quality of exp. phase equilib. data at moderate pressure. Determination and correlation
12.40	12.50	
12.50	14.30	**Lunch**
14.30	14.40	**IV E. Brignole Lecture:** **IL7 - Fèlix Llovell** *The Key Role of Computational Thermodynamics in Developing Sustainable Solutions for the Mitigation of Greenhouse Gases*
14.40	14.50	
14.50	15.00	
15.00	15.10	
15.10	15.20	
15.20	15.30	
15.30	15.40	**O7.1 - Pedro Morgado** PFAS Surfactants – Molecular Modelling and Simulation for Environmental Remediation
15.40	15.50	
15.50	16.00	**O7.2 - Tiago M. Eusébio** Novel Fluorinated Surfactant-Free Microemulsions: Bulk and Interface Behaviour
16.00	16.10	
16.10	16.20	**coffee break**
16.20	16.30	
16.30	16.40	
16.40	18.00	**Poster Session**
18.00	19.00	
19.00		**Conference Dinner**

EQUIFASE 2024
Program

		12th September (Thursday)
9.00	9.10	**IL8 - Aaron M. Scurto** *Ionic Liquid Mixtures with Compressed Hydrofluorocarbon Gases: Thermophysical Properties, Spectroscopy, and X-ray Scattering*
9.10	9.20	
9.20	9.30	
9.30	9.40	
9.40	9.50	**O8.1 - Silvana Mattedi** Thermodynamic and micellization behavior of protic ILs in aqueous medium
9.50	10.00	
10.00	10.10	**O8.2 - Dinis O. Abranches** Combining High Throughput Experiments and Active Learning to Characterize DESs
10.10	10.20	
10.20	10.30	**O8.3 - Neeraj Rai** Thermal and Coverage Effects in Heterogeneous Catalysis using ML Interatomic Potentials
10.30	10.40	
10.40	11.10	**coffee break**
11.10	11.20	**IL9 - Margarida Bastos** *Isothermal Titration Calorimetry as a Tool in Phase Transfer Studies*
11.20	11.30	
11.30	11.40	
11.40	11.50	
11.50	12.00	**O9.1 - Simão P. Pinho** An Overview of the Salt Effect on the Solubility of Biomolecules
12.00	12.10	
12.10	12.20	**O9.2 - Sofia C. Aparício** Natural solvent systems for plastic recycling: dissolution-precipitation
12.20	12.30	
12.30	12.40	**Closing Session**
12.40	12.50	
13.00	13.10	
13.10	14.30	**Lunch**

List of Communications

Invited Lectures

IL1. Walter G. Chapman (Rice University, USA), with Jinxin Lu, Carolina Brindis, Thiago Pinheiro dos Santos, Philip Singer

Towards linking engineering workflows: Phase behavior, self-assembly, and fluctuations from thermodynamic perturbation theory and molecular simulation

IL2. Carlos Vega (Universidad Complutense de Madrid, Spain)

Simulations of water and electrolyte solutions: where are we?

IL3. Frederico Wanderley Tavares (Federal University of Rio de Janeiro, Brazil)

Thermodynamics of Confined Fluids via EoS, DFT, and Molecular Simulation

IL4. J. Palomar (Universidad Autónoma de Madrid, Spain), with S. Dorado-Alfaro, E. Hernández, A. Belinchón, A. Pereira, P. Navarro, J. Lemus

Carbon Capture and Conversion Thermodynamics: How to Promote Process Efficiency

IL5. Clare McCabe (Heriot-Watt University, United Kingdom)

Understanding the Self-Assembly of Skin Lipids from Molecular Dynamics Simulations: A Multiscale Perspective

IL6. Carlos M. Silva (University of Aveiro, Portugal), with José P. S. Aniceto

Advancements in Supercritical Fluid Extraction: Research-Based Strategies for Effective Scale-Up and Design

IL7. F. Llovell (Universitat Rovira i Virgili, Spain)

The Key Role of Computational Thermodynamics in Developing Sustainable Solutions for the Mitigation of Greenhouse Gases

IL8. Aaron M. Scurto (University of Kansas, USA), with Karim S. Al-Barghouti, Rajkumar Kore, Mark B. Shiflett

Ionic Liquid Mixtures with Compressed Hydrofluorocarbon Gases: Thermophysical Properties, Spectroscopy, and X-ray Scattering

IL9. Margarida Bastos (Universidade do Porto)

Isothermal Titration Calorimetry (ITC) as a Tool in Phase Transfer Studies

Oral Presentations

O1.1. Velisa Vesovic* (Imperial College London, UK)
Predicting the Viscosity of Liquid Mixtures

O1.2. Gustavo Chaparro, Erich A. Müller* (Imperial College London, UK)
Multiphase parametrization of quasi-spherical Mie particles

O1.3. Andrés Mejía*, Marcela Cartes, Gustavo Chaparro, Erich A. Müller (Universidad de Concepción, Chile)
Reliable prediction of the Vapor-Liquid-Liquid Equilibria in mixtures using the SAFT VR Mie EoS

O2.1. Germán Pérez-Sánchez*, João A. P. Coutinho (University of Aveiro, Portugal)
Coarse-grain computer simulation approach to unveil interactions between phospholipid membranes and drug nanocarriers

O2.2. Ahmad Eltahlawy, Igor Khmelinskii, **Leslie V. Woodcock*** (University of Algarve, Portugal)
Physical-constant Fluid Equations-of-State Using Boyle and Rigidity-Symmetry Lines: Water-Steam Example

O2.3. Mariana H. Moreira*, Aimone J. C. Duarte, Luís C. Branco, Isabel M. Marrucho, Luís F. G. Martins (University of Évora, Portugal)
Characterizing Potassium-Based Conductive Hydrogels through Experimental and Computational Analysis

O3.1. Felipe M. Coelho, Luís Fernando Mercier Franco* (Universidade Estadual de Campinas, Brazil)
Dielectric Constant Tensor of Electrolyte Solutions Confined by Quartz Crystals via Molecular Dynamics Simulations

O3.2. Andrew J. Schultz, **David A. Kofke*** (University at Buffalo - State University of New York, USA)
Virial Equation of State Using Volume-Dependent Coefficient

O3.3. Nikolas Ferreira de Souza, Federico Ezequiel Benelli, Martina Julieta Quinzio, Sabrina Belén, Rodriguez Reartes, **Luís Fernando Mercier Franco**, Martín Cismondi Duarte* (Universidade Estadual de Campinas, Brazil)
Enthalpy and Entropy of Mixing of Hydrocarbon Mixtures: Insights from Molecular Simulations

O4.1. Arthur B. Weidmann, Luís F. M. Franco, Pedro A. P. Filho*, Amadeu K. Sum (University of São Paulo, Brazil)
Nucleation and growth of mixed carbon dioxide and propane hydrates through molecular dynamics simulations

O4.2. Rafael de P. Soares* (Federal University of Rio Grande do Sul, Brazil)
Addressing Hydrogen Bond Cooperativity in Modern Quasi-Chemical Methods

O4.3. Federico Ezequiel Benelli, Salvador Eduardo Brandolin, Gerardo Oscar Pisoni, **Martín Cismondi-Duarte*** (Universidad Nacional de Córdoba, Argentina)
yaeos: Yet Another Equation of State Library

O5.1. Pedro Velho, Gonçalo Perestrelo, **Eugénia A. Macedo*** (University of Porto, Portugal)
The impact of the nonrandomness factor on biomolecule partitioning in green ATPS

O5.2. Alexandre M. S. Jorge, Gonçalo M. C. Silva, João A. P. Coutinho, **Jorge F. B. Pereira*** (University of Coimbra, Portugal)
New insights into the molecular interactions governing PEG/PPG aqueous two-phase system formation

O5.3. René Gómez-Pineda, Ana Soto, **Oscar Rodríguez*** (Universidade de Santiago de Compostela, Spain)
PEG/sodium citrate ATPS: phase diagrams & fish protein partitioning

O6.1. Murilo L. Alcantara*, Marco Prazeres, Gabriel L. Camilo, Catarina M. S. S. Neves, Paula Navalpotro, Rebeca Marcilla, João A. P. Coutinho (University of Aveiro, Portugal)
Thermodynamic Insights into Thiocyanate-Enhanced Aqueous Biphasic Systems for Redox Flow Batteries

O6.2. Mariana Pereira*, Inês Rocha, Saúl Silva (Hovione Farmaciência S.A., Portugal)
Fluid phase equilibria modelling to enhance downstream processes in the pharmaceutical industry

O6.3. Antonio Marcilla*, Inés Oliver, Paloma Carbonell-Hermida, Eleha Sicilia, María del Mar Olaya (University of Alicante, Spain)
On the quality of experimental phase equilibrium data at moderate pressure. Aspects to be considered for their appropriate determination and correlation

O7.1. Guilherme Damião, André Ramos, Pedro Silva, Luís F. G. Martins, Clare McCabe, Eduardo J. M. Filipe, **Pedro Morgado*** (University of Lisbon, Portugal)
Perfluorinated (PFAS) Surfactants – Molecular Modelling and Simulation for Environmental Remediation

O7.2. Tiago M. Eusébio, Ricardo A. A. Luís, Diogo Machacaz, Pedro Morgado, Eduardo J. M. Filipe* (University of Lisbon, Portugal)
Novel Fluorinated Surfactant-Free Microemulsions: Bulk and Interface Behaviour

O8.1. Gabriela F.D. Ferreira, Tairone S. Paixão, Ana Cristina M. Silva, **Silvana Mattedi***
(Federal University of Bahia, Brazil)
Thermodynamic and micellization behavior of protic ionic liquids in aqueous medium

O8.2. Dinis O. Abranches, William Dean, Miguel Muñoz, Wei Wang, Yangang Liang, Burcu Gurkan, Edward J. Maginn, Yamil J. Colón* (University of Notre Dame, USA)

Combining High Throughput Experiments and Active Learning to Characterize Deep Eutectic Solvents

O8.3. Woodrow Wilson, John Michael Lane, Chinmoy Saha, Jeremy Lugo, and **Neeraj Rai*** (Mississippi State University, USA)

Including Thermal and Coverage Effects in Heterogeneous Catalysis using Machine-Learned Interatomic Potentials

O9.1. Mehriban Aliyeva, José R. B. Gomes, João A. P. Coutinho, Olga Ferreira, **Simão P. Pinho*** (Instituto Politécnico de Bragança Portugal)

An Overview of the Salt Effect on the Solubility of Biomolecules

O9.2. Sofia C. Aparício, Bernardo D. Ribeiro, Isabel M. Marrucho* (University of Lisbon, Portugal)

Natural solvent systems for plastic recycling: dissolution-precipitation

Poster Communications

I-P1. Baptiste Bernicot, Sandrine Dourdain*, Guilhem Arrachart, Nicolas Schaeffer, Gabriel Teixeira Santos (University of Montpellie, France)
Hydrophobic eutectic solvents for liquid-liquid extraction: formulation and modelling

I-P2. Gabriel Teixeira, Paula Brandão, Ana I. M. C. Lobo Ferreira, Dinis O. Abranches, Luís M. N. B. F. Santos, Olga Ferreira*, João A. P. Coutinho (University of Aveiro, Portugal)
Development of biosensors for phenol compounds utilizing Langmuir and Langmuir-Blodgett nano-organized films containing laccase

I-P3. Filipe H. B. Sosa*, Dinis O. Abranches, André M. da Costa Lopes, Mariana C. da Costa, João A. P. Coutinho (University of Aveiro, Portugal)
The impact of hydrotropes on kraft lignin dissolution in aqueous solutions of deep eutectic solvents

I-P4. Nazir Fattahi, Parvin Zohrabi, Fereshteh Shiri, Filipe Hobi Bordón Sosa, and **Beshare Hashemi*** (American International University, Kuwait)
Using COSMO-RS in the designing and screening of different deep eutectic solvents for the extraction of carbaryl

I-P5. Ehsan Heydaryan*, Shohreh Iraji, Saman A. Aryana (University of Wyoming, USA)
WHIA: A Novel Cubic Equation of State for Accurate Modeling of Water Properties

I-P6. José L. Legido*, Eder Peña, Ana M. Robledo, Sergio Salazar, Carmen P. Gómez, M^{a} Lourdes Mourelle (University of Vigo, Spain)
Thermophysical characterization of peloids from the Manizales area in Colombia

I-P7. Annie N. Alves, Priscilla A. Nascimento, Jéssica F. Borges, Rafael C. I. Fontan, Cristiane M. Veloso, Wenrong Yang, Motilal M. Mathesh, **Renata C. F. Bonomo*** (State University of Southwest of Bahia, Brazil)
The impact of nanomaterial on pepsin immobilisation

I-P8. Ricardo T. Pais*, Ana C. Sousa, Pedro J. Carvalho (University of Aveiro, Portugal)
Enhancing CO2 solubility using [C4C1im][DMP] + carboxylate-based Protic Ionic Liquids mixtures

I-P9. J. L. Legido*, J. Vijande, M.M. Mato (University of Vigo, Spain)
Thermophysical properties of ternary mixtures ether + 1-alcohol + n-alkane

I-P10. Rodrigo Kraemer T, Harry Cárdenas, Andrés Mejía* (Universidad de Concepción, Chile)
Adsorption modeling of non-quantum and quantum fluids under confinement using SAFT-VRQ-Mie

I-P11. Juan M. Uceda, Melissa Morales, Marcela Cartes, Andrés Mejía* (Universidad de Concepción, Chile)
Experimental Determination and Theoretical Modelling of Isobaric Vapor-Liquid Equilibria, Liquid Density, Surface Tension and Dynamic Viscosity for the Methyl Butyrate and tert-Butanol Binary Mixture

I-P12. Felipe M. Coelho, Luís Fernando Mercier Franco*, Abbas Firoozabadi (Universidade Estadual de Campinas, Brazil)

CO_2-Water and CO_2-Brine High-Temperature Phase Equilibria: a Multiscale Approach

I-P13. Aline Zambom, João Santos, Priscilla S. Gaschi, Mónia A. R. Martins, João A. P. Coutinho, Olga Ferreira, Simão P. Pinho* (Instituto Politécnico de Bragança, Portugal)

Enhancing acetaminophen solubility in aqueous solutions with hydrotropes

I-P14. Carlos Morales-Díaz, Marcela Cartes, Andres Mejía* (Universidad de Concepción, Chile)

Measurement and Modelling of isobaric vapor-liquid equilibrium and surface tension of methyl butyrate + dibutyl ether binary system

I-P15. André Nogueira, Inês C.M. Vaz, Filipe H.B. Sosa, Nicolas Schaeffer*, João A.P. Coutinho (University of Aveiro, Portugal)

Leveraging machine learning for lithium-ion battery recycling

I-P16. Pedro Velho*, Eduardo Sousa, Eugénia A. Macedo (University of Porto, Portugal)

VPO and liquid density data for binary aqueous solutions of organic salts at 313.15 K and 0.1 MPa: measurement and modelling

I-P17. Paulo V. B. Bonjour, Márcio L.L. Paredes, Pedro H.R. Alijó* (Universidade do Estado do Rio de Janeiro, Brazil)

The influence of thermodynamic modeling on cost assessment in extracting bio-oil value-added compounds

I-P18. Sophia L. S. Santos, Alexandre S. Zimmermann, Raissa C. Ferreira, Lucienne L. Romanielo, Júlio César S. Nascimento, **Silvana Mattedi*** (Federal University of Bahia, Brazil)

Prediction of carbon dioxide solubility in Diethylammonium Butanoate [DEA][Bu] using Monte Carlo Simulations

I-P19. Camila Vallejos_Michea*, Yecid P. Jimenez (Universidad de Antofagasta, Chile)

Liquid-liquid equilibrium of aqueous two-phase systems of ChCl-U with potassium phosphate salts at different temperatures

I-P20. Isaías Huenuvil-Pacheco, Marcela Cartes, Andrés Mejía* (Universidad de Concepción, Chile)

Experimental Determination and Theoretical Prediction of Thermodynamic Properties: Vapor-Liquid Equilibrium, Liquid Densities, Viscosity, and Surface Tensions in Ternary Mixture of n-Hexane + CPME + Propan-1-ol

I-P21. Thallyta G. Fogaça, Caico B. Reis, Lucas O. Cardoso, Rui C. A. Lima, Alana A. da Costa, **Silvana Mattedi* (**Federal University of Bahia, Brazil)

Pressure and Temperature Influence on Viscosity and Density of Binary Mixtures of Ammonium Propionate Ionic Liquids

I-P22. Carlos G. Albà*, Ismail I. I. Alkhatib, Lourdes F. Vega, Fèlix Llovell (Universitat Rovira i Virgili, Spain)

A Comprehensive Framework for Designing Low-GWP Refrigerant drop-ins: A Thermodynamic and Environmental Analysis with Soft-SAFT and LCA

I-P23. Carlos G. Albà*, Ismail I. I. Alkhatib, Lourdes F. Vega, Fèlix Llovell (Universitat Rovira i Virgili, Spain)

Innovative AI Applications in Thermodynamic Modeling of CO_2-based Mixtures

I-P24. J. L. Legido*, M. M. Mato, K. Kashyap, C. P. Gómez, L. M. Mourelle (University of Vigo, Spain)

Study of the density and thermal conductivity of mixtures of bentonite with saline solutions

I-P25. Luís Fernando M. Franco*, **Nathan B. de Souza** (Universidade Estadual de Campinas, Brazil)

A novel equation of state for mixtures of cylindrically-symmetric hard-core fluids of different aspect ratios

I-P26. Francisco Paes, Romain Privat*, Baptiste Sirjean, Jean-Noël Jaubert (Université de Lorraine, France)

Coupling the tc-PR and COSMO-RS approaches to get a purely predictive equation of state: application to the prediction of the phase behavior of +200 complex systems

I-P27. L.V.T.D. Alencar*, S.B. Rodriguez-Reartes, F.W. Tavares, F. Llovell **(**Universitat Rovira i Virgili, Spain)

Combining soft-SAFT and Neural Networks to address the Thermophysical Properties of Choline Chloride DES with Co-solvents

I-P28. Fabio P. Nascimento*, Ladislane S. Bastos, Verônica J. Pereira, Gloria M. N. Costa, Silvio A. B. Vieira de Melo **(**Universidade Federal da Bahia, Brazil)

Investigation of interfacial tension and minimum miscibility pressure between a Brazilian dead oil and a CO_2:CH_4 mixture

I-P29. Gerard Alonso*, Marcela Cartes, Andrés Mejía **(**Universidad de Concepción, Chile)

Vapor-Liquid-Liquid Equilibrium for the Water + Butanol + CPME Mixture

I-P30. Gabriela Caetano, Bernardo Dias, Isabel M. Marrucho* **(**Universidade de Lisboa, Portugal)

Analysis of saponin extraction from beet leaves using the ultrasound-assisted

I-P31. Gabriel Teixeira, Olga Ferreira, Nathanaël Guigo, João A. P. Coutinho* **(**University of Aveiro, Portugal)

Fast calorimetry scanning for degrading quaternary ammonium compounds

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Aneotropy: Unusual interfacial behaviour of mixtures of hydrogenated and fluorinated substances

II-P49. José Santos Pereira, Gonçalo M. C. Silva, Pedro Morgado, Eduardo J. M. Filipe* (Universidade de Lisboa, Portugal)

Self-Assembly of Compartmentalized Micelles

II-P50. Ricardo A. A. Luís, Tiago M. Eusébio, Diogo Machacaz, Pedro Morgado, Eduardo J. M. Filipe* (Universidade de Lisboa, Portugal)

New Fluorinated Surfactant-Free Microemulsions: experimental and molecular dynamics simulations

Abstracts

Towards linking engineering workflows: Phase behavior, self-assembly, and fluctuations from thermodynamic perturbation theory and molecular simulation

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A goal of our research program has been to link engineering workflows with molecular theory across scales for bulk fluid properties and phase behavior, interfacial properties, and prediction of self-assembly. The vision is to have models and transferable model parameters that scale across these systems, allowing the user to move seamlessly from engineering models for bulk fluid phase behavior to mesoscale models of self-assembly and finally to molecular simulation, matching the level of model complexity to the system and properties of interest. We base the approach on rigorous statistical mechanics based theory for these systems that has been validated versus molecular simulation. An advantage of this approach is that the theories are predictive with known approximations and limitations.

In this talk, we will provide an overview of recent advances and applications from our research group. Our recent research has moved in two directions: firstly, simplifying our molecular theories to provide accurate statistical mechanics based engineering models with known approximations. At the same time, we have discovered unrecognized approximations in current engineering models. In a second direction, we have extended molecular theory by incorporating new degrees of realism, such as diblock and triblock surfactants / copolymers and patchy colloids, enabling calculations of self-assembly in ever more complex systems. Other directions and advances in our research program will be highlighted.

Simulations of water and electrolyte solutions: where are we?

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Simulations of water started around 1970 [1,2]. Intermolecular interactions were described using the Lennard-Jones (LJ) potential and partial charges as first suggested in 1933 [3]. Potential parameters were determined to reproduce the experimental density and the energy of liquid water. The study of phase equilibria arrived later: vapor-liquid equilibria in the 90s and fluid-solid equilibria in the XXI century and that allowed the proposal of improved water models as for instance TIP4P /2005 [4]. This model is not able to describe all properties of water and the reasons for this failure will be discussed. However, it allows to study a number of interesting physical problems as nucleation, the quasi-liquid layer and the possible existence of a liquid- liquid transition in supercooled water. The attempt to improve the predictions for the dielectric constant (as in the OPC model) seems to deteriorate the overall performance of a water non-polarizable model [5]. Electrolytes in water are both important and interesting. In simulations they are commonly described using integer charges and single LJ centers for the ions but the results are far from being satisfactory. It will be shown, that the use of scaled charges for the ions along with TIP4P /2005 (as done in the Madrid force field [6]) allows for a decent (although still not fully satisfactory) description of electrolyte solutions for properties such as densities, maximum in density, structure, freezing point depression and transport properties. Probably we reached the limit of can be done with simple non-polarizable force fields in modeling water and electrolyte solutions. To go beyond that we need a more sophisticated description (including polarizability and/or ab initio input). However, for certain type of problems the simple approach can be enough to learn some physics.

References

[1] J. A. Barker and R. O. Watts,Chem.Phys.Lett.,3,144,(1969)
[2] A. Rahman and F.H. Stillinger,J.Chem.Phys.,55,3336,(1971)
[3] J. D. Bernal and R. H. Fowler,J.Chem.Phys.,1,515,(1933)
[4] J.L.F.Abascal and C.Vega, J.Chem.Phys., 123 ,234505,(2005)
[5] L.F.Sedano, S.Blazquez and C.Vega, J.Chem.Phys.,161,044505,(2024)
[6] I.M.Zeron,J.L.F.Abascal,C.Vega,J.Chem.Phys.,151 134504 (2019)

Thermodynamics of Confined Fluids via EoS, DFT, and Molecular Simulation

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The 1-D and 3-D classical Density Functional Theory (cDFT), consistent with the PC-SAFT and Peng-Robinson equations of state, are used to investigate the adsorption isotherms and local densities of pure hydrocarbons, H2, and CO2 and their mixtures in crystalline-structure materials (like MOF-5) and amorphous materials (like nanoporous carbons). The cDFT calculations reveal that the adsorption process is influenced by the fluid-fluid spatial correlations between the fluid molecules and the external potential produced by the solid structure. These findings are supported by a comparison with experimental data and Grand Canonical Monte Carlo (GCMC) simulations of the adsorbed amount and density profiles of the adsorbed fluid inside the solid. We also explore the impact of the non-crystalline structure of amorphous carbon nanopores on fluid structure and adsorption isotherms, as well as fluid-fluid and fluid-solid interactions. The c-DFT approach provides local fluid structure and then permits the description of the dynamic behavior of non-uniform fluids at confined or non-confined conditions. We offer insights into how hard-sphere nanoparticles behave when confined to an external oscillate potential and the different forms that appear during crystallization.

References

[1] Elvis Soares, Amaro G. Barreto Jr., Frederico W. Tavares, “Classical Density Functional Theory Reveals Structural Information of H2 and CH4 Fluids Adsorption in MOF-5”, *Fluid Phase Equilibria*, 574, 113887 (2023). DOI: 10.1016/j.fluid.2023. 113887

[2] Lucas J. dos Santos, Elvis Soares, Amaro G. Barreto Jr., Frederico W. Tavares "Comparison of 3D-cDFT and GCMC Simulations for Fluid-Structure Analysis in Amorphous Carbon Nanoporous Materials", Adsorption, 30, 583 – 594 (2024). DOI: 10.1007/s10450-024-00444-z

[3] Vítor de Morais Sermoud, André de Freitas Gonçalves, Amaro Gomes Barreto Jr., Luís Fernando Mercier Franco, Frederico Wanderley Tavares, Marcelo Castier “Classical density functional theory of confined fluids: from getting started to modern applications” Fluid Phase Equilibria, 586, 114177 (2024). DOI: 10.1016/j.fluid.2024.1141177

Carbon Capture and Conversion Thermodynamics: How to Promote Process Efficiency

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Carbon capture and utilization (CCU) are main strategies to promote industrial decarbonization, with the goal to address the climate challenge of net-zero by 2050. Therefore, big efforts are being made by academic and industry for developing new efficient and cost-effective carbon capture (CC) technologies. It involves a wide range of industrial applications and CC systems, from the high CO_2 concentrated streams in low-carbon footprint energy production (H_2 production, pre-combustion, biogas upgrading) to relatively diluted (post-combustion) and highly diluted (direct air capture, DAC) carbon sources. The process performance of CC technologies is determined for several factors, highlights the CO_2 partial pressure of treated industrial streams, the sorbent material properties, the operating conditions, the process configuration and used utilities. Subsequent carbon utilization (CU) to produce added-value chemical products is also widely explored to decrease the carbon emission rates and promote carbon circular economy. This additional process must be optimized to reach neat CO_2 fixation in sustainable CCU applications. It implies the development of efficient catalyst and the design of reaction/separation process to produce commercial CO_2-based product at competitive cost and minimized environmental impacts.

In the last years, Ionic Liquids (ILs) have become promising CO_2 chemical absorbent and CO_2 catalysts in the CO_2 cycloaddition to epoxides for cyclic carbonates production. Sequential CC and CU process designed using ILs as absorbent/catalyst were reported with lower energy consumption, process cost and environmental impacts than those based on benchmark industrial processes. Additionally, bifunctional ILs -able to chemically absorb and activate the CO_2 compound- were designed for new integrated CCU processes, allowing process intensification with corresponding decreasing of operating and capital costs.

Despite the huge research work in this field, there is a lack of knowledge regarding how reaction and phase equilibrium thermodynamics of CO_2-based systems determine the CCU process performance. Obtaining deeper insight in the relationships between key performance indicators (KPIs) and CO_2-IL-based systems would clearly contribute to develop more efficient CCU technologies by means of simultaneous absorbent/catalyst material and process design. Taking advantage of “designer compound” characteristics of ILs, in this work several molecular simulations tools (density functional theory, COSMO-RS, molecular dynamics), combined with process simulations and life cycle assessment, will be applied to explore the thermodynamic limits of CCU strategies for cyclic carbonate production based on ILs, with the aim of overviewing the role of material and process thermodynamic properties on KPIs as cyclic capacity, product yield, energy/chemical/water consumptions, environmental impacts, net CO_2 fixation, and process costs, involving relevant industrial CC systems (pre-combustion, biogas, post-combustion, DAC) and different cyclic carbonate products (ethylene, propylene, hexylene, styrene, glycerol).

Understanding the Self-Assembly of Skin Lipids from Molecular Dynamics Simulations: A Multiscale Perspective

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The barrier function of the human skin is primarily located in the stratum corneum (SC), which is composed of skin cells (corneocytes) surrounded by a dense, lamellar lipid matrix made up of ceramides (CERs), cholesterol (CHOL), and free fatty acids (FFAs) of various lengths. While the lipid structure of intact SC can be reproduced experimentally with model systems using synthetic lipids,[1] the organization and role of each lipid in determining the barrier properties of skin, is not well understood due to the complex nature of the SC lipid matrix. To address this need, atomistic molecular dynamics (MD) simulations of pre-assembled lipids in primarily bilayer configurations have been used to study the behavior of the SC lipids.[2,3] However, such simulations can suffer from initialization bias due to low lipid mobility. Furthermore, simple bilayers are not representative of the complex multilayer structure of the SC. In order to access the long timescales and large system sizes needed to self-assemble multilamellar structures, we have developed computationally efficient coarse-grained (CG) models using the Multi-State Iterative Boltzmann Inversion (MS-IBI) method2 based on simulation data from fully atomistic models for commonly studied SC lipids.[3] The self-assembly of mixtures of CERs, CHOL, and FFAs are subsequently studied into multilayer assemblies. Atomistic configurations are then generated by back-mapping the self-assembled multilayer CG configurations and in turn provide insight into lipid organization and structure of SC lipid systems.

References

[1] J. A. Bouwstra and M. Ponec, "The Skin Barrier in Healthy and Diseased State," Biochimica et Biophysica Acta – Biomembranes, 1758, 2080-2095 (2006).

[2] P. Shamaprasad, C. O Frame, T. C. Moore, A. Yang, C. R. Iacovella, J. A. Bouwstra, A. L. Bunge and Clare McCabe, "Using Molecular Simulation to Understand the Skin Barrier" Progress in Lipid Research, 88, 101184 (2022).

[3] T.C. Moore, C. R. Iacovella, and Clare McCabe, "Derivation of Coarse-Grained Potentials via Multistate Iterative Boltzmann Inversion," J. Chem. Phys, 140(22) 224104 (2014).

Advancements in Supercritical Fluid Extraction: Research-Based Strategies for Effective Scale-Up and Design

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Supercritical fluids (SCF) exhibit properties that are intermediate between those of liquids and gases, such as null surface tension, low viscosity and high diffusivity, which enhance mass transfer and penetration into matrices. Additionally, their solvent power can be adjusted by slight variations in pressure and temperature, as well as by adding small amounts of organic cosolvents. These properties make SCFs versatile and eco-friendly fluids for a wide range of applications, including: extraction of bioactive compounds or pollutants from biomass; extraction of metals by coordination with dissolved ligands; as a favorable medium for chemical reactions; as solvents in chromatographic processes; reducing oils viscosity to speed up sedimentation processes; impregnation of biomolecules and dyes; drying of aerogels; and more.

In the case of supercritical fluid extraction (SFE), the SCF acts as a solvent to extract valuable compounds (e.g., oils and bioactive molecules) or contaminants (e.g., anisoles and pesticides) from biomass, or is used in the pretreatment of materials for subsequent processing (*e.g.*, increasing biomass accessibility, reducing lignin content, and facilitating enzymatic hydrolysis).

In the conventional SFE process, the SCF (pure or modified with a cosolvent) passes through a vessel containing the biomass and solubilizes the extractable compounds, which are then recovered from the SCF by precipitation after sudden depressurization. The SCF, free of solutes, is then repressurized and reheated to reach the extraction conditions again, which, at an industrial scale, represents significant energy consumption. The industrial operation of these processes poses additional challenges, such as channeling, which causes the flow to short-circuit and reduces extraction efficiency. New extraction approaches have emerged as the SFE process is implemented industrially. For example, in the decontamination of cork, the regeneration of the SCF is conducted under the same operating conditions through an adsorbent bed capable of retaining the undesired compounds and allowing the recycling of the fluid, thus avoiding the costly pump and heating systems required in the conventional process.

The effective scale-up and design of supercritical processes requires a strong research background to maximize the chances that laboratory studies can ultimately reach an industrial scale. This implies a multi-step process covering preliminary extraction and characterization, experimental optimization of operating conditions, measurement of kinetic extraction curves and their phenomenological modeling, scale-up studies, and techno-economic analysis of industrial processes.

This plenary lecture focuses the SFE for the selective recovery of bioactive compounds or the removal of contaminants, employing both conventional and innovative cycles. Insights to guide research into the successful industrial implementation of these processes will also be presented. The strengths and weaknesses of various methods are identified, along with the current state-of-the-art mechanistic and statistical modeling approaches and scale-up challenges.

The Key Role of Computational Thermodynamics in Developing Sustainable Solutions for the Mitigation of Greenhouse Gases

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The use of molecular-based equations of state (EoSs), rooted in statistical mechanics, has been perceived with a certain degree of skepticism from the industry. However, the combination of these models with molecular simulations has proven capable of accurately predicting the thermophysical properties of a wide range of systems. This accuracy is particularly valuable as new industrial processes increasingly involve complex fluids and extreme operating conditions, where extrapolations are required and classical models and correlations often fall short. In addition, the exponential development of computer capabilities has facilitated the development of a diverse of additional options, ranging from quantum chemistry methods to machine learning approaches, which can be used to complete the thermophysical picture of any system. Overall, this multiscale theoretical approach becomes a powerful basis to address many remaining challenges, offering the necessary information to progress towards a process simulation scale, even facilitating further environmental and technoeconomic analyses.

In this very special talk for the *Esteban Brignole* Award, it is intended to follow the steps of the pioneering work of Prof. Brignole and show how accurate thermodynamic methods can be used as an excellent platform to provide a methodology for designing technological solutions to the industry nowadays, spotlighting the key role of Thermodynamics and Phase Equilibria. In particular, the focus of this contribution will be related to the immense challenge of the reduction of greenhouse gas emissions. The proposed approach has its core on the robust polar soft-SAFT EoS to predict thermodynamic properties, but also includes other theoretical tools ranging from the quantum molecular scale via COSMO-RS, till the microanalysis using neural networks.

Indeed, this talk will try to emphasize how it is possible to carry out a technical screening for the selection of adequate solvents for CO_2 capture and high Global Warming Potential (GWP) refrigerants separation. In terms of recovery, a study based on the capabilities of ionic liquids and deep eutectic solvents to selectively separate the most common hydrofluorocarbons (HFCs) present in commercial mixtures is addressed, with a practical example on real blends, such as R410A and R407F. Additionally, a detailed example focused on the use of Thermodynamics for the selection and development of new low GWP refrigerant mixtures will be shown, highlighting the calculation of several Key Performance Indicators to provide a drop-in replacement study of current high GWP systems. Some examples will be given, with applications on refrigeration cycles, discussing the impact of different variables. The direct connection with the process scale, showing how economic and environmental calculations are highly dependent on the technical evaluation will also be highlighted. In summary, it is expected to emphasize the pivotal role of Thermodynamics to find solutions to global issues, contributing to the sustainability of industrial processes.

Ionic Liquid Mixtures with Compressed Hydrofluorocarbon Gases: Thermophysical Properties, Spectroscopy, and X-ray Scattering

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Ionic liquids (ILs) have been proposed as entrainers in novel extractive distillation technologies to separate azeotropic and near-azeotropic hydrofluorocarbon (HFC) refrigerant blends with high global warming potential (GWP). Design and optimization of extractive distillation engineering units require a comprehensive evaluation of a multitude of thermodynamic and transport properties of the pure components as well as the biphasic gas/IL mixtures. In addition, a molecular-level understanding of ionic liquid mixtures, in general, continues to be a challenge.

In this work, we measure thermophysical properties of several imidazolium-based ILs saturated with the hydrofluorocarbon gases difluoromethane (R-32), 1,1,1,2-tetrafluoroethane (R-134a), and pentafluoroethane (R-125) to elevated pressures and temperatures. Investigated properties include phase equilibrium thermodynamics (solubility and density), and transport properties (viscosity, diffusivity, and thermal conductivity). Our results indicate highly non-ideal behavior across the array of properties measured. All systems investigated exhibit large negative excess molar volumes. The viscosity of all systems exhibits a sharp decrease with even low loadings of the HFCs illustrating a general dilution effect with the low viscosity HFCs. Diffusivities are investigated using a pulsed field gradient stimulated echo NMR technique at elevated pressures. Simple Stokes-Einstein relationships using measured mixture viscosity generally follow the experimental data, however, with fractional Stokes-Einstein coefficients deviating up to 15% from unity. However, unlike the dilution effect found in viscosity (diffusivity), thermal conductivity remains dominated by that of the IL even to very high HFC loadings. The ramifications of the complex behavior in thermophysical properties on unit design are assessed in comparison to simple mixing rules commonly employed in process design.

To examine some of the molecular behavior leading to these often divergent behaviors, several spectroscopic and x-ray scattering techniques have been investigated and combined with molecular dynamics simulation results. A high-pressure x-ray scattering technique is utilized to investigate the molecular level interactions responsible for the observed behavior in transport properties. Small angle and wide angle X-ray scattering (SWAXS) results indicate a persistent ordered IL structure to elevated dissolved HFC compositions. High-pressure spectroscopic techniques including electrochemical impedance spectroscopy and UVvis spectroscopy are utilized to investigate the solution *ionicity* and *polarity*.

Isothermal Titration Calorimetry (ITC) as a Tool in Phase Transfer Studies

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When a calorimeter is used, the heat associated with a process is measured, and thus this experimental technique can be used to follow and quantitate the process under study.

Among the available calorimetric techniques, Isothermal Titration Calorimetry (ITC) is a widely used one, encompassing a wide range of applications. Being mostly known these days for the biological applications, (Biocalorimetry), it can indeed be used to follow and characterize many other processes.

In this talk, I will address the use of different ITC instruments to achieve various goals in phase transfer studies, broadly organized into TRANSFER OF SOLUTE between phases and PARTITION (partition of solutes to membranes (liposomes, lipid nanodiscs, vesicles).

Different approaches and experimental designs will be shown, as an introduction to a broad view of possibilities for this calorimetric technique.

Fig. 1. Different calorimeters available nowadays

Predicting the Viscosity of Liquid Mixtures

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In numerous industrial applications that involve the flow of fluids, knowledge of viscosity of mixtures is an essential pre-requisite for good design and optimal operations. Modern trends for viscosity prediction are moving away from empirically based methods to those that make use of a sound theoretical framework and are validated against primary experimental data. The present talk will focus on one such method, namely the extended hard-sphere (EHS) model [1,2].

The model is based on the postulate that the behavior of pure fluids is essentially conformal and that the reduced viscosity is a universal function of the reduced molar volume. In order to apply the EHS model to calculate the viscosity of mixtures, one either requires mixing rules or an estimate of the effective molecular mass. The latter relies on representing the viscosity of the multicomponent mixture by a viscosity of a single pseudo-component, which is characterized by an appropriate molecular weight. It is particularly suitable for predicting the mixtures encountered in industrial applications that have an ill-defined composition or consist of a very large number of species.

The predictive capability of the developed model will be demonstrated for the plethora of liquid mixtures in a wide range of temperature and pressure [3-6]. Namely, (i) mixtures containing alkane and aromatic molecules; (ii) synthetic crude oil; (iii) deep eutectic solvents and (iv) mixtures of esters relevant to biodiesel characterization. The results obtained demonstrate that the developed EHS model is capable of generating viscosities within 5-10% of the experimental values. The observed good agreement with experimental data indicates that the proposed approach offers a tangible way forward in developing the molecular based models for predicting the viscosity of industrially relevant liquid mixtures, of well-defined or ill-defined composition, over a required range of temperature and pressure.

References

[1] M.J. Assael, A.R.H. Goodwin, V. Vesovic, W.A. Wakeham (edts.), Experimental Thermodynamics Volume IX: Advances in Transport Properties of Fluids, The Royal Society of Chemistry, (2014).
[2] F. Ciota, J.P.M. Trusler, V. Vesovic, *Fluid Phase Equil.* **2014**, 363, 239.
[3] B. Nguyen, V. Vesovic, *Fluid Phase Equil.* **2019**, 487, 58.
[4] J.A.M.S.C. Malta, C. Calabrese, B. Nguyen, J.P.M. Trusler, V. Vesovic, *Fluid Phase Equil.* **2020**, 505, 112343.
[5] N.F. Gajardo-Parra, V.P. Cotroneo-Figueroa, P. Aravena, V. Vesovic, R.I. Canales, *J. Chem. Eng. Data* **2020**, 65, 5581.
[6] J. Jovanović, D. Majstorović, I. Milošević, N. Grozdanić, E. Živković, V. Vesovic, *J. Molec. Liq.* **2023**, 382, 121930.

Oral Presentation 1.2: Monday, September 9th, 16:30h - 16:50h

Multiphase parametrization of quasi-spherical Mie particles

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The Mie potential [1] has been postulated as a versatile semi-empirical function to model intermolecular forces and, by extension, the thermophysical properties of simple quasi-spherical molecules. Although the Mie potential has been successfully used for modeling molecules of industrial interest [2], the parameterization of the potential is an interesting question that Lennard-Jones [3] himself had when studying this potential. Depending on the type of data used during the parameterization, one can obtain significantly distinct molecular parameter sets. Single-phase and/or equilibrium fluid data are standard for this purpose; however, it is common to discard any data involving the solid state since most equations of state (EoSs) cannot describe this phase.

In a recent work [4], we have trained an artificial neural network-based EoS capable of continuously modeling the fluid-fluid and solid-fluid transition of a Mie particle (FE-ANN(s) EoS). In this contribution, we leverage this EoS to compare the merits of two parameterization strategies. The first utilizes only Vapor-Liquid Equilibria (VLE) data, while the second employs VLE, Solid-Liquid Equilibria (SLE), and Solid-Vapor Equilibria (SVE) data. The results of parametrizing three simple quasi-spherical molecules are shown in Fig. 1. For Argon, Fig. 1(a), both approaches lead to a similar predicted phase diagram. Conversely, for Methane, Fig. 1(b), and Tetrafluoromethane, Fig. 1(c), a region of the reference VLE data lies below the predicted triple point when the molecular parameters are estimated with only VLE data. This defect can be partially corrected for Methane by including SVE and SLE data in the parametrization. For Tetrafluoromethane, whilst the inclusion of the solid-phase data does fix this issue, this comes at the expense of accuracy in the predicted VLE and grossly overestimating the critical point. Ultimately, these limitations on the Mie potential are not noticed when regressing from only VLE data. They suggest that the Mie potential alone might not be suitable to describe quasi-spherical molecules when they exhibit more complex interactions.

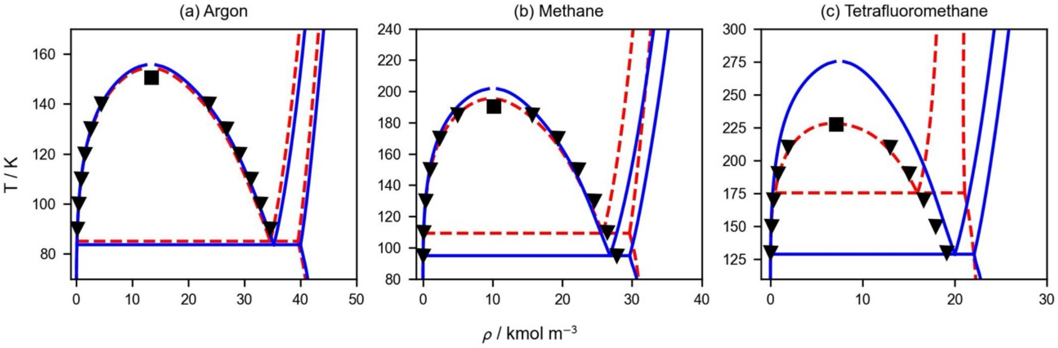

Fig. 1. Temperature-density diagram of (a) Argon, (b) Methane, and (c) Tetrafluoromethane. Lines: results from FE-ANN(s) EoS. Red dashed lines: molecular parameters from using VLE data only. Solid blue lines: parameters from using VLE, SLE, and SVE data. Symbols: data obtained from NIST TRC [5].

References

[1] J. Fischer, M. Wendland, *Fluid Phase Equilibria*, **2023**, 573, 113876.
[2] C. Herdes, T.S. Totton, E. A. Müller, *Fluid Phase Equilibria*, **2015**, 406, 91–100.
[3] J.E. Jones, *Proceedings of the Royal Society of London*, 1924, 106(738), 463–477.
[4] G. Chaparro, E. A. Müller, **2024** (in preparation)
[5] NIST/TRC Web Thermo Tables (WTT), **2011,** http://wtt-pro.nist.gov/ (Accessed March 11, 2024)

Oral Presentation 1.3: Monday, September 9th, 16:50h - 17:10h

Reliable prediction of the Vapor-Liquid-Liquid Equilibria in mixtures using the SAFT VR Mie EoS

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The determination of the vapor-liquid-liquid equilibria (VLLE) plays a relevant role in diverse industrial applications. The accurate and correct thermodynamic description of the VLLE is key information needed to design and improve some advanced separation unit operations, such as the Fischer-Tropsch synthesis and heterogeneous azeotropic distillation. The latter has shown a renewed interest in the dehydration of bio-alcohols to reach technically acceptable levels of water content (< 1%) for biofuel use.

However, the VLLE determination is challenging from an experimental and modeling perspective. The experimental determination of VLLE is complex due to the heterogeneous liquid-liquid phase in contact with the vapor. Fortunately, this problem is overcome by incorporating an ultrasonic homogenizer in the phase equilibria cell and using a recycle line for the vapor phase. This composed device has been used for us to explore alternative entrainers for the dehydration of bio-alcohols [1,2]. From a theoretical modeling view, the VLLE can be calculated from a multiphase flash algorithm, but it needs an appropriate initialization to avoid its failure to compute the whole VLLE range, especially when a ternary heterogeneous azeotrope is present. To overcome this problem, some authors have proposed alternative algorithms [3,4], which are complex to incorporate in the VLLE calculations, especially when a molecular-based equation of state is used.

This work aims to overcome this limitation by incorporating phase stability criteria under the multiphase flash algorithm. This strategy provides not only a route to detect all possible (one, two, and three) coexisting phases but also initial values for the VLLE calculation. This combined algorithm is illustrated with the SAFT VR Mie EoS and selected examples are given for mixtures where different heterogeneous azeotropy types are detected, as it is shown in Figures 1 and 2 for the water + CPME + propan-1-ol mixture.

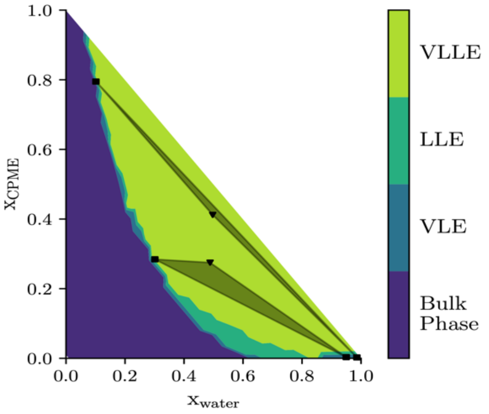

Fig. 1. Phase stability test results at 355 K and 101.3 kPa. Coloring refers to possible equilibria type. Dark triangles denote true VLLE phase composition.

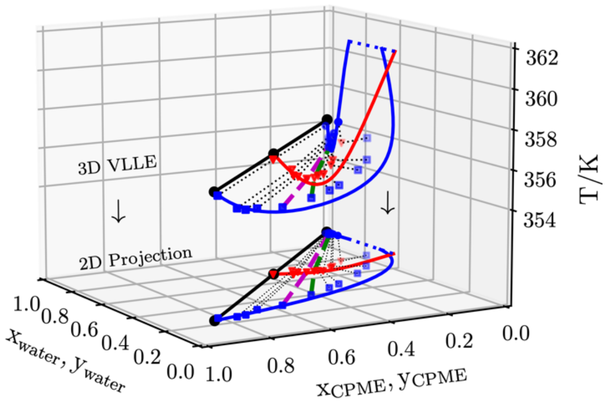

Fig. 2 VLLE in T-x^w-x^o-y projection at 101.3 kPa

References

[1] A. Mejía, M. Cartes, G. Chaparro, *Fluid Phase Equilib.*, **2020**, 523, 112768
[2] A. Mejía, M. Cartes, G. Chaparro, E. A. Müller, *J. Mol. Liq.*, **2024**, 397, 124087
[3] P. S. Reddy, K. Y. Rani, *Ind. Eng. Chem. Res.* **2012**, *51*, 10719−10730
[4] A. Wyczesany, *Ind. Eng. Chem. Res.* **2014**, *53*, 2509–2519

Coarse-grain computer simulation approach to unveil interactions between phospholipid membranes and drug nanocarriers

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One of the main challenges that researchers must face in theragnostic therapies is the efficiency of drug nanocarriers.[1] Interactions between drug nanocarriers and target cells are crucial, however many issues remain such as early drug releases and multi drug resistance. Unfortunately, nanotechnology is still a small portion in the pharmaceutical industry and only small companies and start-ups are the primary developers.[2] Computer simulations, with reliable force fields, became a valuable tool to explore this topic.[3] In this work, a coarse-grain molecular dynamics simulation (CG-MD) framework is used to investigate the interactions between biological phospholipid membranes and diverse nature antitumoral drugs-nanocarriers. The 1-palmitoyl-2-oleoyl-glycero-3-phosphocholine POPC + 1-palmitoyl-2-oleoyl POPG (4-POPC:1-POPG) (resembles tumoral cell walls) and the dipalmitoyl phosphatidylcholine (DPPC), related to the infection of adenocarcinoma human alveolar lung tissue cells, membranes were selected. Two antitumoral drugs were considered, Doxorubicin (DOX) and Gemcitabine (GEM) and the 5th generation of poly(amidoamine) dendrimer (G5 PAMAM) besides two nonionic Pluronic, P123 and F68, were chosen. CG-MD simulations were performed for each phospholipid membrane in aqueous solution in contact with the selected preloaded nanocarriers at two drug-loading capacities under physiological conditions. Fig. 1a-d shows the CG-MD simulation snapshots for the G5 dendrimer, P123, F68 and P123/F68 mixed micelles loaded with DOX and Fig. 1e-h with GEM. CG-MD simulations disclosed the role of coulombic forces and the nature of the systems in their drug loading/release capacities.

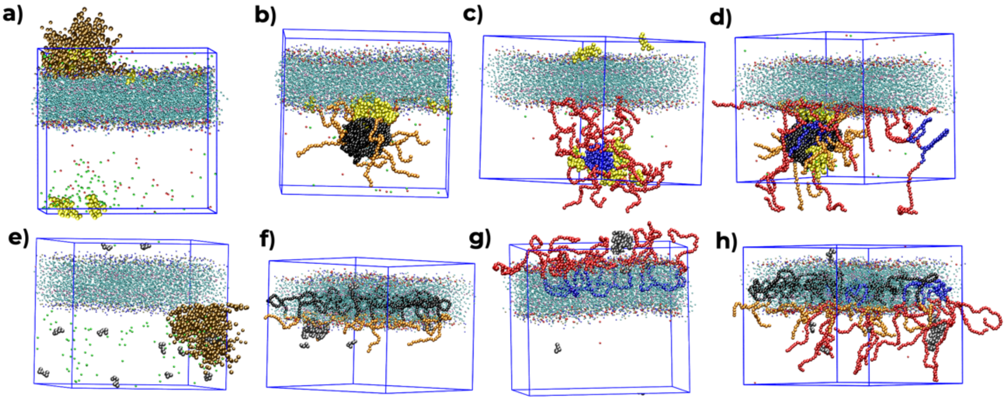

Fig. 1. MD-CG simulation snapshots for 4-POPC:1-POPG membrane (beads in cyan) with a) and e) G5 PAMAM dendrimer (ochre), b)and f) P123 micelle (PPO and PEO groups in black and orange, respectively), c) and g) F68 (PPO and PEO groups in blue and red, respectively) micelle and d) P123&F68 micelle, all of them loaded with DOX (yellow) in the top and GEM (grey) at the bottom. Water molecules were removed for clarity.

References

[1] R. Langer, *Nature Drug delivery and targeting* **1998**, *392*, 5–10.
[2] A. Hafner, J. Lovrić, G. P. Lakoš, I. Pepić, *Int. J. Nanomed Nanotherapeutics in the EU: an overview on current state and future directions* **2014**, *9(1)*, 1005–1023.
[3] G. Pérez-Sánchez, F. A. Vicente, N. G. Schaeffer, I. S. Cardoso, S. P. M. Ventura, M. Jorge, J. A. P. Coutinho, *J. Phys. Chem. B Unravelling the Interactions between Surface-Active Ionic Liquids and Triblock Copolymers for the Design of Thermal Responsive Systems* **2020**, *124*, 7046–7058.

Physical-constant Fluid Equations-of-State Using Boyle and Rigidity-Symmetry Lines: Water-Steam Example

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Modern equations-of-state require up to 100 or more fitted parameters to reproduce experimental p-V-T data to within their measurement precision [1]. Following the discovery [2] of a coexisting critical density hiatus and a supercritical mesophase defined by percolation transitions, the state functions density $\rho(p,T)$, and Gibbs energy $G(p,T)$, of pure fluids are seen to exhibit a symmetry characterised by the rigidity, $\omega = (dp/d\rho)$ along isotherms from triple point (T_t) to Boyle temperature (T_B), on either side of the supercritical mesophase for $T > T_c$ and the coexistence range $T_t < T < T_c$. Along any isotherm, the lower virial coefficients that describe the gas region also describe the liquid range in an expansion about a rigidity symmetry line with experimental precision for simple fluids, e.g. argon [3].

Here, we report an investigation into the cluster physics of steam and water over the range of experimental data from 273K to the Boyle temperature (T_B), which we re-determine to be 1598±15 K and pressures up to 1000 MPa. Cluster expansions in powers of density relate steam virial coefficients to a supercritical liquid-phase rigidity symmetry (RS) line, $\omega_{RS} = (dp/d\rho)_T = RT$ to gas phase virial coefficients. We show that it is continuous in all derivatives, and linear within stable fluid phase of steam and water. Simple relationships arise from the observation that the higher virial coefficients (b_n, $n \geq 4$) cancel due to cluster equilibria, or are negligible ($0 < T < T_B$) in the steam regions. Our zero-fit symmetric equation-of-state for the isotherm shown (Figure 1), for example, is as accurate as the data from the Wagner-Pruss equation-of-state [1] for water with its countless fitted parameters.
The RS line, $\omega(T) = RT$, defines a water/ice-density ground-state physical constant that relates to the Boyle work line ($w_{BW} = (p/\rho)_T = RT$) via the lower virial coefficients. Given the gas-liquid rigidity symmetry, all thermodynamic state functions below T_B are obtainable from lower $b_n(T)$ with $n \leq 4$.

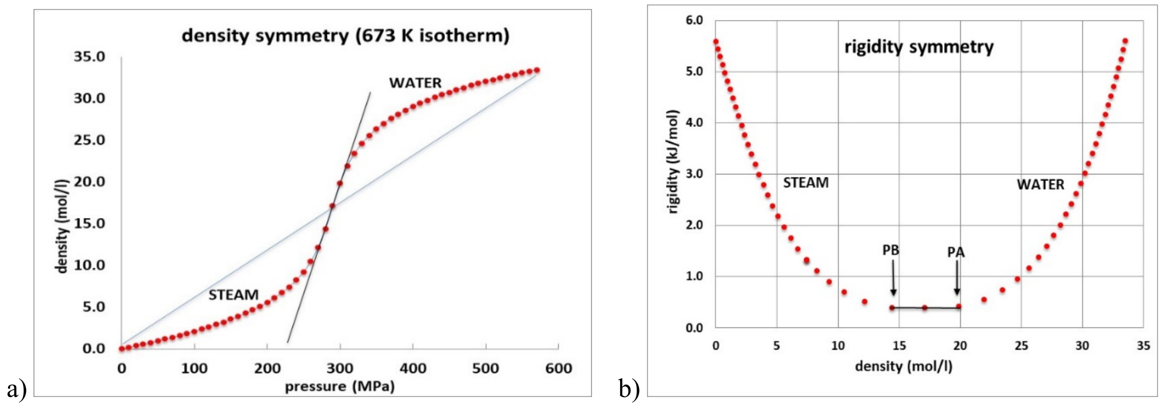

Fig. 1. A supercritical isotherm of steam and water 673 K (T_c = 647K): a) showing the axis of density symmetry crossing at the rigidity symmetry point $(dp/d\rho)_T = RT$ at 32.5 mol/l: b) the rigidity showing the mesophase by the percolation of bonded gas clusters of (PB) and by empty available volume pockets in the liquid state (PA).

References

[1] *Thermophysical Properties of Fluid Systems* in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, NIST Gaithersburg USA https://doi.org/10.18434/T4D303, (retrieved May 2024).
[2] I. Khmelinskii and L. V. Woodcock, Supercritical gaseous and liquid states: a review of experimental results, Entropy, 22, 437-463 (2020) https://doi.org/10.3390/e22040437
[3] L. V. Woodcock, *J. Mod. Phys. Rigidity Symmetry Line for Thermodynamic Fluid Equations of State,* 2024,15, 613-633. https://doi.org/10.4236/jmp.2024.155029

Characterizing Potassium-Based Conductive Hydrogels through Experimental and Computational Analysis

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In pursuit of achieving the energy transition towards lower carbon footprint sources, scientific efforts are focused on developing more durable, flexible, and efficient energy storage devices [1-4]. Currently, the predominant component in electric batteries and capacitors is lithium metal; however, its limited availability and accessibility have induced the search for possible substitutes [5]. This study investigates the physicochemical properties of novel potassium-based hydrogels, to evaluate their potential suitability as electrolytes. Experimental measurements included electrical conductivity and self-diffusion coefficients, which were conducted using Nuclear Magnetic Resonance (NMR). Rheology tests were performed to assess the stability of the hydrogels, with a particular emphasis on the influence of alkyl chain length. Additionally, we used Molecular Dynamics (MD) Simulations to deepen our comprehension of their molecular arrangement. The findings highlighted the role of system composition, particularly the proportion between the acid and salt molecules, in determining the stability and characteristics of the hydrogels. Overall, this study provides insights that may support the development of novel hydrogels.

References

[1] Z. F. Wang et al., *Adv. Funct. Mater.,* **2018**, *28*, 1804560.
[2] H. Wang, W. Zhao, *Next Materials*, **2023**, *1*, 100049.
[3] Y. Chen et al., *Journal of Energy Storage*, **2023**, *73*, 109023.
[4] D. Meena et al., *Journal of Energy Storage*, **2023**, *72*, 109323.
[5] M. Grohol, C. Veeh, European Comission, *Study on the critical raw materials for the EU 2023 – Final report*, Publications Office of the European Union, Brussels (2023).

Oral Presentation 3.1: Tuesday, September 10th, 11:50h - 12:10h

Dielectric Constant Tensor of Electrolyte Solutions Confined by Quartz Crystals via Molecular Dynamics Simulations

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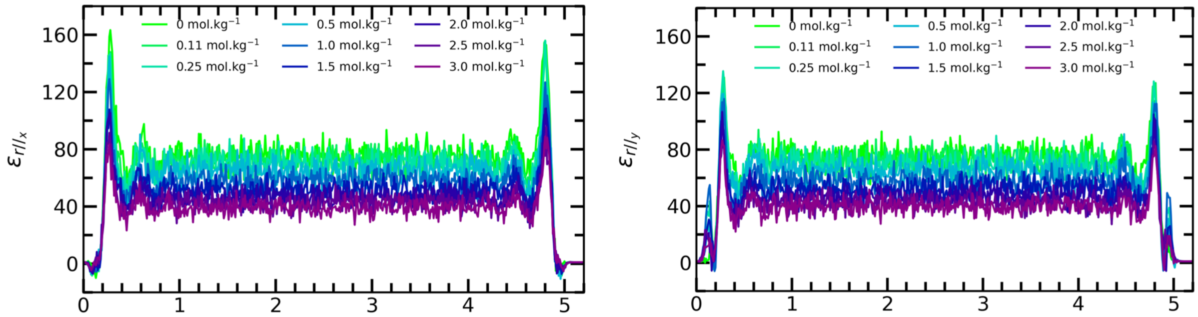
Macroscopically, the effect of a solvent on fluid electrostatics can be quantified by its dielectric constant, which represents its ability to screen charges and attenuate external electric fields. In homogeneous media, the dielectric constant is a scalar. Close to interfaces, however, it is a tensor. Our work aims at studying the dielectric behavior of NaCl aqueous solutions under confinement via equilibrium molecular dynamics simulations. Quartz minerals are chosen to represent the confined medium. By deprotonating terminal hydroxyls, a partial negative charge is embedded at the surface to represent the effect of salinity and pH. The local dielectric constant tensor is determined through the fluctuation-dissipation theorem, which relates the permittivity to fluctuations of the total polarization density [1]. At the center of the pore, the dielectric saturation effect is observed in the parallel components of the dielectric constant tensor. Electrolytes reduce the solution permittivity because the orientation of water dipoles is partially restricted within the hydration spheres to shield ions. The same behavior is not observed in the perpendicular direction. In fact, the perpendicular dielectric constant is about an order of magnitude lower than the parallel and bulk dielectric constant, and it slightly increases with salinity. The presence of ions disturbs the water-water and water-quartz interactions, in such a way that the mobility of water in the direction of the confinement increases. Adjacent to the surface, there is an anisotropy in the dielectric constant parallel components (Fig. 1). Due to the mineral surface topology, water molecules present more rotational mobility in the *y* parallel direction. By further increasing salinity, the dipoles of water tend to be parallel oriented in the *y* direction, resulting in less vibration of molecules around this direction, which vanishes the first dielectric constant peak observed before. With our work, we hope to expand the knowledge of the electrical double layer, especially the permittivity under confinement, which represents an important property for the development of materials such as capacitors and batteries.



(A) *(B)*

Fig. 1. Dielectric constant of NaCl solutions confined by quartz minerals: parallel components in the *(A) x* and *(B) y* directions.

References

[1] D. J. Bonthuis, S. Gekle, R. R. Netz, *Langmuir*, **2012**, *28*, 7679-7694.

Oral Presentation 3.2: Tuesday, September 10th, 12:10h - 12:30h

Virial Equation of State Using Volume-Dependent Coefficient

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The conventional development of the virial equation of state (VEOS) invokes the thermodynamic limit, and consequently the virial coefficients, which are integrals involving only a few molecules (typically fewer than ten in practice) are independent of volume. On the one hand, at conditions where the series is converged this allows the VEOS to describe behavior in the thermodynamic limit, while treating just a few molecules. On the other hand, the absence of volume effects renders the VEOS unable to describe, in principle, condensation and condensed phases. Attempts exist in the literature to examine this issue, but they are largely based on conjectures about the volume dependence of the coefficients. In this presentation we address the question with correct volume-dependent coefficients that we have computed for some simple models.

We discuss how the VEOS is modified when applied using volume-dependent coefficients. We first examine the development when expressed as a series in the activity, where convergence is poor even in the absence of a phase transition. Considering the one-dimensional hard-rod model, we examine steps in the development of the activity VEOS that introduce inaccuracy that leads it to form a divergent series. We discuss the role of volume dependence of the virial coefficients, and present expressions and calculations for volume-dependent coefficients for the model, up to order n = 200 [1]. We examine alternative methods for computing properties from the activity-series coefficients. We then turn to the Lennard-Jones model in three dimensions, and compute values of volume-dependent coefficients and apply them to estimate the equation of state. We examine the series behavior in comparison to small-system simulations to ascertain the source of observed inaccuracies, considering also complications resulting from propagation of stochastic error in the computed coefficients. Finally, we consider ways to approximate higher-order coefficients, and their volume dependence, aiming to achieve the capability to calculate behavior in the thermodynamic limit.

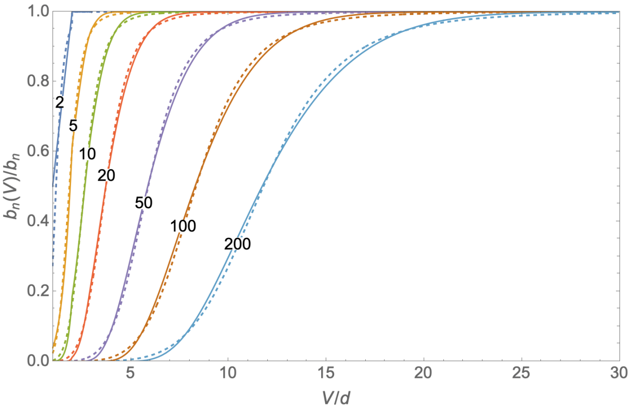

Fig. 1. Exact volume-dependent activity-series virial coefficients for the hard-rod model in 1-D, reduced by infinite-system values. Numbers indicate the order (n) of the coefficient. Abscissa is system volume (length).

References

[1] D.A. Kofke, *J. Phys. Chem. B* **2023**, *127*, 3690-3700.

Enthalpy and Entropy of Mixing of Hydrocarbon Mixtures: Insights from Molecular Simulations

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The entropy of mixing plays a central role in the thermodynamic description of mixtures. This property is essential to understand the entropic contribution to the mixture, and is embedded in virtually all thermodynamic models. Particular interest exists for highly asymmetric mixtures, for which a significant difference in molecular sizes is present, for example: binary mixtures between small and large alkanes. Recently, some publications put into discussion the previously established idea that cubic equations of state (EoS) necessarily fail in predicting the type of non-ideality in nearly athermal mixtures like the ones formed by *n*-alkanes [1-3]. In particular, it was shown that a cubic EoS like RKPR, with a third parameter in a way analogous to the number of segments in SAFT models, not only predicts the right trends for infinite dilution activity coefficients in asymmetric *n*-alkane mixtures, but it also performs quantitatively equal or better than PC-SAFT, when using null interaction parameters [1, 3]. Nevertheless, a good description of the excess Gibbs energy does not necessarily translate to the decomposition into S^E and H^E, and it is well known that certain compensation of errors may take place in the prediction of some properties by cubic EoS's. In addition, based on experimental data, it remains unclear how the G^E curves distribute into these components. Therefore, an insight from molecular simulation would be highly valuable in these analyses. Computing the entropy of mixing from equations of state (EoS), regardless of the molecular sizes, is fairly straightforward. Nevertheless, from a molecular simulation standpoint, this calculation is quite challenging and not fully described in the open literature. In this work, we propose a robust methodology to compute the entropy of mixing for polyatomic molecules from molecular dynamics simulations. Using molecular dynamics (MD) simulations and the two-phase thermodynamic (2PT) method, we investigate *n*-alkanes entropy of mixing and compare it to traditional cubic EoS, such as Peng-Robinson and also to the RKPR equation of state. The approach is based on an effective decomposition of translational, rotational, and internal degrees components of the entropy, providing detailed insights into molecular level interactions captured by MD, and improving the predictive calculations for the thermodynamic behaviour of large molecules mixtures. By comparing the entropy contributions from both methodologies, we aim to elucidate the underlying mechanisms driving non-ideality in mixtures. This hybrid methodology offers a bridge for the gap between macroscopic models (EoS) and microscopic behaviour (MD), resulting in a powerful tool for studying entropy in multi-component systems and a robust framework for future thermodynamic predictions.

References

[1] N.G. Tassin, S.B. Rodríguez Reartes, M. Cismondi, Activity coefficients in nearly athermal mixtures predicted from equations of state: don't blame the cubic when it is the lack of a third parameter!, Fluid Ph. Equilib. 522 (2020) 112753, https://doi. org/10.1016/j.fluid.2020.112753.

[2] J.N. Jaubert, R. Privat, SAFT and cubic EoS: type of deviation from ideality naturally predicted in the absence of BIPs. application to the modelling of athermal mixtures, Fluid Phase Equilib. 533 (2021), https://doi.org/10.1016/j. fluid.2020.112924.

[3] M.J. Quinzio, S.B. Rodriguez-Reartes, M. Cismondi-Duarte, Phase behavior and type of non-ideality in n-alkanes mixtures predicted from equations of state: The role of a third parameter, Fluid Phase Equilib. 577 (2024) 113963. https://doi.org/10.1016/j.fluid.2023.113963.

Oral Presentation 4.1: Tuesday, September 10th, 15:10h - 15:30h

Nucleation and growth of mixed carbon dioxide and propane hydrates through molecular dynamics simulations

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Gas hydrates are crystalline structures composed of water and light gases, in which cavities formed by hydrogen bonds of water molecules are occupied by guest gas molecules. The most common structures, types I and II, are formed respectively by the presence of small and large guest molecules. Molecular dynamics simulations constitute a powerful tool to study the nucleation mechanisms of these systems, as it is unfeasible to experimentally observe this process, which occurs on scales of nanometers and nanoseconds. Hydrate nucleation simulations were performed for the water/CO_2/C_3H_8 system with GROMACS. Three gas composition conditions were analyzed, with ratios of 1:1, 1:2 and 2:1 (CO_2:C_3H_8). Each system had a total number of 432 gas molecules and 3672 water molecules. The TIP4P/Ice, OPLS/UA, and EPM2 models were used to describe water, propane, and carbon dioxide, respectively. To ensure a statistical analysis of the results, 10 production simulations (from 3 to 8 μs) were performed for each composition. Pressures between 1000 and 1500 bar were applied to the systems so that the driving force was sufficient to nucleate the hydrate on the microsecond scale.

Hydrate nucleation was observed in 100%, 70% and 40% of the 1:1, 2:1 and 1:2 simulations, respectively. The LCC OP code was used to detect each type of cage and the clusters formed in simulations [1,2]. Post processing codes were developed to extract information on cage connectivity, domains, and transitions. An extensive analysis of the simulations was carried out through the evaluation of the number, type, and occupancy of the cavities. The first stable clusters and their compositions were determined. Domains only up to 17 cages of Structures I and II were observed. Irregular cages with squared faces prevailed on the clusters instead of the characteristic large cages of sI and sII. Although no long range ordered clusters were detected, the analyzes of non-nucleated simulations, pre nucleation periods and the initial clusters formed provided relevant information on how propane and CO2 interact to form gas hydrates.

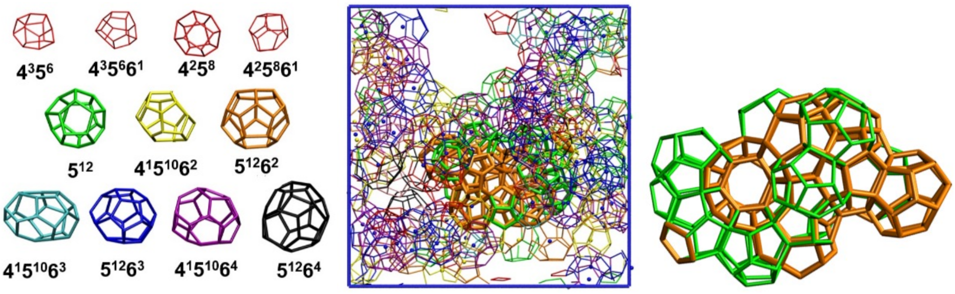

Fig. 1. Cages detected in the simulations through the LCC OP code [1,2]; example of a nucleated simulation box; largest sI domain detected in all simulations.

References

[1] Y. Chen, C. Chen, A. K. Sum, *J. Phys. Chem. B,* **2020**, *124*, 4661-1671.
[2] Y. Chen, C. Chen, A. K. Sum, *Cryst. Growth Des.,* **2021**, *21*, 960-973.

Oral Presentation 4.2: Tuesday, September 10th, 15:30h - 15:50h

Addressing Hydrogen Bond Cooperativity in Modern Quasi-Chemical Methods

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The increasing interest in modern quasi-chemical methods, such as COSMO-RS and COSMO-SAC, seems to be driven by their robust ability to predict the thermodynamic properties of complex mixtures. Quantum chemical calculations are combined with a statistical thermodynamic treatment to predict various types of phase equilibria—such as vapor-liquid, liquid-liquid, and solid-liquid—usually achieving semi-quantitative quality. This category of models effectively explains the behavior of different types of mixtures, including polar, apolar, and associating compounds, which exhibit positive, negative, or s-shaped excess enthalpy and/or entropy [1]. However, these models are based on pairwise (two-body) interactions and cannot directly handle hydrogen bond (HB) cooperativity [2], potentially limiting their accuracy in systems where such interactions are significant. A notable example is ether-water mixtures, where COSMO-based models struggle to predict the s-shaped excess enthalpy and pronounced negative excess entropy at room temperature. Moreover, they tend to miss the experimental observations in both liquid-liquid and vapor-liquid equilibria for such systems. This issue could be addressed by molecular clusters [3] or by devloping a second-order theory [4] for HB cooperativity. In this work, a more practical approach is proposed: we assume that the water-ether HB energy has an additional *cooperativity* term that is composition-dependent. A special treatment to keep the model Gibbs-Duhem consistent is necessary and a simple composition dependency of the form $C\,\theta_w^p$ is initially proposed, where C and p are constants to be adjusted for a particular HB type, and θ_w is the water area fraction. Fig. 1 shows the results for vapor-liquid and liquid-liquid equilibria for the tetrahydrofuran-water mixture, comparing a recent COSMO-SAC parametrization available in JCOSMO [5] with the one proposed in this work. A single set of parameters was enough to improve results for all ether-water systems tested.

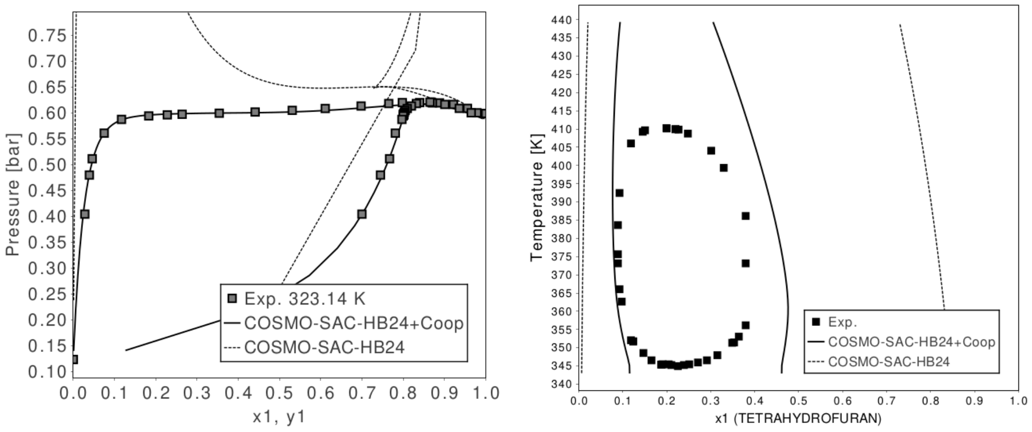

Fig. 1. Vapor-liquid(left) and liquid-liquid (right) equilibria for tetrahydrofuran/water, calculated with a recent COSMO-SAC parametrization with and without the proposed cooperativity effect.

References

[1] Soares R. de P, Staudt P. B., *Fluid Phase Equilibria*, **2024**, *583*, 114113.
[2] Urbic, T.; Dill, K. A., *Journal of Physical Chemistry B*, **2021**, *125*, 1611-1617.
[3] Andersson, M. P., Journal of Molecular Liquids, **2023**, *383*, 122169.
[4] Klamt, A., *Journal of Physical Chemistry A*, **2016**, *120*, 2049-2056.
[5] JCOSMO, *available at* https://ufrgs.br/lvpp, **2024**

yaeos: Yet Another Equation of State Library

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An essential aspect of modelling fluid mixtures using equations of state involves obtaining the interaction parameters of the mixture's components through experimental data fitting procedures. Phase equilibrium experimental data serve as the primary source for fitting parameters, typically accomplished through single saturation point or flash calculations.

While this can be a straightforward and generally useful approach to simple mixtures, more complex mixtures can present algorithmic challenges, particularly when encountering non-converging saturation points or trivial solutions. A more robust approach is based on the calculation of the entire phase equilibrium diagram for specified conditions [1, 2].

While there has been a considerable emergence of open-source libraries capable of performing phase equilibrium calculations with a wide range of models, the implementation of the mentioned methods and a friendly framework for parameter optimization is still absent and depends on the user to be implemented.

In this work, we present a thermodynamic library capable of doing EOS-based phase equilibria and thermodynamic properties calculations for multicomponent mixtures, like saturation points and flash calculations. It also provides the tracing of complex phase diagrams with robust mathematical methods.

While at the moment it only includes cubic EoS like Peng-Robinson, Soave-Redlich-Kwong and RKPR, as well as a single NRTL excess Gibbs energy model, it also presents a simple framework to include new models, which can be done with analytical derivatives provided by the user or through automatic differentiation (either by operator overloading or source-to-source translation).

Fortran excels as a programming language in the scientific world thanks to its high numerical performance and simplicity compared to other more complex languages. In recent years there has been a rise in the tooling around it, with the most notorious addition of the package manager fpm, which improves the user experience of Fortran programmers. It makes it easier to build your Fortran program or library, run the executables, tests, and examples, and distribute it as a dependency on other Fortran projects. *yaeos* is being distributed as a fpm-compatible package and its source code, with some examples and instructions. It is available on the GitHub platform (https://github.com/ipqa-research/yaeos).

References

[1] Cismondi, Martín, and Michael L. Michelsen. "Global Phase Equilibrium Calculations: Critical Lines, Critical End Points and Liquid–Liquid–Vapour Equilibrium in Binary Mixtures." *The Journal of Supercritical Fluids* 39, no. 3 (January 2007): 287–95. https://doi.org/10.1016/j.supflu.2006.03.011.

[2] Deiters, Ulrich K., and Ian H. Bell. "Calculation of Phase Envelopes of Fluid Mixtures through Parametric Marching." AIChE Journal 65, no. 11 (November 2019). https://doi.org/10.1002/aic.16730.

The impact of the nonrandomness factor on biomolecule partitioning in green ATPS

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Aqueous Two-Phase Systems (ATPS), also known as Aqueous Biphasic Systems (ABS), provide biocompatible and eco-friendly extractive media for the recovery of biomolecules such as vitamins (*e.g.*, cyanocobalamin and folic acid) and antioxidants (*e.g.*, catechin and chlorogenic acid), which constitute vital value-added products for pharmaceuticals and cosmetics [1,2]. Moreover, ATPS composed of green solvents such as ethyl lactate allow to reduce the environmental impact of the extractive processes while ensuring non-toxic and biodegradable media [3].

The nonrandomness factor (α) is a parameter which quantifies the randomness of spatial orientation of molecules, being normally defined or fitted between 0.20 and 0.47 [1]. Nevertheless, in this work, the nonrandomness factors of the studied biomolecules were determined using a novel methodology based on computational chemistry [1], namely Density Functional Theory (DFT), providing component-specific parameters and taking advantage of the well-known relationship between this parameter and polarity. More precisely, this *ab initio* method was used with a combination of the hybrid functional B3LYP [4,5] with the basis set 6-311++G**(d) [6], applying the Polarizable Continuum Model (PCM), which simulates the solute cavity via a set of overlapping spheres [1].

Being solute polarity a crucial property in liquid-liquid extraction, in this work, the nonrandomness factors (α) were used to ease the interpretation of the performance indicators (partition coefficients and extraction efficiencies) obtained in the recovery of biomolecules (such as cyanocobalamin and chlorogenic acid) in green ATPS based on ethyl lactate, combining experimentation and simulation.

References

[1] P. Velho, L. R. Barroca, E. A. Macedo, *J. Chem. Eng. Data* **2023** (in press).
[2] C. S. Rebelo, P. Velho, E. A. Macedo, *Ind. Eng. Chem. Res.* **2024**, *63,* 2885-2894.
[3] P. Velho, E. A. Macedo, *J. Chem. Eng. Data* **2023**, *68*, 2385-2397.
[4] A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648-5652
[5] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[6] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77,* 3654-3665.

Oral Presentation 5.2: Wednesday, September 11th, 10:00h - 10:20h

New insights into the molecular interactions governing PEG/PPG aqueous two-phase system formation

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Aqueous two-phase systems (ATPS), also known as aqueous biphasic systems (ABS), are mixtures that can be used in liquid–liquid extraction (LLE) processes, where at least two water-soluble compounds form two immiscible aqueous phases when their concentrations exceed certain levels defined by a binodal curve [1]. Since their discovery, polymer/polymer systems have been extensively studied for their capability to separate, extract and purify biomolecules and other valuable compounds [2, 3]. However, the understanding of molecular interactions that control phase separation in polymer/polymer aqueous two-phase systems (ATPS) has been a subject of debate up to this day. In light of this, we investigated the molecular interactions occurring in ternary mixtures composed of polyethylene glycol (PEG600), polypropylene glycol (PPG400) and water. The ternary phase diagram was plotted at two temperatures (298 K and 323 K), revealing a transition from a type 0 to a type I diagram. Molecular dynamics (MD) simulations were performed to elucidate the polymer–polymer and polymer–water interactions occurring at different temperatures and water concentrations. COnductor-like Screening Model for Realistic Solvents (COSMO-RS) was used to assess the thermodynamic properties of the polymer–water binary mixtures and their correlation with ATPS formation. The MD simulations clearly demonstrate the effect of segregation/separation with increasing water content and temperature, highlighting a significant reduction in PPG–water interactions compared to PEG–water counterparts. Polymer–water interactions were identified as those controlling the phase separation mechanism, and the thermodynamic properties determined with COSMO-RS for the polymer–water binary systems further support this view.

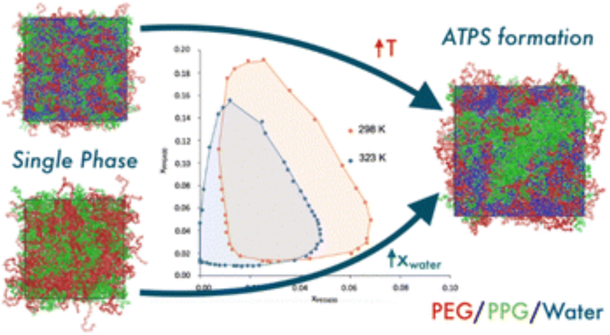

Figure 1. *Snapshots from MD simulations showing the transition from single phase mixtures up to biphasic mixtures by the increase in temperature and water content, and the phase diagrams of the PEG/PPG ATPS for 298K and 323K.*

Acknowledgements

CERES is supported by the Fundação para a Ciência e a Tecnologia (FCT) through the projects UIDB/ EQU/00102/2020 and UIDP/EQU/00102/2020. This work was partly developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). J.F.B. Pereira and A. M. S. Jorge acknowledge FCT for funding the project DRI/India/0044/2020 (DOI: 10.54499/DRI/India/0044/2020).

References

[1] J. F. B. Pereira and J. A. P. Coutinho, Aqueous Two-Phase Systems, in Liquid-Phase Extraction, Elsevier, 2020, pp. 157–182, https://doi.org/10.1016/B978-0-12-816911-7.00005-0

[2] J. A. Asenjo and B. A. Andrews, J. Chromatogr. A, 2011, 1218, 8826 —8835, https://doi.org/10.1016/j.chroma.2011.06.051

[3] A. M. Ferreira, H. Passos , A. Okafuji , A. P. M. Tavares , H. Ohno , M. G. Freire and J. A. P. Coutinho , Green Chem., 2018, 20 , 1218 —1223, https://doi.org/10.1039/C7GC03880A

PEG/sodium citrate ATPS: phase diagrams & fish protein partitioning

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Aqueous Two-Phase Systems (ATPS) have been investigated for about half a century as mild biphasic systems for extraction processes in biotechnology and wet metallurgy. Polymer/polymer and polymer/salt are the conventional formulations, with polyethylene glycols (PEG) being the most used polymer. Inorganic salts such as phosphates and sulphates are the most common, but in recent years organic salts (such as citrates, tartrates, oxalates, etc) have been investigated due to concerns in high concentration inorganic salt disposal [1-3]. Also in the last 20 years, ionic liquids have introduced new salts into the formulation, opening for salt/salt ATPS. Alternative ATPS with organic solvents, carbohydrates and other chemicals have also raised academic interest [4-6].

The characterization of an ATPS is based on the phase diagram together with physical properties of interest for the extraction process such as density, viscosity or interfacial tension. For the application to extraction processes, it is necessary to obtain the distribution of the solutes to be separated among the equilibrium phases. In biotechnological applications, solute concentration is most often low and thus partition coefficients are used. In this work we have measured the complete liquid-liquid phase envelope of PEG/sodium citrate ATPS, with PEG molecular weights of 6, 10 and 20 kDa. While the common practice in the literature is to obtain a few tie-lines of the ATPS, in general close to the plait point, here the complete liquid-liquid region is covered, up to the limit of phase-forming component precipitation (in these systems, salt precipitation). Moreover, rigorous determination of the tie-lines was carried out using physical properties of the equilibrium phases (density and refractive index). The complete phase diagram of ATPS (with all solid and liquid phases) has been scarcely determined because it is time-consuming and the difficulties of solid phase analysis. Besides, knowledge of the solid phases is not necessary for extraction processes (but important for thermodynamic modelling) [7]. Nevertheless, characterization of the complete liquid-liquid region is never carried out in ATPS, despite it is the standard practice in all other biphasic systems. Knowledge of the complete liquid-liquid phase envelope is important for extraction processes since it indicates the composition limits that can be used for extraction.

The ATPS investigated have been tested for recovery of fish proteins from fishmeal. Total protein partition coefficients were measured in the selected ATPS, using the BCA method to quantify the protein concentration in both ATPS equilibrium phases. For each ATPS and tie-line investigated, different protein concentrations were tested to ensure that partitioning was independent of protein concentration, a proof of infinite dilution and that true partition coefficients are obtained. The results obtained show the preference of fish proteins for the PEG-rich phase, where they can be concentrated.

References

[1] B.Y. Zaslavsky, *Aqueous Two-phase Partitioning: Physical Chemistry and Bioanalytical Applications*, CRC Press, (1994).
[2] R. Hatti-Kaul, *Aqueous Two-phase Systems: Methods and Protocols*, Springer Science & Business Media, (2000).
[3] J.A. Asenjo, B.A. Andrews, *J. Chromatogr. A* **2011**, *1218*, 8826-8835.
[4] M.G. Freire, A.F.M. Claudio, J.M. Araujo, J.A. Coutinho, I.M. Marrucho, J.N.C. Lopes, L.P.N. Rebelo, Chem. Soc. Rev. **2012,** *41*, 4966-4995.
[5] M.G. Freire, J.F. Pereira, M. Francisco, H. Rodríguez, L.P.N. Rebelo, R.D. Rogers, J.A. Coutinho, *Chem. Eur J.* **2012**, *18*, 1831-1839.
[6] M.G. Freire, *Ionic-Liquid-Based Aqueous Biphasic Systems: Fundamentals and Applications*, Springer, Berlin Heidelberg (2016).
[7] M. González-Amado, O. Rodríguez, A. Soto, P. Carbonell-Hermida, M.M. Olaya, A. Marcilla, *Ind. Eng. Chem. Res.* **2020**, *59*, 6318−6328.

Thermodynamic Insights into Thiocyanate-Enhanced Aqueous Biphasic Systems for Redox Flow Batteries

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In the quest for sustainable technologies suitable for large-scale energy storage, redox flow batteries (RFB) have emerged as particularly promising for extensive applications. Membrane-free systems offer the potential for reduced resistance and costs in comparison to traditional battery technologies. Yet, achieving an equilibrium in the thermodynamic balance of species is critical to minimize cross-contamination and self-discharge issues. To this end, most of the research has concentrated on modifying the redox-active species, with only a limited exploration of electrochemical additives. Thyocyanate has been recognized as an effective electrolyte additive in various electrochemical energy storage devices such as capacitors and solar cells due to its ability to enhance stable performance. Thiocyanate ($[SCN]^-$) ions have been recognized for their role in aqueous battery applications as effective low-viscosity stabilizers, contributing to enhanced ionic conductivity [1, 2]. This study was dedicated to identify aqueous biphasic systems (ABS) using chloride-based ionic liquids (ILs), ammonium sulphate salt and incorporating thiocyanate anion able to improve the partition of methyl viologen (MV) and 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) as redox pairs. Employing the Conductor-like Screening Model for Real Solvents (COSMO-RS) [3], a thorough screening of ILs was undertaken, with the optimal systems subsequently assessed through experimental evaluation. Mixture points were carefully selected based on their ABS binodal curves at room temperature. COSMO-RS calculations showed the quaternary ammonium and phosphonium ILs to be the most promising for the partition of TEMPO and MV in the ABS containing $[SCN]^-$. The experimental results showed that the presence of a low concentration of $[SCN]^-$can enhance MV/TEMPO selectivity, whereas a high concentration tends to reduce it. Moreover, the introduction of $[SCN]^-$predominantly resulted in its accumulation in the IL-rich upper phase and the subsequent displacement of water to the lower phase. Additionally, all systems incorporating $[SCN]^-$exhibited upper phases with increased viscosity and decreased density relative to their counterparts devoid of $[SCN]^-$. In summary, this work shows the incorporation of $[SCN]^-$stabilizing agent in the IL-rich phase can also improve the partition of the redox molecules.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC). This work has received funding from the European Innovation Council (EIC) under grant agreement 101046742. The EIC receives support from the European Union’s Horizon Europe research and innovation programme.

References

[1] Suyama, H., Y. Hirose, H. Nakayama, et al., “Improvement of Discharge Characteristic of Primary Al-Air Battery Anode By Sodium Thiocyanate Electrolyte Additive”, ECS Meeting Abstracts MA2016-02(5), 2016, pp. 878–878.
[2] Gorska, B., P. Bujewska, and K. Fic, “Thiocyanates as attractive redox-active electrolytes for high-energy and environmentally-friendly electrochemical capacitors”, Physical Chemistry Chemical Physics 19(11), 2017, pp. 7923–7935.
[3] Wojeicchowski, J.P., C.M.S.S. Neves, P. Navalpotro, R. Rubio-Presa, E. Ventosa, R. Marcilla, J.A.P. Coutinho, *Journal of Energy Storage*, **2023**, *72,* 108584.

Fluid phase equilibria modelling to enhance downstream processes in the pharmaceutical industry

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The downstream process is crucial in the pharmaceutical industry as it encompasses quench, purification and isolation of the desired drug substance or synthetic intermediates. Overall, it ensures product quality, regulatory compliance, scalability, cost effectiveness, sustainability, among other features [1]. Given its criticality and extension, it is crucial to optimize process development and its scale-up. By accurately modelling equilibrium behaviour of various phases involved in downstream operations such as extractions, distillations, and crystallizations, one can optimize conditions for maximum yield, purity and cost. This model-oriented approach has a positive impact in streamlining the downstream process while reducing the need for experimental trial and error and, ultimately, accelerates new drugs time to market [2].

In this work it is presented how phase equilibrium modelling interplays in conceiving and developing downstream processes. Several case-studies will be presented, for instance, a distillation to remove residual reagent upon reaction completion. In this example, two different approaches were applied with the final aim of developing 1-bromo-2-chloroethane azeotropic distillation using n-heptane. First, vapor-liquid equilibrium (VLE) was predicted using Non-Random Two-Liquid (NRTL) model and COSMO-RS and, in parallel, modified UNIFAC was also used for the same purpose. Both strategies were compared against experimental data to validate predictions, demonstrating comparable results. *Fig. 1* portrays the comparison of modified UNIFAC predicted and experimental liquid vapour equilibrium (P-x-y). Based on this data, it was possible to optimize distillation conditions, conceiving an optimized process based on waste generation and time-at-scale criteria.

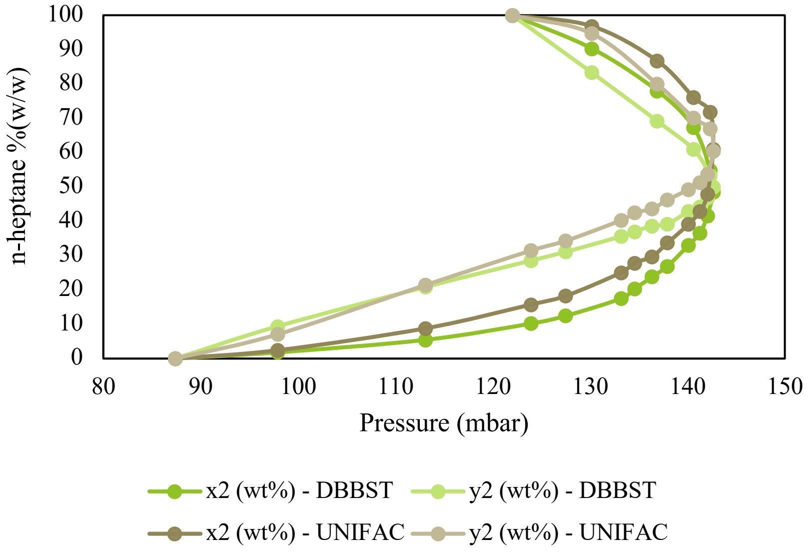

Fig. 1. Experimental data (Dortmund Data Bank) comparison with UNIFAC prediction of P-x-y equilibrium.

References

[1] Guo, C., Ye, W., Kauffman, J., & Doub, W. H., Journal of pharmaceutical sciences, 2009, 98, 8.
[2] Jönsson, S., Henningsson, A., Edholm, M., & Salmonson, T., Clinical pharmacokinetics, 2012, 51, 69-76.

On the quality of experimental phase equilibrium data at moderate pressure. Aspects to be considered for their appropriate determination and correlation

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In previous papers and meetings, we have analyzed the quality of the published experimental phase equilibrium data at moderate pressures, concluding that many of them, and for different reasons, show inconsistencies and inaccuracies making them inadequate for designing purposes. Also, the many correlations reported are not adequately checked and may lead to spurious results. Nevertheless, both the quality of the experimental data as well as the correlations, and consequently the models enabling them, may easily be and must be improved in order to solve this pressing situation, affecting to phase equilibrium and design problems.

In this presentation we present the diagnosis of the situation and emphasize on some aspects to be considered in order to check and improve the quality of the experimental data as well as how to improve the models and the corresponding correlations from the point of view of the Gibbs energy of mixing and the phase stability analysis.

Acknowledgments

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Perfluorinated (PFAS) Surfactants – Molecular Modelling and Simulation for Environmental Remediation

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Per- and polyfluoroalkyl substances (PFAS) are synthetic compounds with exceptional characteristics of chemical inertness, simultaneous hydrophobicity and lipophobicity, surfactant activity, among others. PFAS have thus found countless uses, from surface coatings to fire-fighting foams. This widespread use, allied to the extreme chemical inertness, has led to the accumulation of these compounds in the environment and to the epithet of "Forever Chemicals". Although PFAS were initially considered biocompatible, studies have shown their bio-accumulative potential and found links between PFAS exposure and severe health issues including cancer. For this reason, states are restricting PFAS production and use, and tightening the limits on their presence in food, water, and effluents. The number of PFAS remediation plants is thus growing rapidly in several countries and is expected to continue accelerating.

The current remediation processes include adsorption on solids, membrane processes, flocculation, and more recently the foam fractionation process, which separates PFAS by adsorption to the interface of rising air bubbles in a column of water. These form a concentrated foam at the top of the column and are extracted. Knowing the thermophysical behaviour of PFAS is crucial for the design and optimization of all these technologies but, however, large gaps and inconsistencies exist in the available experimental data, and development must still rely on trial-and-error.

In this work, a molecular modelling approach is used to gain a molecular-level understanding of the behaviour of PFAS. Molecular models and simulation methods are tested, validated against the available literature results, and then used to obtain properties for related compounds, extrapolate beyond the experimentally studied conditions or to provide reliable estimates of thermophysical data whenever experimental values are unavailable, disperse or inconsistent. Examples are presented for diffusion coefficients [1] and surfactant properties of carboxylate and sulfonate PFAS in water, including the calculation of adsorption isotherms and structural analysis of the Gibbs films formed.

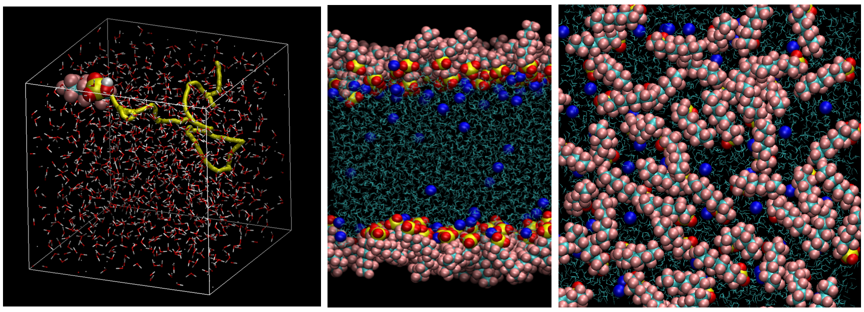

Fig. 1. Left to right: 1 ns diffusion of perfluorohexanesulfonic acid in water; side- and top-view of a film of NaPFOS adsorbed at the surface of water.

References

[1] G. Damião, P. Morgado*, P. Silva, L.F.G. Martins, C. McCabe, E.J.M. Filipe*, Perfluorinated pollutants in water: Diffusion coefficient of perfluorosulfonic acids by molecular dynamics simulations, *Fluid Phase Equilib.* **2023**, *575*, 113928

Oral Presentation 7.2: Wednesday, September 11th, 15:50h - 16:10h

Novel Fluorinated Surfactant-Free Microemulsions: Bulk and Interface Behaviour

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The tendency for phase separation in binary mixtures of a hydrophobic organic compound and water can be mitigated by adding a hydrotrope, such as a short-chain alcohol, instead of a classical surfactant. Such ternary mixtures have been found to form thermodynamically stable surfactant-free microemulsions (SFMEs), characterized by the formation of nanometric micelle-like aggregates, at compositions near the plait point of the liquid-liquid equilibrium phase diagram [1]. This unique type of microemulsion offers distinct properties and advantages over conventional surfactant-based systems, with applications in numerous commercial products. SFMEs are particularly well-suited as a medium for chemical and enzymatic reactions and for nanoparticle synthesis [2].

In this study, we present the first report of a fluorinated SFME. Our study focused on the (1H,1H-perfluoroheptanol + ethanol + water) ternary system, for which we experimentally determined the liquid-liquid equilibrium phase diagram. A comprehensive approach, integrating both experimental and computational methods, was used to explore the system's bulk and interfacial behaviour. Dynamic light scattering (DLS), ^{129}Xe NMR spectroscopy, and interfacial tension measurements confirmed the formation of a fluorinated SFME. Molecular dynamics (MD) simulations provided a detailed molecular-level description of the system that corroborated the experimental data. MD results further suggest that the 1H,1H-perfluoroheptanol aggregates are stabilized by ethanol molecules adsorbed on their surface.

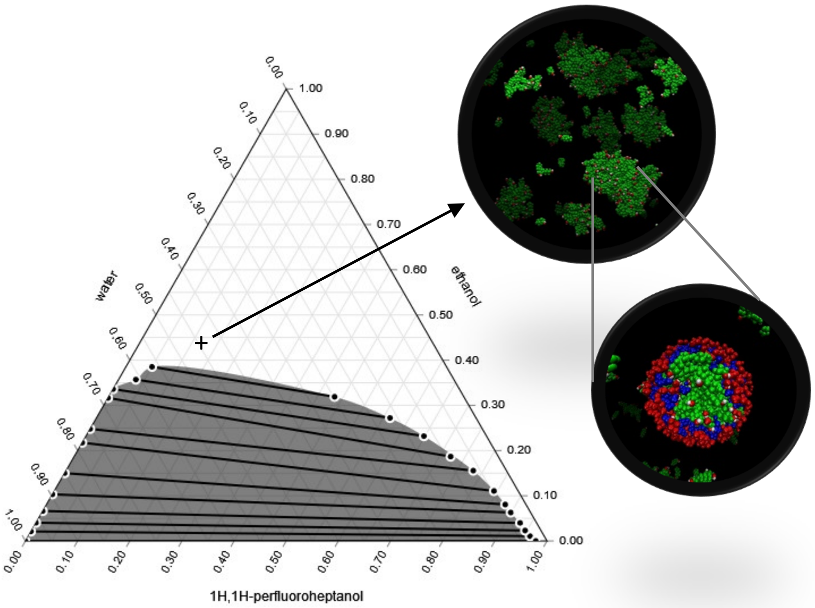

Fig. 1. Liquid-liquid equilibrium phase diagram of the (1H,1H-perfluoroheptanol + ethanol + water) mixture. The insets show representative MD simulation snapshots of the 1H,1H-perfluoroheptanol aggregates, exhibiting a fluorous core (green), surrounded by ethanol (blue) and water (red).

References

[1] S. Schöttl, D. Horinek, *Current Opinion in Colloid & Interface Science* **2016**, *22*, 8–13.
[2] W. Hou, J. Xu, *Current Opinion in Colloid & Interface Science* **2016**, *25*, 67–74.

Thermodynamic and micellization behavior of protic ionic liquids in aqueous medium

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In recent years, micellization has been the subject of extensive studies due to the multiple applications of micellar systems in fields as diverse as chemistry, petrochemistry, pharmaceuticals, and the environment. Micelles arise from the assembly of amphiphilic substances known as surfactants or surfactants. Furthermore, ionic liquids (ILs) are composed of organic salts with surfactant properties, which provides them with a wide range of applications in micelles. Consequently, several studies have investigated the micelle formation process using these elements. This work focuses on the precise evaluation of the thermodynamic process of micelle formation, based on the minimization of Gibbs free energy to determine the critical micelle concentration. Geometric characteristics of the ionic liquids are obtained using semi-empirical quantum mechanics calculations using MOPAC [1]. The values obtained through minimization will be contrasted with previously published data on critical micelle concentration of ionic liquids [2] containing ammonium and long alkyl chain acids to validate the proposed method. Validation of this method offers the opportunity to analyse the micelle formation behaviour in a set of ILs without the demand for exhaustive and expensive experiments. This advance opens new perspectives to expand the generation of data on the micellization of ionic liquids, representing a significant contribution to the scientific area.

References

[1] MOPAC2016, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, available in HTTP://OpenMOPAC.net, **2016,** Consulted in October 2nd, 2023.
[2] A.A. C. Toledo Hijo et al. *J. Phys. Chem. B* **2017,** *121*, (14), 3177–3189. *https://doi.org/10.1021/acs.jpcb.7b01384.*

Oral Presentation 8.2: Thursday, September 12th, 10:00h - 10:20h

Combining High Throughput Experiments and Active Learning to Characterize Deep Eutectic Solvents

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The high tunability of deep eutectic solvents (DESs) stems from the ease of changing their precursors and relative compositions. However, measuring physicochemical properties across large composition and temperature ranges, necessary to properly design target-specific DESs, is tedious, error-prone, and represents a bottleneck in the advancement and scalability of DES-based applications. As such, active learning (AL) methodologies based on Gaussian Processes (GPs) were developed in this work to minimize the experimental effort necessary to characterize DESs. Owing to its importance for large scale applications, the reduction of DES viscosity through the addition of a low molecular weight solvent was explored as a case study.

A high throughput experimental screening was performed to measure the viscosity of three neat DESs – ChCl:EG, ChCl:AN (1:4), and ChCl:AN (1:6) – and their mixtures therein with three low molecular weight co-solvents – water, acetonitrile, and DMSO. GPs were able to fully interpolate and describe the viscosity data measured for the nine ternary DES systems studied. Owing to their ability to capture both composition and temperature dependencies, the usage of GPs allowed the identification of the best co-solvents to decrease the viscosity of a particular neat DES, as well as unexpected non-monotonic trends between the amount of added co-solvent and DES viscosities.

Finally, the ability of GPs to estimate the uncertainty of their predictions was leveraged in an AL workflow, aiming at minimizing the amount of experimental data necessary to describe the relationship between DES viscosity and co-solvent composition/temperature. A substantial efficiency increase was attained for several systems, particularly those based on ethylene glycol where only five experimental data points, acquired through AL, were necessary to fully describe the overall viscosity dataset in each case. This represented a six-fold increase in efficiency when compared with the high throughput experimental screening based on a pre-determined temperature/composition grid. We demonstrate that leveraging the combined approach of AL and high throughput screenings greatly enhances the efficiency of experimentally characterizing the physicochemical properties of DESs.

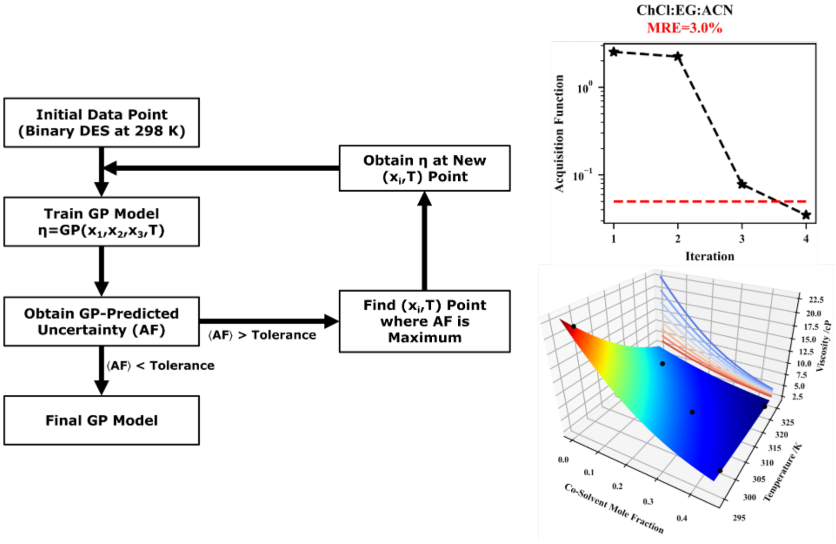

Fig. 1. Schematic illustration of the active learning workflow employed in this work and example of its performance for the system ChCl:EG:ACN.

Including Thermal and Coverage Effects in Heterogeneous Catalysis using Machine-Learned Interatomic Potentials

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Transforming one chemical species into another using catalysts is an inherently complex process at the core of chemical process industries. In the case of heterogeneous catalysis, reactants in the gas phase interact with the catalytic sites on the transition metal surface through a complex set of elementary steps influenced by thermodynamic variables such as temperature and pressure. Thermodynamic conditions dictate the nature of coverage on the catalytic surface, which can significantly affect the catalytic process. Computational modeling of these catalytic processes has proven to be a significant challenge. In this presentation, we will share some of our early work on the modeling thermal and coverage effects on the surface of transition metal carbides using machine-learned interatomic potentials (ML-IAPs). ML-IAP allows one to carry out large-scale molecular dynamics simulations while maintaining quantum mechanical accuracy, which is necessary for reactive systems. While highlighting the model's success, we will also share the limitations.

Oral Presentation 9.1: Thursday, September 12th, 11:50h - 12:10h

An Overview of the Salt Effect on the Solubility of Biomolecules

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Aqueous solutions containing electrolytes are the natural environment of many biomolecules, which is important in regulating their structure and physico-chemical behaviour, governing numerous biochemical processes. The knowledge of the solubility of amino acids, peptides, and proteins in the presence of salts is of utmost importance from a biological perspective in many food and pharmaceutical applications. Even if relevant data on amino acid solubility in aqueous electrolyte solutions can be found, the gaps are evident, particularly for aromatic amino acids and those presenting more than one amino or carboxylic group.

This work aims to contribute to understanding solvation phenomena, selecting ions from the Hofmeister series covering a wide range in the series to check their effects on the solubilities of AAs with different polarities [1-4]. It considers the solubility of L-aspartic acid, L-phenylalanine, glycine, and L-leucine in aqueous inorganic solutions containing the anions chloride, nitrate, sulfate or thiocyanate, and the cations sodium, potassium or ammonium, and the divalent magnesium or calcium cations. As shown in Figure 1, amino acids with many consistent and reliable solubility data are also included and interpreted, as well as optical isomerism and pH effect, extending the studies to peptides and glycine derivatives.

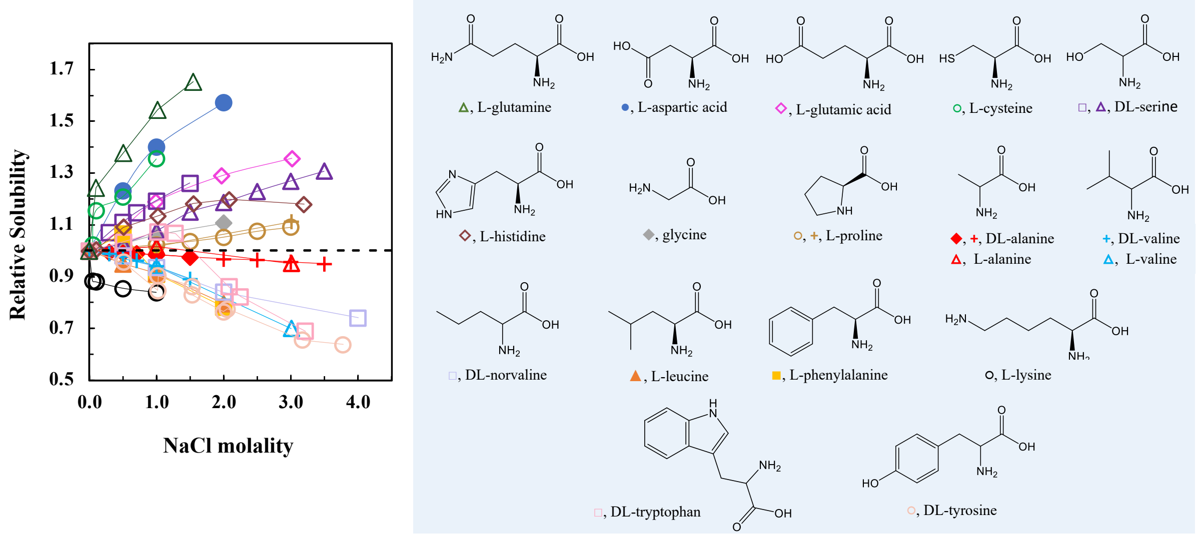

Fig. 1. The effect of NaCl on the solubility of different amino acids at 298.15 K.

References

[1] M. Aliyeva, P. Brandão, J. R. B. Gomes, J. A. P. Coutinho, O. Ferreira, S. P. Pinho, *Ind. Eng. Chem. Res.* **2022**, *61*, 5260-5631.

[2] M. Aliyeva, P. Brandão, J. R. B. Gomes, J. A. P. Coutinho, O. Ferreira, S. P. Pinho, *J. Chem. Eng. Data* **2022**, *67*, 1565-1572.

[3] M. Aliyeva, P. Brandão, J. R. B. Gomes, J. A. P. Coutinho, O. Ferreira, S. P. Pinho, *J. Chem. Thermodyn.* **2023**, *177*, 106929.

[4] M. Aliyeva, P. Brandão, J. A. P. Coutinho, O. Ferreira, S. P. Pinho, *J. Sol. Chem.* **2024**, *53*, 527-537.

Natural solvent systems for plastic recycling: dissolution-precipitation

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The plastic sector generates an enormous amount of waste each year, with the yearly consumption surpassing 460 Mt, in 2019[1]. However, recycling rates remain below 15%[1]. The urge to shift to a more circular paradigm is intertwined with the need for greener sustainable recycling processes, that yield polymers of sufficient quality to fulfil the requirements of most applications, including those with severe restrictions, such as food packaging. The recycling of polyolefins, a class that accounts for 40% of plastic usage[1], is particularly difficult, since its chemical recycling is inefficient, and mechanical routes usually result in downcycling, failing to handle complex plastic streams containing various additives or polymer mixtures. Physical recycling, and particularly dissolution-precipitation, has the potential to fill this gap. It allows the purification, separation, and recovery of polymers similar to the pristine, while still consisting of an overall simple process[2]. Despite being a promising solution, it is urgent to replace conventional hazardous solvents that are commonly used in these processes, by replacing them with natural alternatives.

The design of these polymer-solvent-antisolvent systems needs to take into account the interactions of the polymer with the solvent and the antisolvent, as well as the solubility of both components, a key factor for obtaining a pure polymer, without solvent contaminations, and for the efficient recovery of the solvent, allowing it to be reused. This work aimed to develop physical recycling of polyolefins and PET by addressing the necessity for new natural solvent alternatives, while delving into solvent-antisolvent equilibria, to ensure efficient solvent recovery, which is key to a sustainable and economically viable process. COSMO-RS was used as a screening tool to select the solvents used experimentally and to study the interactions between compounds. Several natural terpenes were able to dissolve polyolefins, while their precipitation was conducted using various alcohols. PET was dissolved in a thymol:carvacrol NaDES (natural deep eutectic solvents)[3]. The same systems were proved to allow the selective dissolution of HDPE from mixtures containing PET. Characterization via TGA, FTIR, DSC, and NMR confirmed that all recovered polymers and solvents maintained the properties of the pristine materials, and it was possible to reuse the recovered solvents multiple times.

Acknowledgements: This work was financed by FCT/MCTES (Portugal) through CQE (UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020)) and IMS (LA/P/0056/2020(https://doi.org/10.54499/LA/P/0056/2020).

References

[1] OECD, Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options, 2022.
[2] U. Arena, F. Ardolino; *Resources, Conservation and Recycling* **2022**, *183*, 106379.
[3] S. Pestana, J. Machado, R. D. Pinto, B. D. Ribeiro, I. M. Marrucho; *Green Chemistry* **2021,** *23*, 9460-9464.

Hydrophobic eutectic solvents for liquid-liquid extraction: formulation and modelling

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The separation of chemical elements is a major challenge in mining extraction or in the recycling of nuclear and electronic wastes. Hydrometallurgical processes such as liquid-liquid extraction is highly exploited for such purposes, but requires considerable amounts of solvents, that are often polluting, and volatile organic compounds. Today, liquid-liquid extraction is facing an unprecedented challenge environmental concern. New systems as Deep Eutectic Solvents (DES) are considered as "green" alternatives to conventional organic diluents,[1] due to their lower volatility, higher flash point, and in some cases higher extraction performance. Hydrophobic DES (HDES) systems are generally composed of two components: a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). Although very promising, they are currently little applied because they need to be optimized and better understood.[2] The aims of this study was therefore to synthetize and characterize new hydrophobic DES (HDES) based on well known extractants molecules. As HBA, we used extractants as Trioctylphosphine oxide, Tributyl phosphate, N,N′-Dimethyl,N,N′-dioctylhexylethoxymalonamide (DMDOHEMA) or N,N ,N',N' Tetraoctyl Diglycolamide (TODGA), associated with a HBD as carboxylic acids. A detailed characterization of these systems was studied using complementary characterization techniques and modelling (DSC, FT-IR, MD…) to highlight the potential of these HDES for solvent extraction.

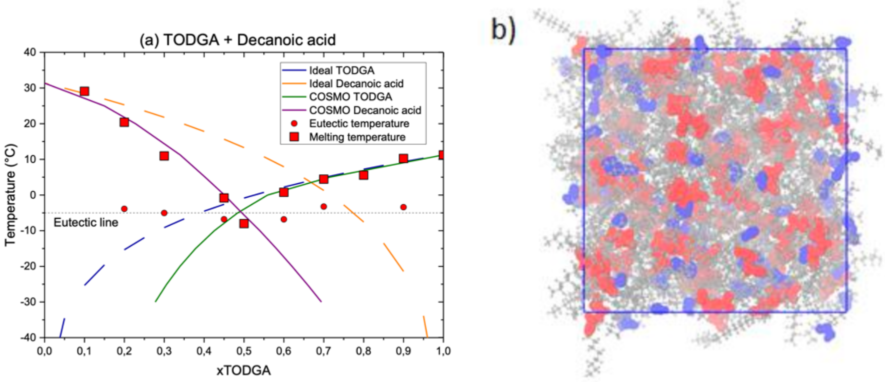

Fig. 1. Solid-liquid phase diagram of TODGA and decanoic acid ,(b) Snapshot of molecular dynamics results for the system TODGA 45% Decanoic acid 55% , blue : Decanoic acid red : TODGA and in grey : alkyl chain.

References

[1] G. Arrachart, J. Couturier, S. Dourdain, C. Levard, S. Pellet-Rostaing, Recovery of Rare Earth Elements (REEs) Using Ionic Solvents, Processes, 9 (7) 1202, 2021.

[2] J. Cao et E. Su, « Hydrophobic deep eutectic solvents: the new generation of green solvents for diversified and colorful applications in green chemistry », *J. Clean. Prod.*, vol. 314, p.127965, sept. 2021

Designing type V deep eutectic solvents with antimalarial pharmaceutical ingredients

Gabriel Teixeira[a], Paula Brandão[a], Ana I. M. C. Lobo Ferreira[b], Dinis O. Abranches[a], Luís M. N. B. F. Santos[b], Olga Ferreira[c,d,*], João A. P. Coutinho[a]

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Solid-liquid equilibrium (SLE) data including active pharmaceutical ingredients (APIs) and excipients can greatly contribute to the pre-formulation and development stages of these drugs. Excipients can enhance target properties such as solubility within relevant matrices, absorption rates, and formulation stability [1]. In this context, formulations based on deep eutectic solvents (DES) emerge as a promising approach in pharmaceutical development. DES-based formulations primarily aim at enhancing the solubility of the target drug, which is especially interesting since approximately 40% of APIs have poor water solubility [2]. Moreover, mixtures involving metabolites or permeative enhancers can also augment drug bioavailability and facilitate efficient delivery. Such formulations find applications in both topical and oral administration routes [3].

The focus of this work is to study and develop DES formulations that incorporate one of three APIs: quinine and pyrimethamine, two antimalarial drugs, and 2-phenylimidazopyridine, a representative model structure for nonbenzodiazepines [4–6]. Initial screening using the COSMO-RS thermodynamic model identified three promising excipients (thymol, propyl gallate, and butylated hydroxyanisole). Subsequently, by combining the drugs with the selected excipients, nine solid-liquid equilibrium (SLE) phase diagrams were measured using a visual melting method and differential scanning calorimetry. Negative deviations from the ideal solution model were observed across all systems. Furthermore, four novel cocrystals were identified through powder and single crystal X-ray diffraction analyses to confirm their unique diffraction patterns. Additionally, the thermodynamic modelling of the SLE diagrams was carried out using two COSMO-RS parametrizations (TZVP and TZVPD-FINE), with no consistent superiority observed between both approaches.

Acknowledgements

This work was developed within the scope of the project CICECO - Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020, CIQUP, Centro de Investigação em Química da Universidade do Porto (UIDB/00081/ 2020); IMS, Institute of Molecular Sciences (LA/P/0056/2020), and CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); and SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020), financed by national funds through the Portuguese Foundation for Science and Technology FCT/MCTES (PIDDAC). AIMCLF is financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5, and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July. G.T. thanks FCT for his Ph.D. grant (UI/BD/151114/2021).

References

[1] H.G. Morrison, C.C. Sun, S. Neervannan, *International Journal of Pharmaceutics* **2009**, *378*, 136–139.
[2] K.T. Savjani, A.K. Gajjar, J.K. Savjani, *ISRN Pharmaceutics* **2012**, 1–10.
[3] P.W. Stott, A.C. Williams, B.W. Barry, *Journal of Controlled Release* **1998**, *50*, 297–308.
[4] J. Achan, A.O. Talisuna, A. Erhart, A. Yeka, J.K. Tibenderana, F.N. Baliraine, P.J. Rosenthal, U. D'Alessandro, *Malaria Journal* **2011**, *10*, 144.
[5] R.R. Ben-Harari, E. Goodwin, J. Casoy, *Drugs in R&D* **2017**, *17*, 523–544.
[6] J. Wagner, M.L. Wagner, *Sleep Medicine Reviews* **2000**, *4*, 551–581.

Poster Communication I-P3: Tuesday, September 10th, 16:40h - 18:00h

The impact of hydrotropes on kraft lignin dissolution in aqueous solutions of deep eutectic solvents

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Lignin has the potential to generate valuable aromatic compounds, but effective dissolution methods are necessary. Previous research has shown that hydrotropes can enhance the aqueous solubility of lignin. Notably, deep eutectic solvents (DESs) have exhibited hydrotropic behaviour, significantly increasing the aqueous solubility of hydrophobic compounds, making them an attractive option for lignin dissolution. Inspired by the recently proposed cooperative mechanism of hydrotropy, this study explores the influence of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) on the performance of DESs as hydrotropes for lignin dissolution in aqueous solutions. Possible lignin solubility mechanisms in different water/DES compositions are also proposed. The capacity of six alcohols (glycerol, ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol) and choline chloride to enhance the aqueous solubility of Kraft Lignin was primarily investigated. The obtained results revealed a correlation between the size of alkyl chains in alcohols and their ability to improve the solubility of Kraft Lignin (Figure 1). This can be explained by the competition between hydrotrope-hydrotrope and solute-hydrotrope aggregates. The latter is maximized by 1,4-butanediol. Interestingly, in the diluted region, the hydrotropic behaviour exhibited by DESs is well represented as the independent sum of the contributions from the corresponding HBAs and HBDs. In contrast, lignin solubility is higher with pure hydrotropes in the concentrated region than with their combined form (DES).

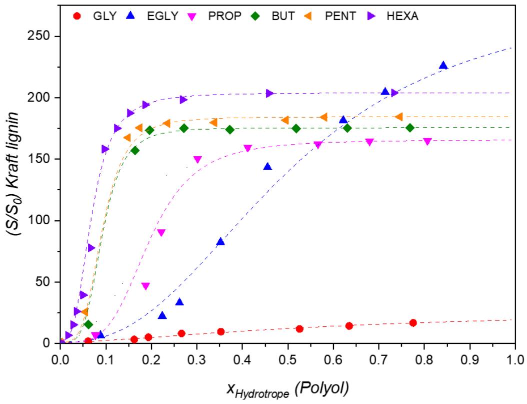

Figure 1. Solubility data for Kraft lignin in aqueous solutions of glycerol (GLY), ethylene glycol (EGLY), 1,3-Pronanediol (PROP), 1,4-Butanediol (BUT), 1,5-Pentanediol (PENT) and 1,6-Hexanediol (HEXA) at 313.15 K fitted using the cooperative hydrotropy model (- - -).

Acknowledgements

This work developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 and LA/P/0006/2020, financed by national funds through the FCT/ MCTES (PIDDAC). Filipe H. B. Sosa acknowledge FCT I.P. for the researcher contract CEECIND/07209/2022. André M. da Costa Lopes acknowledges project CENTRO-04-3559-FSE-000095—Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

Using COSMO-RS in the designing and screening of different deep eutectic solvents for the extraction of carbaryl

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This work aims to evaluate the efficiency of the Conductor-Like Screening Model for Real Solvents (COSMO-RS) in designing and screening different deep eutectic solvents (DESs) for the extraction of carbaryl from water samples [1]. Carbaryl belongs to carbamate pesticides that are used in agriculture to control insects and can enter the aquatic environment leading to water contamination. Thirty-three hydrogen bond acceptors (HBAs) and sixty-four hydrogen bond donors (HBDs) were selected for the initial design and screening using the COSMO-RS. The possible equimolar combination of HBAs and HBDs resulted in the design of 2112 mixtures. The initial COSMO-RS evaluations showed that DESs composed of thymol, decanoic acid, and citric acid as HBAs, and oxalic acid, maleic acid, octanoic acid, and 4-chlorophenol as HBDs extracted carbaryl with the highest efficiency based on the calculation of the activity coefficient of carbaryl at infinite dilution in all mixture designed (Fig. 1). Then, the composition of the DESs led to the highest extraction efficiency was predicted using COSMO-RS and the results were in good agreement with the experimental values (up to 85% extraction recovery). Finally, both binary and ternary DESs were used in the extraction of carbaryl from water samples.

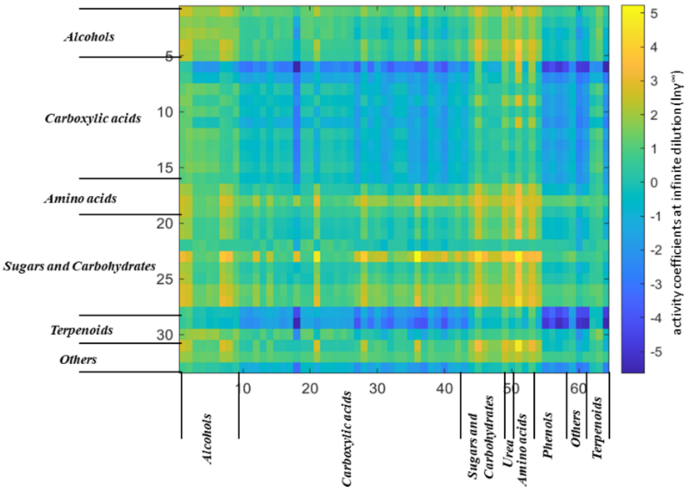

Fig. 1. Predicted solubility of carbaryl in different DESs (1:1) designed by COSMO-RS.

[1] L.M. de Souza Mesquita, F.H.B. Sosa, L.S. Contieri, P.R. Marques, J. Viganó, J.A.P. Coutinho, A. C.R.V. Dias, S.P.M. Ventura, M.A. Rostagno. Food Chem. **2023**, 406, 35093.

Acknowledgements

This work developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 and LA/P/0006/2020, financed by national funds through the FCT/ MCTES (PIDDAC). Filipe H. B. Sosa acknowledge FCT I.P. for the researcher contract CEECIND/07209/2022.

WHIA: A Novel Cubic Equation of State for Accurate Modeling of Water Properties

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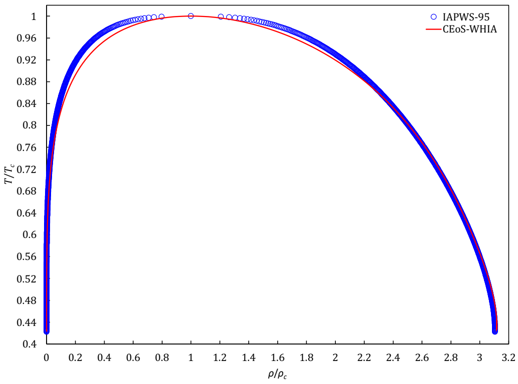
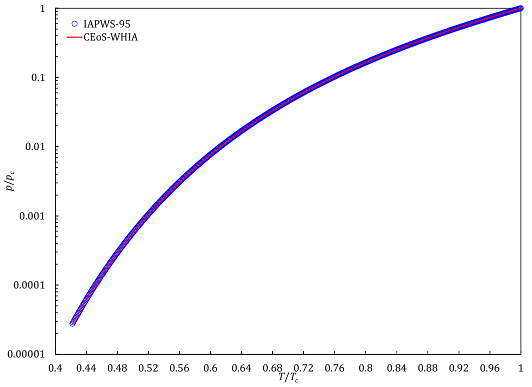
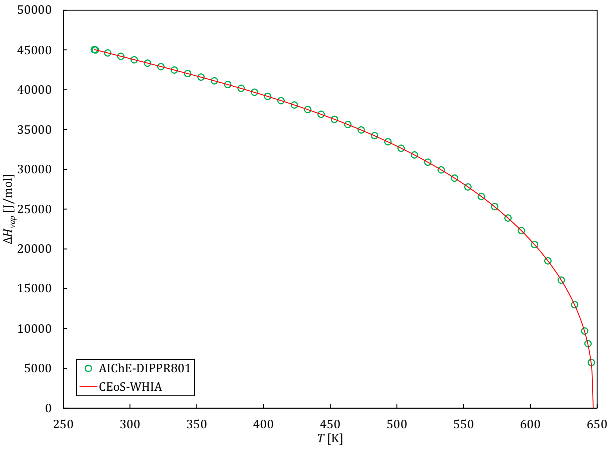
This study proposes a corresponding state cubic equation of state (CEoS-WHIA) to address the limitations inherent in classical cubic, volume translation, and association extension methodologies for predicting the thermophysical properties of pure water. It focuses on calculating non-derivative properties, including entropy, enthalpy, internal energy, volume, and derivative properties, such as heat capacities, compressibilities, and the speed of sound. These properties of water were evaluated across various equations of state and compared against the IAPWS-95 [1], a specialized formulation for water, as well as experimental data from AIChE-DIPPR801 [2]. While all models yielded acceptable results for non-derivative properties, the association extension approaches encountered challenges in the near-critical region. Moreover, none of the methodologies effectively predicted the properties in supercooled and compressed liquid regions. Additionally, all approaches exhibited significant shortcomings in predicting derivative properties across all regions. The results indicate that CEoS-WHIA appropriately predicts thermodynamic properties in saturated liquid-vapor and superheated regions.







References

[1] IAPWS-95 https://doi.org/10.1063/1.1461829
[2] DIPPR801 https://app.knovel.com/kn/resources/kpDIPPRPF7/toc

Thermophysical characterization of peloids from the Manizales area in Colombia

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Peloids are heterogeneous mixtures of a solid phase, generally a clay, and mineral-medicinal water or seawater, which are applied in thermal centres for both therapeutic and cosmetic uses [1]. This work presents the thermophysical characterization (density, specific heat, thermal conductivity and thermal diffusivity) of two peloids from the Manizales area in the municipality of Caldas in Colombia.

The thermal spa Tierra Viva is located at an altitude of 3,500 meters above sea level, and the water emerges at about 63°C, channelling over a path of 14 kilometres. In thermal pools the water temperature fluctuates between 35°C and 41°C and a pH of 2.2. The peloid has a proportion of mineral-medicinal water of 36.2% and the clay is mainly formed by Silica (72%), Kaolinite (22%) and Phlogopite (3%).

The thermal spa El Ruiz is located at 3,530 meters above sea level. It has 13 outcrops of mineral-medicinal waters with temperatures from 40°C to 65°C, with very low pH 2.2 and electrical conductivity of 96 mS/cm. The peloid has a proportion of mineral-medicinal water of 30% and the clay is mainly formed by Silica (12%), Albite (50%), Edenite (30%) and Corrensite (8%).

The description of the measurement equipment is described in Casas et al. 2013 [2]. The measurements were made at 298.15 K and atmospheric pressure.

Density range is between 1,500 and 1,800 kg/m^3; specific heat is between 1,950 and 2,150 $J/kg\cdot K$; thermal conductivity is between 0.7 and 0.9 $W/m\cdot K$, and thermal diffusivity is between $2\cdot 10^{-7}$ and $3\cdot 10^{-7}$ m^2/s. On the other hand, pH of the peloids ranges is between 4 and 5.

The studied peloids present thermophysical properties similar to other peloids applied in thermotherapy in Thermal Centres. The pH is slightly low, but compatible with skin applications.

Acknowledgements

We appreciate the financial support provided by the project ED431C 2020/06 V055 of the Xunta de Galicia of Spain.

References

[1] C. Gomes, M.I. Carretero, M. Pozo, F. Maraver, P. Cantista, F. Armijo, J.L.Legido, F. Teixeira, M. Rautureau, R. Delgado. *Applied. Clay Science.* **2013**, 75–76, 28–38.
[2] L.M. Casás, M. Pozo, C.P. Gómez, E. Pozo, D. Bessières, F. Plantier, J.L. Legido. *Applied Clay Science*. **2013**, 72, 18-25.

The impact of nanomaterial on pepsin immobilisation

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Pepsin is a proteolytic enzyme, that can naturally be found in the stomach of animals. Once it plays an important role in the digestive system, pepsin is widely used in the treatment of digestive disorders [1]. Recent research shows the relationship between pepsin and the viruses that affect human health, such as HIV and hepatitis. In the food industry, pepsin is commonly used to decrease the allergenic properties of protein-based food and nutraceuticals [2]. Due to the relevance of enzymes for industry, the development of techniques to enhance enzyme performance by increasing its stability, reducing inhibition, and enabling reusability is crucial. These aims can be achieved through techniques such as enzyme immobilization, which consists of confining the enzyme on a solid support [1]. The efficacy of the enzyme immobilization is significantly impacted by the choice of support utilized and its interactions once it can induce critical alterations in enzyme conformation. Among the different materials that can be used for enzyme immobilization, the production of biocatalysts using nanomaterials is addressed in the literature [3,4].

In this study, graphene oxide (GO), chemically reduced GO (RGO), boron nitride nanosheets (BN), and NH_2 functionalized BN (BN-NH_2) were used as supports for immobilizing pepsin. The synthesis of these materials is described in [4] and [5]. For the immobilisation, 0.5 mL of the enzyme (10^{-6} M) in buffer glycine-HCl (0.05 M at pH 3.0) was added to 1.5 mL of GO, BN, or BN-NH_2 solution (2 mg/mL) and mixing the resulting solution for 1 hour in an ice bath. The immobilization efficiency (E%) and relative activity of immobilized pepsin were evaluated against the free enzyme. Casein from bovine milk was used as a substrate for enzyme activity.

The study found that immobilization of pepsin in GO (graphene oxide) and RGO (reduced graphene oxide) reduced the enzymatic activity, despite showing high efficiency of immobilization at $90.00 \pm 1.57\%$ and $85.00 \pm 0.11\%$, respectively. The inactivity of pepsin immobilized in RGO may be attributed to the hydrophobic interactions between the support and the active site of the enzyme. GO is hydrophilic and its reduction using acid L-ascorbic reduces the oxygenated groups on the surface of GO, and consequently reduces its hydrophilicity [3]. The BN and BN-NH_2 were able to immobilise approximately 99% of the content of the enzyme initially added to the supports. The high value of functionalized BN may be attributed to the amino groups present on the surface of the supports, which interact covalently with pepsin surface groups. After the immobilisation in BN and BN-NH_2, pepsin shows an increase in proteolytic activity from 0.050 ± 0.05 U to 0.09 ± 0.05 U and 0.098 ± 0.015, respectively. The findings of this study provide a significant advancement towards the development of new and improved biocatalysts through the immobilization of enzymes in nanomaterials.

References

[1] M.P.F. Santos, M.C.P. Porfírio, E.C. Sousa Júnior, R.C.F. Bonomo, C.M. Veloso, *International Journal of Biological Macromolecules* **2022**, *203*, 67-79.

[2] R. Morellon-Sterling, O. Tavano, J.M. Bolivar, A. Berenguer-Murcia, G. Vela-Gutiérrez, J.S.M. Sabir, V.G. Tacias-Pascacio, R. Fernandez-Lafuente, *International Journal of Biological Macromolecules* **2022**, *210*, 682-702.

[3] T. R. B. Ramakrishna, T.D. Nalder, W. Yang, S.N. Marshall, C.J. Barrow, *Journal of Materials Chemistry B* **2018**, *6*, 3200-3218.

[4] M. Mathesh, B. Luan, T.O. Akanbi, J.K. Weber, J. Liu, C.J. Barrow, Z. Ruhong, W. Yang, *ACS Catalysis* **2016**, *6*, 4760-4768

[5] L.H. Li, Y. Chen, G. Behan, H. Zhang, M. Petravic, A.M. Glushenkov, Journal of Materials Chemistry **2011**, *21*, 11862

Poster Communication I-P8: Tuesday, September 10th, 16:40h - 18:00h

Enhancing CO_2 solubility using $[C_4C_1im][DMP]$ + carboxylate-based Protic Ionic Liquids mixtures

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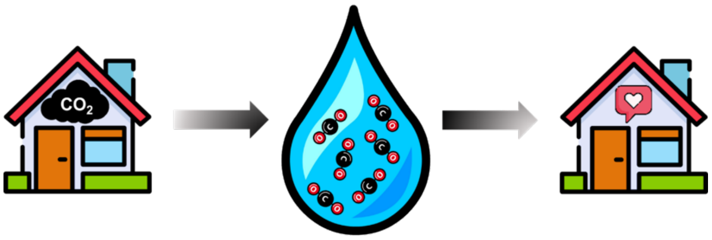
According to the World Health Organization, access to clean air is considered an essential human right [1]. Nonetheless, air pollution is a serious threat to human health, being responsible for around 7 million deaths per year [1]. This mortality is associated to several pollutants with both ambient and household emissions, such as gases, particulate matter, and volatile organic compounds [1]. As poor air quality is responsible for various diseases, improving indoor air quality (IAQ) must be a priority [1]. Despite the existing guidelines to guarantee IAQ, other strategies must be employed whenever possible, including the reduction of pollutants at their source, air ventilation, and, if necessary, indoor air treatment [2]. Although several technologies can be considered for indoor air treatment, these possess relevant disadvantages, such as high energy consumption, waste generation and harmful by-products production [2]. Therefore, new indoor air technologies are required to overcome such limitations. Among several new technologies and solvents, ionic liquids (ILs) and eutectic solvents have gathered special attention due to their high sorption capacity and unique thermophysical properties, easily tuneable by the simple combination of anions and cations, in the case of ILs, and hydrogen bond donor and acceptor species, in the case of the eutectic mixture [3]. On top of their inherent characteristics, one can further enhance gas physisorption and transport properties by preparing mixtures with positive deviations to ideality and, therefore, positive excess volumes [4]. In a previous work, we have shown that mixtures of $[C_4C_1im][DMP]$ or $[C_4C_1im][NTf_2]$ with carboxylate-based protic ILs present positive excess volumes [4]. Here, the sorption capability of $[C_4C_1im][DMP]$ with the carboxylate-based protic ILs will be evaluated through their CO_2 solubility measurement using an isochoric equilibrium cell.



ILs as a solution for capturing CO_2 and improve air quality

References

[1] World Health Organization, WHO global air quality guidelines. Particulate matter (PM2.5 and PM10), ozone, nitrogen dioxide, sulfur dioxide, and carbon monoxide, Geneva, **2021**.
[2] A. Luengas, A. Barona, C. Hort, G. Gallastegui, V. Platel and A. Elias, A review of indoor air treatment technologies, Rev. Environ. Sci. Biotechnol., **2015**, 14, 499.
[3] X. Yan, S. Anguille, M. Bendahan and P. Moulin, Ionic liquids combined with membrane separation processes: A review, Sep. Purif. Technol., **2019**, 222, 230.
[4] M. Martins, G. Sharma, S. Pinho, R. Gardas, J. Coutinho, and P. Carvalho, Selection and characterization of non-ideal ionic liquids mixtures to be used in CO2 capture, Fluid Ph. Equilibria, **2020**, 518, 112621.

Thermophysical properties of ternary mixtures ether + 1-alcohol + n-alkane.

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There are numerous articles on thermophysical properties of ternary mixtures ether + 1-alcohol + n-alkane [1-10], these mixtures have numerous applications, including the possibility of applications as fuels in mixed combustion and electric engines [11], They are also of interest from the point of view of molecular interactions, since contacts occur between alkyl, alcohol and ether groups, with data on thermophysical properties being important for the development of different physical models [12-14]. In this work, different thermophysical properties such as density, viscosity, refractive index, speed of sound, excess enthalpies, excess volumes and liquid vapor equilibrium of the ternary mixtures formed by ether + 1-alcohol + n-alkane are reviewed.

Acknowledgements

We appreciate the financial support provided by the project ED431C 2020/06 V055 of the Xunta de Galicia of Spain

References

[1] I. Abala, M. Lifi, F. E. Alaoui, N. Muñoz-Rujas, F. Aguilar, E. A. Montero, *Journal of Chemical Thermodynamics*. **2021**, 161, 106549.
[2] A.Mejía, M.Cartes, A.Velasquez, G.Chaparro, V.Sanhueza, *Fluid Phase Equilibria*. **2022**, 558, 113444.
[3] M. Cartes, G. Chaparro, G. Alonso, A. Mejía, *Journal of Molecular Liquids*. **2022**, 359, 119353
[4] K. Kammerer, G. Oswald, E. Rezanova, D. Silkenbaumer, R.N. Lichtenthaler, *Fluid Phase Equilibria*. **2000** 167:223-241
[5] C. Leppla, E. N. Rezanova, R.N. Lichtenthaler, *Journal of Chemical and Engineering Data,* **2000**, 45(6), 1019–1026
[6] E. Jimenez, L. Segade, C. Franjo, M.M. Piñeiro, M.I. Andrade. *Fluid Phase Equilibria*. **2001**;179, 363-383
[7] P.V. Verdes, M.M. Mato, M.I. Paz Andrade, J.L. Legido, *J Chemical Thermodynamic*. **2014**; 73, 224-231.
[8] E. Mascato, L. Mussari, M. Postigo, A. B. Mariano, M. M. Piñeiro, J. L. Legido, M. I. Paz Andrade. *Journal of Chemical and Engineering Data*. **2009**, 54(2), 453-458.
[9] M.M. Piñeiro, E. Mascato, L. Mosteiro, J.L. Legido, Journal of Chemical and Enginering Data. 2003, 48(4), 758-762
[10] E. Mascato, L. Mosteiro, M.M. Piñeiro, B.E. de Cominges, M. M. Mato, J.L. Legido. *Journal of Thermal Analysis and Calorimetry*. **2002**, 70(1), 235-241.
[11] S. Seyam, I. Dincer, M. Agelin-Chaab, *Energy,* **2023**, 283, 128488
[12] F. Shaahmadi, S.A.M. Smith, C.E. Schwarz, A.J. Burger, J.T. Cripwell, *Fluid Phase Equilibria*. **2023**; 565:113674.
[13] A. Fredenslund, Fluid Phase Equilibria, **1989**, *52*, 135-150.
[14] A. Klamt, F. Eckert, W. Arlt, *Annual Review of Chemical and Biomolecular Engineering* **2010**, 1, 101-122.

Poster Communication I-P10: Tuesday, September 10th, 16:40h - 18:00h

Adsorption modeling of non-quantum and quantum fluids under confinement using SAFT-VRQ-Mie

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The use of Hydrogen (H_2) as an energy vector or directly as a fuel has been shown a renewed scientific and technical interest due to its advantageous properties, versatility, and potential production from low-cost renewable energy. However, the main challenge associated with the H_2-fuel is its safe and reversible storage, where one of the most promising alternatives is to confine H_2 in adsorbent solids. To characterize the H_2 storage, it is essential to have adsorption models that consider the quantum effects of H_2 as well as the characteristics of the solid in a broad range of conditions.

In this contribution, a thermodynamic method is developed to calculate adsorption isotherms for non-quantum and quantum fluids. Herein, the fluid–fluid interactions are modelled by using the statistical associating fluid theory for a Mie potential for non-quantum and quantum fluids with a variable range (i.e., SAFT-VR-Mie [1] and SAFT-VRQ-Mie [2], respectively), whereas the solid–fluid interactions are described by a model that considers the square-well potential and the pairwise correlation function.[3]

The capability of the model is initially tested by modeling the adsorption isotherms of neon at 77 K and helium at 77 K and 298 K on MSC5A, where non-quantum and quantum effects are compared for the case of helium. The validated model is applied to describe the adsorption isotherms of hydrogen on two Metal Organic Frameworks (IRMOF-1, and IRMOF-6) and one activated carbon (JX101).
Figure 1 displays selected results, where it is possible to observe that at high temperatures, both the SAFT-VR-Mie and SAFT-VRQ-Mie equations display similar outcomes for adsorption isotherms, but at low temperatures, the SAFT-VRQ-Mie improves the results significantly, displaying a better agreement with the experimental values.

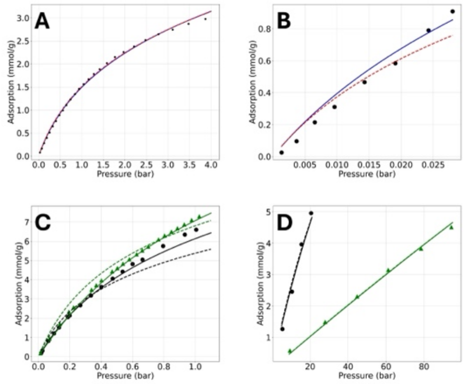

Fig. 1. Adsorption isotherms in different solids. Solid symbols represent experimental data [6]. Adsorption of neon (A) and helium (B) on MSC5A at 77 K. Adsorption of hydrogen on IRMOF-1 (black line) and IRMOF-6 (green line) at 77 K (C) and 298 K (D). Solid and dashed lines represent the results from SAFT-VRQ-Mie and SAFT-VR-Mie EoS, respectively.

References

[1] T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. Adjiman, E. Müller, G. Jackson, *J Chem Phys* **2013**, *139*, 154504.
[2] A. Aasen, M. Hammer, A. Ervik, E. Müller, O. Wilhelmsen, *J Chem Phys* **2019**, *151*, 064508.
[3] L. Franco, I. Economou, M. Castier, *Langmuir* **2017**, *33*, 11291-11298.
[6] Y. Ming, J. Purewal, D. Liu, A. Sudik, C. Xu, J. Yang, M. Veenstra, K. Rhodes, R. Soltis, J. Warner, M. Gaab, U. Müller, D. Siegel, *Microporous and Mesoporous Materials* **2014**, *185*, 235–244
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Experimental Determination and Theoretical Modelling of Isobaric Vapor-Liquid Equilibria, Liquid Density, Surface Tension and Dynamic Viscosity for the Methyl Butyrate and *tert*-Butanol Binary Mixture

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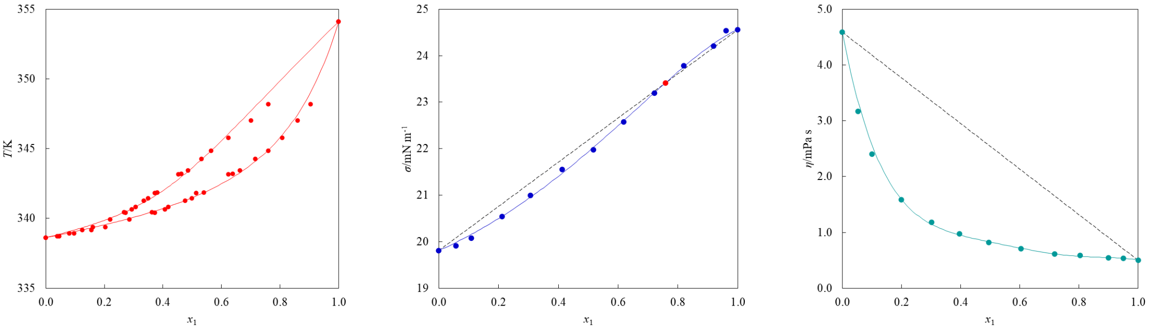
In the last decades, an extensive characterization of alternative renewable fuels and oxygenate gasoline additives has been carried out to explore new eco-friendly compounds in the transport sector. Low-molecular-weight alcohols and esters play a central role in generating renewable fuels and biofuels. Specifically, bioalcohols have been applied as oxygenate gasoline additives, whereas the use of biodiesel has been proposed as a direct alternative to diesel. In the latter case, methyl butyrate is the simplest ester capable of preserving the qualities of biodiesel and has been regarded as a promising surrogate for it [1]. On the other hand, *tert*-butanol, which is widely used as a fuel agent, has become relevant in biodiesel production [2]. In this context, a potential new biodiesel-type mixture is likely to be formed from these species, hence it is desirable to measure some fundamental physical properties, namely vapor-liquid equilibria (VLE), liquid density, dynamic viscosity, and surface tension.

To the best of our knowledge, no experimental data on these properties are currently available in the literature for this mixture, with the sole exception of Ortega's work [3] concerning its VLE, although measured at a single condition. Therefore, a more generalized approach is still needed to describe and predict the physical properties of this system. In this work, our goal is to explore the VLE at the isobaric conditions of 50.00, 75.00 and 94.00 kPa, the density, the viscosity, and the surface tension at 298.15 K and 101.3 kPa for this mixture within the whole composition range. Some results are displayed in Fig. 1 where zeotropic behavior with positive deviation from Raoult's law, the bimodal trend of its surface tension and the monotonic behavior of its dynamic viscosity can be appreciated. The data are correlated, while models based on the Wilson equation [4,5] coupled to the results obtained in the VLE calculations predict its surface tension and dynamic viscosity with acceptable overall accuracy.



(a) (b) (c)

Fig. 1. Characterization of the system methyl butyrate (1) + tert-butanol (2). (a) VLE at 50.00 kPa: experimental data (●) and Redlich-Kister expansion (—). (b) Surface tension at 298.15 K and 101.3 kPa: experimental data (●), Chunxi model (—) and linear behavior (– –). (c) Liquid dynamic viscosity at 298.15 K and 101.3 kPa: experimental data (●), Redlich-Kister-type expansion (—) and linear behavior (– –).

References

[1] A. D. Lele, S. K. Vallabhuni, K. Moshammer, R. X. Fernandes, A. Krishnasamy, K. Narayanaswamy, *Combust. Flame* **2018**, *197*, 49-64.
[2] X. Zhao, F. Qi, C. Yuan, W. Du, D. Liu, *Renew. Sust. Energ. Rev.* **2015**, *44*, 182–197.
[3] J. Ortega, F. Espiau, M. Postigo, *J. Chem. Eng. Data* **2004**, *49*, 1602-1612.
[4] L. Chunxi, W. Wenchuan, W. Zihao, *Fluid Phase Equilib* **2000**, *175*, 185-196.
[5] R. Macías-Salinas, F. García-Sánchez, G. Eliosa-Jiménez, *Fluid Phase Equilib.* **2003**, *210*, 319-334.

CO_2-Water and CO_2-Brine High-Temperature Phase Equilibria: a Multiscale Approach

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The CO_2-water and CO_2-brine systems represent one of the main geological mixtures in the subsurface. For some applications, such as heat extraction in super-hot geothermal formations at high pressure, and high temperature conditions, phase equilibria of the CO_2-water and CO_2-brine mixtures become key elements in engineering. Modeling and optimization of the processes are based on partitioning of the species between the phases. Depending on the subsurface conditions, the species mutual solubility vary over a wide range. Experiments in these extreme conditions are not trivial and only limited data are available. Accurate modeling techniques entail a vital alternative. In our work, we analyze the CO_2-water and CO_2-brine phase equilibria using molecular simulation and equation of states (EoS).

Gibbs Ensemble Monte Carlo (GEMC) simulations are applied as the molecular simulation approach. In this method, beyond the typical Monte Carlo moves, there is molecule swap between two simulation boxes, and when equilibrium is established, each box represents a phase of the mixture with equal chemical potential. SPCE and EPM2 force fields are used to represent water and CO_2 molecules. By using optimized cross-interaction parameters [1] CO_2-water interactions are described without correcting the SPCE overpolarization. We obtain the phase diagrams at 573 K in good agreement with experiments. At this temperature, SPCE-EPM2 represents the mixture phase behavior more accurately than the Exp6-Exp6, TIP4P2005-Trappe and TIP4P2005-EPM2 force fields [2]. However, at 623 K no phase separation is detected for the range of global composition and pressure analyzed. In the CO_2-brine mixture, the salting-out effect decreases CO_2 solubility in the aqueous phase and good agreement is achieved with experiments.

In our work, we use the CPA EoS [3] to model CO_2-water mixtures. The cubic Peng-Robinson EoS is coupled with an association term derived from the perturbation theory to describe directional interactions, such as hydrogen bonds. CO_2 molecules do not self-associate but may cross-associate with water through weaker hydrogen bonds. At lower temperatures, good agreement between the original CPA and experiments has been reported for the solubility of both CO_2 and water in the aqueous and CO_2-rich phases, respectively. However, at higher temperatures, there are significant deviations using the literature parameters. At 573 K, for instance, the mixture critical pressure is overestimated by a factor of 3. We observe a pronounced dependency of the binary interaction and cross-association parameters on the phase equilibria close to the critical point. By considering a wide range of conditions, such parameters are adjusted to represent CO_2-water phase equilibria at higher temperatures. In the presence of brine, e-CPA [4] may be used to represent the CO_2 phase diagram, considering the electrostatic interactions represented by the Debye-Huckel and Born equations. However, at temperatures different from the one used for the parameterization, the e-CPA may not accurately describe the brine-CO_2 mixtures.

With our work, we hope to expand the knowledge of the phase equilibria modeling of CO_2-water mixtures, especially at high temperatures, in which limited work is available.

References

[1] L. Vlcek, A. A. Chialvo, D. R. Cole. *Journal of Physical Chemistry B*, **2011**, *115*, 8775-8784.
[2] Y. Liu, A. Z. Panagiotopoulos, P. G. Debenedetti. *Journal of Physical Chemistry B*, **2011**, *115*, 6385-6810.
[1] Z Li, A. Firoozabadi. *AIChE Journal*, **2009**, *55*, 1803-1813.
[4] M. D. Olsen, G. K. Kontogeorgis, X. Liang, N. von Solms. *Fluid Phase Equilibria*, **2021**, *548*, 113167-16.

Enhancing acetaminophen solubility in aqueous solutions with hydrotropes

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Hydrotropes are compounds capable of enhancing the solubility of sparingly soluble molecules in aqueous media, thereby expanding their effective use in many applications [1]. Typically, these compounds exhibit amphiphilic properties, characterized by both hydrophilic and hydrophobic domains within their molecular structure. And while an increase in solubility indicates hydrotrope efficiency, it also holds significance for water activity. In fact, the addition of hydrotropes is known to alter the free water within the system, potentially impacting its activity in pharmaceutical formulations [2,3].

Within the pharmaceutical industry, several traditional hydrotropes are commonly used to enhance the solubility of poorly water-soluble drugs, namely sodium-based salts like benzoate or salicylate, short alkylbenzene sulfonates, and selected small organic compounds such as urea or nicotinamide [2].

Acetaminophen (ACP), a widely used analgesic recognized as an essential medicine by the World Health Organization, remains surprisingly understudied in the hydrotropy field. Previous works have explored the use of organic solvents, biomolecules, salts, ionic liquids, and eutectic mixtures. Due to its significance as a model compound, ACP has been selected as the subject of study to explore different types of hydrotropes under similar conditions, aiming to establish connections between hydrotropes molecular structure and the increase in solubility.

The main goal of this study is to investigate the effect of several hydrotrope families (traditional organic compounds, ionic liquids, and organic or inorganic salts) at different concentrations on the solubility of ACP. New solubility data in aqueous solutions of sixteen hydrotropes were experimentally measured at 298.2 K using the shake-flask method coupled to UV-Vis spectroscopy or gravimetry as analytical techniques. The COSMO-RS model was used to analyze the hydrotrope effect on the solubility increase, through the determination of the hydrotrope charge density (the donor DF, apolar AF, and acceptor AcF factors). Experimental water activity data at 298.15 K for some specific organic salts are also included to better understand if the hydrotrope-induced depression of water activity is related to the solubility increase. Overall, the findings showed that among the tested hydrotropes, organic compounds (acetone or ethanol) had the highest potential for increasing solubility, followed by salts and ionic liquids. In general, according to COSMO-RS, compounds with higher AF values tend to increase solubility more effectively. Besides that, in the aqueous solutions of salts that promoted the highest ACP solubility increase, the highest water activity was observed.

These findings provide a deeper understanding of the critical role of hydrotropes in improving drug solubility, with significant implications in the development of pharmaceutical formulations.

References

[1] D.O. Abranches et al., *Chem. Commun.* **2020**, *56*, 7143–7146.
[2] J.J. Booth et al., *Phys. Chem.* **2015**, *17*, 8028–8037.
[3] S. Shimizu et al., *Phys. Chem.* **2013**, *15*, 20625–20632.

Measurement and Modelling of isobaric vapor-liquid equilibrium and surface tension of methyl butyrate + dibutyl ether binary system

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In a world of raising concerns about the negative impact of fossil fuels, finding alternatives with less impact on the environment is important. In this context, alcohols, ethers, esters, and their mixtures have been widely studied throughout the years as oxygenated gasoline additives or as important components of biofuels [1]. The first step to explore new alternates of potential candidates for biofuel additives is to quantify the mixture's phase equilibria and surface tension. This work explores the latter thermophysical properties for an ether + ester mixture.

Specifically, this work is focused on the methyl butyrate + dibutyl ether binary mixture. Dibutyl ether (DBE) is a symmetric ether that uses a wide range of applications such as pharmaceutical, food industry, and gasoline blends. Moreover, DBE displays a very promising application as a gasoline additive or even as a biofuel itself [2]. On the other hand, methyl butyrate (MB) is an ester with a large record as a solvent and is broadly used in cosmetic and food industries due to its fragrance and flavor and is classified as a potential candidate as a biofuel additive [3].

This work focuses on the experimental measurements and modeling of the vapor-liquid equilibria (VLE) of the MB + DBE mixture at isobaric conditions of 50, 75, and 94 kPa and the surface tensions at 298.15 K and 103.33 kPa in the whole mole fraction range. The VLE data are validated using thermodynamic consistency and modelled through the traditional activity coefficient models. The surface tensions are correlated by a Scott-Mayer expression. According to partial results, Figure 1 displays the VLE at the explored isobaric conditions, where it is possible to observe a zeotropic behavior with a positive deviation of Raoult's Law. Figure 2 shows the mixture's surface tension, where a monotonic behavior is observed.

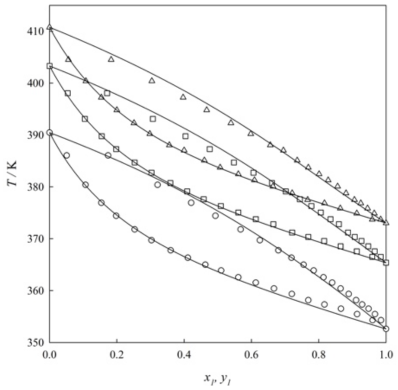

Fig. 1. Isobaric phase diagrams for the MB (1) + DBE (2) mixture. Experimental data: ○:50 kPa, □: 75 kPa, and △:94 kPa. (—) One parameter Redlich-Kister.

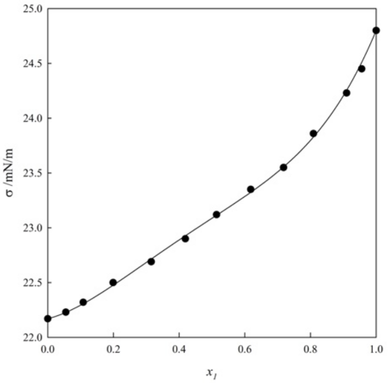

Fig. 2. Surface tension for MB (1) + DBE (2) mixture at 298.15 K and 101.3 kPa.(●) experimental data, (—) two Scott-Mayer parameters.

References

[1] R. Luque et al., *Handbook of Biofuels Production: Processes and Technologies*. Woodhead Publishing (2022).
[2] A. Mejía, M. Cartes, A. Velásquez, *Journal of Chemical & Engineering Data*, **2021**, 66, 2783.
[3] K.C. Lin, J.Y.W. Lai, A. Violi, *Fuel*, **2012**, 92, 16.

Leveraging machine learning for lithium-ion battery recycling

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The electrification of the modern world led to the widespread adoption of lithium-ion batteries (LIBs) as energy storage devices. As the lifespan of the electronic devices being produced approaches its end, solutions are needed to manage the growing volume of waste that is being generated. End-of-life LIBs may however be considered not as only waste, but as a valuable source of critical and useful materials – mitigating the need for conventional mining techniques and securing an alternative supply of these resources. However, given the range of battery chemistries and leaching agents, it is often difficult to identify the best combinations for a given objective.

In this work, a methodical data-driven approach is taken to model the leaching of key metals (Li, Ni, Mn, Co) from LIB cathodes, exploiting the literature available on this subject to create a more versatile leaching model built using machine learning algorithms. By using a wide range of experimental conditions and battery cathode chemistries, the model provides a flexible platform for LIB cathode leaching useful for the development of novel LIB recycling technologies. A diverse range of machine learning algorithms is screened using Orange and further optimized with MATLAB. Preliminary results using a feed-forward artificial neural network with one hidden layer, optimized with the Levenberg-Marquardt backpropagation algorithm to model leaching in HCl showed great promise, with a test R2 of over 0.95.

Acknowledgements

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VPO and liquid density data for binary aqueous solutions of organic salts at 313.15 K and 0.1 MPa: measurement and modelling

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The optimization of chemical processes involving strong electrolytes is remarkably complex due to their very distinct behaviour, for which reliable vapour-liquid equilibria (VLE) data are essential to enhance the description of these systems and foster more accurate thermodynamic models [1,2].

The Pitzer equations [3] include an empirical modification of the Debye-Hückel (DH) term expressing the DH limiting law and provide valuable tools for the determination of a comprehensive suite of thermodynamic properties over a wide range of temperatures and pressures [1]. In particular, the description of osmotic coefficients (ϕ) by the Pitzer equations was improved by Archer [4,5] by adding a dependence of the third virial coefficient with ionic strength, which has proven application in the modelling of binary vapour-liquid equilibria (VLE) involving molten and metallic inorganic salts [6]. Nevertheless, even though organic salts (*e.g.*, disodium succinate and sodium formate) provide a more sustainable alternative than the inorganic ones, the former have rarely been studied, for which there is a significant lack of data concerning VLE measurements.

In this work, vapour pressure osmometry (VPO) was used to determine the osmotic coefficients (ϕ) of aqueous binary solutions containing organic salts at T = 313.15 K and P = 0.1 MPa. Then, these results were described with the Extended Pitzer Model of Archer for mixed electrolytes, achieving a very satisfactory description of the systems. Furthermore, mean molal activity coefficients ($\gamma_\pm$) and excess Gibbs free energies (G^E/RT) were calculated for these binary solutions, and liquid densities (ρ) were measured and correlated at T = 298.15 and 313.15 K and P = 0.1 MPa.

References

[1] P. Velho, E. Sousa, E. A. Macedo, *J. Chem. Thermodyn.* **2024**, *194*, 107287.
[2] K. Wysoczanska, N. Calvar, E. A. Macedo. *J. Chem. Thermodyn.* **2016**, *97*, 183-190.
[3] K. S. Pitzer. Activity Coefficients in Electrolyte Solutions, 2nd ed., CRC Press, FL, USA (1991).
[4] D.G. Archer, *J. Phys. Chem. Ref. Data* **1991**, *50*, 509-555.
[5] D.G. Archer, *J. Phys. Chern. Ref. Data* **1992**, *21*, 793-829.
[6] N. Calvar, A. Domínguez, E. A. Macedo, *J. Chem. Eng. Data* **2016**, 61, 4123-4130.

The influence of thermodynamic modeling on cost assessment in extracting bio-oil value-added compounds

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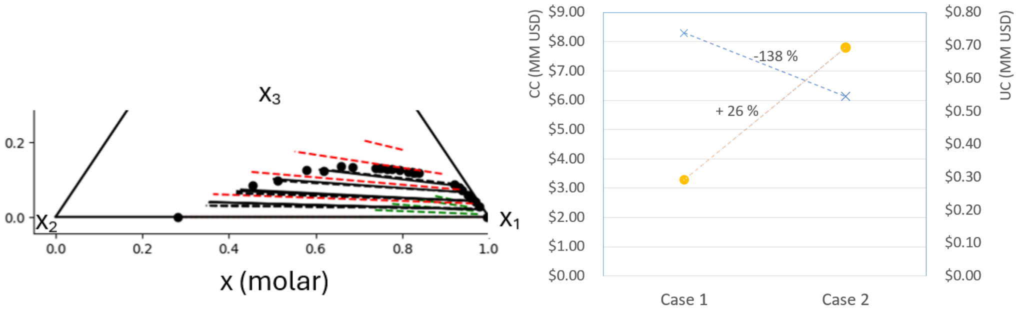
The extraction of valuable compounds from bio-oil, a byproduct of biomass pyrolysis, is gaining increasing attention due to its potential as a sustainable feedstock for various industrial applications [1]. This study investigates the influence of thermodynamic modelling on cost assessment in two distinct cases of bio-oil compound extraction processes using Aspen Plus v12.1 and Aspen Process Economic Analyzer: one employing the NRTL model with default parameters in conjunction with UNIFAC (case 1) and the other utilizing NRTL with estimated parameters coupled with UNIFAC (case 2). The cost evaluation encompasses capital cost (CC) and utility cost (UC).

In case 1, the default process simulator parameters may not always accurately represent the specific thermodynamic behavior of bio-oil extraction systems. In contrast, case 2 explores the use of estimated parameters for the NRTL model, in which all three binary parameters of the subsystem water – guaiacol – acetic acid, were adjusted to improve the accuracy of thermodynamic predictions.

Results indicate that 95.3% of guaiacol recovery with 99.60 w.t. % of purity was obtained in case 1. On the other hand, in case 2, the guaiacol recovery was reduced to 92.07% while the purity increased up to 99.97 w.t. %. The economic impact of this rigorous thermodynamic modelling (*i.e.*, comparing case 2 with case 1) was -26.2% and 137.6%, for CC and UC, respectively, as shown in Figure 1-b.

Our findings quantify the effect of choice of thermodynamic models and parameterization methods in the outcome of cost evaluations in bio-oil value-added compound extraction processes. While the default parameters of the NRTL model may offer reasonable estimates under certain conditions, employing estimated parameters customized to the specific characteristics of bio-oil extraction systems provides greater accuracy and reliability in cost assessments.



(a) *(b)*

Figure 1- (a) Ternary Liquid-Liquid equilibrium of water (x_1)+ guaiacol (x_2)+ acetic acid (x_3) at 293.15 K. (●) Experimental binodal data, (---) Case 1, (---) Case 2, (---) UNIFAC model; (b) Comparison of CC (×) and UC (●) for both cases.

References

[1] Aicha Mabrouk, Xabier Erdocia, Maria González Alriols, Jalel Labidi,Journal of Cleaner Production, 2018, Volume 198, Pages 133-142.

Prediction of carbon dioxide solubility in Diethylammonium Butanoate [DEA][Bu] using Monte Carlo Simulations

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The emission of greenhouse gases, such as carbon dioxide, due to an increasing demand for energy, is particularly concerning and has prompted the search for new technologies to capture and store this gas. In this context, the pursuit of alternative solvents for use in CO_2 capture processes by absorption methods has been driven in recent years. Ionic liquids deserve special attention due to the unique characteristics that can be achieved by combining different cations and anions. However, given the vast number of possible ionic liquids to be synthesized, it is impractical to conduct experiments with all of them to assess their potential in given applications. Molecular simulation has proven to be a powerful tool in material selection. However, its effectiveness is directly related to the ability of the force field to describe the species' properties. Several force fields with proven efficacy in describing volumetric and equilibrium properties for CO_2 behavior are already established in the literature, including the TraPPE force field. However, no general force fields exist in the literature for protic ionic liquids. In previous work, a simplified force field was proposed to represent experimental density data of a carboxylate ammonium ionic liquid at different water content [1]. The force field was tested in the prediction of CO_2 solubility in N-methyl-2-hidroxyethylammonium propaonate [2mHEA][Pr] with good results. Therefore, in this work, a newly proposed force field, which has shown excellent results in describing volumetric properties of protic ionic liquids formed by the combination of cations based on R1-$NH2^+$-R2 with carboxylic acid anions, is applied to predict the solubility of CO_2 with the ionic liquid diethylammonium–butanoate [DEA][Bu], which vapor-liquid equilibria and density data are available. Simulations were conducted in the GEMC ensemble using the Monte Carlo method implemented in the CASSANDRA software. Figure 1 presents simulation results at 303K. The agreement of simulations with experimental data reported in the literature are very good.

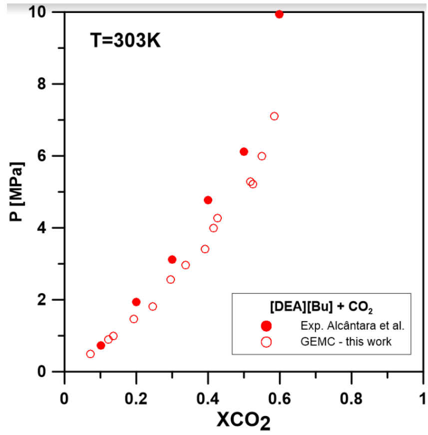

Figure 1. CO_2 Solubility in [DEA][BU] at 303K:

References

[1] M. L. Alcantara, P.H.R. Silva, L. L. Romanielo, L. Cardozo-Filho, S. Mattedi. *J. Mol. Liq.*, **2020**, *306*, 112775.

Liquid-liquid equilibrium of aqueous two-phase systems of ChCl-U with potassium phosphate salts at different temperatures

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Currently the types of aqueous two-phase systems (ATPS) that are formed by deep eutectic solvents (DESs) have attracted attention due to the attractive characteristics of DESs such as, properties similar to ionic liquids [1], economical [2], non-toxic and biodegradable. [3,4]. Therefore, they are considered environmentally friendly depending on whether the types of compounds to be used for DES formation have a low environmental impact. The information about ATPSs with DESs that is usually presented is DES with the K_2HPO_4 salt [5]. Therefore, in this work the liquid-liquid equilibrium of ATPSs formed by ChCl/Urea and different potassium phosphate salts at T= (288.15 and 308.15) K are presented in order to observe the effect of temperature, concentration and anion (type of potassium phosphate) on the ATPS. The KH_2PO_4 salt did not form ATPS, so a comparison is made with two potassium phosphate salts (K_2HPO_4 and K_3PO_4). The biphasic region expands with decreasing temperature, also the effect of anion (potassium phosphate salts) was observed in the binodal curves where it can be observed that when the concentration of K_3PO_4 increases, the formation of the biphasic area is greater than that of K_2HPO_4. In addition, the binodal curves were fitted by least squares regression with Merchuk's equation, the fitting data are presented in Table 1, observing an average absolute deviation (AAD) between 0.1081 to 0.1992%.

	Temperature (K)	**a**	**b**	**c**	**AAD (%)**
K_3PO_4	288.15	1.1586	-2.2988	14.8059	0.1838
	308.15	1.2263	-2.3646	13.4109	0.1801
K_2HPO_4	288.15	1.1026	-2.0962	10.7744	0.1081
	308.15	1.0257	-1.8512	10.2798	0.1905

Table 1.Parameters of least-squares regression fit with Merchuk's equation.

References

[1] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids : Versatile Alternatives to Ionic Liquids, (2004) 9142–9147.
[2] E. Słupek, P. Makoś, J. Gębicki, Theoretical and Economic Evaluation of Low-Cost Deep Eutectic Solvents for Effective Biogas Upgrading to Bio-Methane, Energies 2020, Vol. 13, Page 3379 13 (2020) 3379. https://doi.org/10.3390/EN13133379.
[3] K. Radošević, M. Cvjetko Bubalo, V. Gaurina Srček, D. Grgas, T. Landeka Dragičević, R.I. Redovniković, Evaluation of toxicity and biodegradability of choline chloride based deep eutectic solvents, Ecotoxicol. Environ. Saf. 112 (2015) 46–53. https://doi.org/10.1016/J.ECOENV.2014.09.034.
[4] P. Xu, G.W. Zheng, M.H. Zong, N. Li, W.Y. Lou, Recent progress on deep eutectic solvents in biocatalysis, Bioresour. Bioprocess. 4 (2017) 1–18. https://doi.org/10.1186/S40643-017-0165-5/FIGURES/1.
[5] E.A. Oke, S.P. Ijardar, Advances in the application of deep eutectic solvents based aqueous biphasic systems : An up-to-date review, Biochem. Eng. J. 176 (2021) 108211. https://doi.org/10.1016/j.bej.2021.108211.

Poster Communication I-P20: Tuesday, September 10th, 16:40h - 18:00h

Experimental Determination and Theoretical Prediction of Thermodynamic Properties: Vapor-Liquid Equilibrium, Liquid Densities, Viscosity, and Surface Tensions in Ternary Mixture of n-Hexane + CPME + Propan-1-ol

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Over the past three decades, environmental regulations have continuously pressured petroleum refineries worldwide to modify gasoline composition to produce more environmentally friendly and efficient fuels. During this period, various ethers (e.g., ETBE, TAME, DIPE, DPE) and aliphatic alcohols (e.g., methanol, butanol, propanol) have been considered for producing reformulated enhanced oxygen gasoline. Cyclopentyl methyl ether (CPME) has been proposed as a potentially utilizable gasoline oxygenate additive due to its renewable nature and promising technical and environmental properties [1]. This work aims to provide new experimental data and corresponding theoretical modeling for the thermodynamic evaluation of vapor–liquid equilibria, bulk liquid mass density, bulk liquid viscosity, and surface tension for a ternary mixture comprising n-hexane (1) + cyclopentyl methyl ether (2) + propan-1-ol (3).

Experimental vapor-liquid equilibrium (VLE) at 94 kPa was conducted using a VLE cell based on Guillespie's principle, validated through thermodynamic consistency tests. Liquid density, viscosity, and surface tension were measured under isobaric (101.3 kPa) and isothermal (298.15 K) conditions in the whole mole fraction range. Theoretical modeling of VLE utilized the statistical associating fluid theory with a Mie intermolecular potential (SAFT-VR-Mie EoS) [2], incorporating free volume theory for viscosity [3] and square gradient theory for interfaces [4]. The study provides comprehensive insights into non-isothermal vapor-liquid equilibrium (VLE) through detailed data presented in Fig. 1, including graphical representation and density diagrams for the ternary mixture. Theoretical calculations predict the surface tension and dynamic viscosity with an overall acceptable level of accuracy.

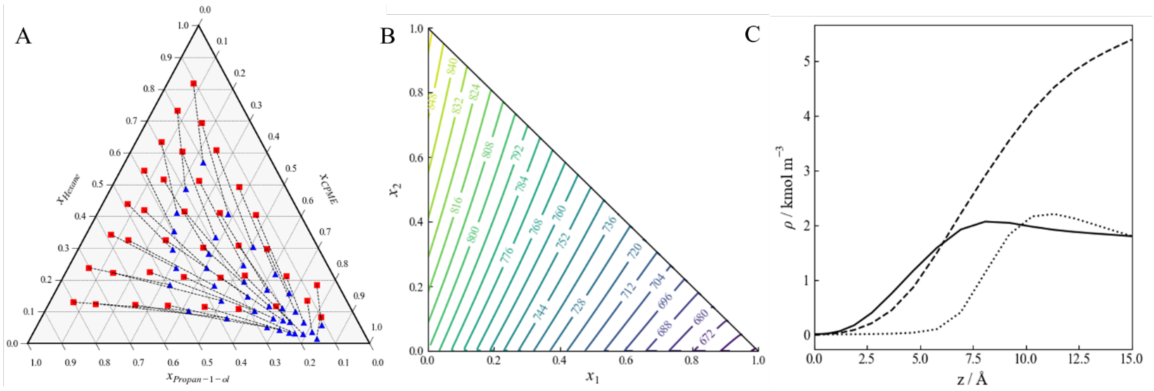

Fig. 1. (A) Experimental Vapor–Liquid equilibria diagram for n-hexane (1) + CPME (2) + propan-1-ol (3) ternary mixture at 94.00 kPa. (▲) liquid bulk phase; (■) vapor bulk phase; (--) tie lines. (B) Contour plot of the isothermal (298.15 K) – isobaric (101.3 kPa) liquid densities (ρ in kg m^{-3}). (C) Interfacial concentration of species, ρ_i, along the interfacial region, z, for (—) $x_1 = 0.2$, (--) $x_2 = 0.6$ y (···) $x_3 = 0.2$.

References

[1] K. Rehák, M. Klajmon, M. Strejc, *J. Chem. & Eng. Data* **2017**, 62, 3878-3888.
[2] T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. Adjiman, E. Muller, G. Jackson, *J. Chem. Phys* **2013**, 139, 154504
[3] A. Allal, M. Moha-Ouchane, C. Boned, *Physics and Chemistry of Liquids* **2001**, 39, 1-30.
[4] J.D. van der Waals, *Z. Phys. Chem* ***1894***, 13, 657-725

Pressure and Temperature Influence on Viscosity and Density of Binary Mixtures of Ammonium Propionate Ionic Liquids

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In the production and flow of natural gas, the presence of water and acid gases directly impacts the quality of the gas, which must comply with the specifications provided by the agency regulator before being marketed. In this sense, due to their hygroscopic characteristic, ionic liquids (ILs) appear as promising solvents in the absorption of acid gases and dehydration of natural gas. Although protic ILshave advantages such as low vapor pressure and high water affinity, among other properties, it is essential to investigate their transport properties, as they directly affect mass transfer and are connected with process efficiency, especially at high pressures. This work investigates the effect of high pressureand temperature on the viscosity and densities of pure ILs and their mixtures. The studied binary IL mixtures are formed by N-methyl-2-hydroxi ethyl ammonium propionate ([m2HEA][Pr]) and dietylammonium propionate ([DEA][Pr]) or butylammonium propionate ([Buta][Pr]). Viscosity data were measured using a Viscometer PVT model SPL 440 at pressures ranging from 30 to 300 bar and temperatures from 303.15 to 333.15 K. The density was determined with an Anton Paar DMA 4500, operating with a high-pressure cell DMA 512P at temperatures from 303.15K to 333.15K and pressuresfrom 30 to 300 bar. Atmospheric data were measured with an Anton Paar SVM 3000. Results reveal that the viscosity of [DEA] is significantly lower than [m2HEA] due to hydroxyl group interactions. Mixing the liquids at a 1:1 gravimetric ratio yields viscosity closer to [DEA], showing that the presence of non-hydroxylated LI in the mixture partially undoes the hydrogen network created with the presence of hydroxyl group, the same effect is not observed with [Buta]. [Buta] and [DEA] cations exhibit isomeric differences affecting density and viscosity, with [DEA] displaying symmetrical distribution around nitrogen favoring fluidity. High-pressure effects mirror atmospheric trends. Figures 1 and 2 depict samples of the obtained data viscosity and behavior, demonstrating the impact of pressure on [m2HEA][Pr] + [DEA][Pr].

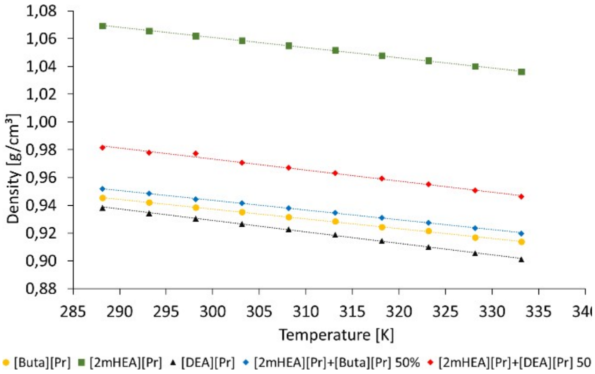

Fig.1. Density as a function of temperature for pure ionic liquids and those with 50% mixture at atmospheric pressure. Dotted ines are result from a linear data correlation

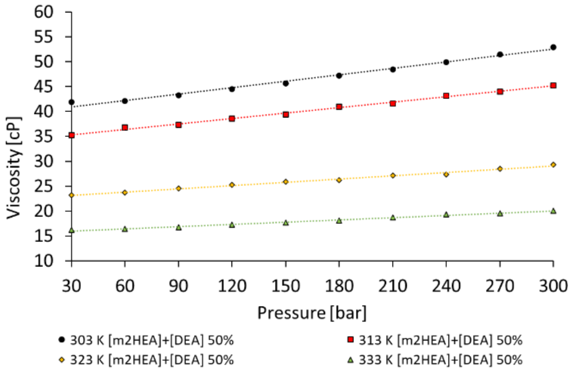

Fig. 2. Influence of temperature and pressure on dynamic viscosity for ionic liquids in [m2HEA] [Pr] + [DEA] [Pr] 50% mixtures. Dotted lines are result from a linear data correlation.

Acknowledgements

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A Comprehensive Framework for Designing Low-GWP Refrigerant drop-ins: A Thermodynamic and Environmental Analysis with Soft-SAFT and LCA

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Considering the future prospects of F-gases emissions, the Kigali Amendment has committed to reducing the use of high global warming potential (GWP) third-generation refrigerants in current refrigeration and air conditioning (RAC) systems. Notably, about 20% of existing RAC units using hydrofluorocarbons (HFCs) are anticipated to be replaced within this decade, in line with European environmental directives [1]. In response, the polar soft-SAFT molecular-based equation of state (EoS) has been used to identify and develop low-GWP fluorinated refrigerant alternatives, specifically targeting top-produced HFC R134a (GWP=1300) [2]. A detailed thermodynamic model has been established for this aim, effectively simulating refrigerants' properties, including vapor-liquid equilibrium and thermophysical characteristics, as well as binary mixtures on a coarse-grain scale [3]. The model is systematically applied to evaluate the suitability of alternative refrigerants, considering retrofitting needs through a comprehensive energy and exergy analysis, in addition to evaluating safety and technical aspects across multiple commercial RAC systems.

The compatibility KPIs are also reproduced for R513A (GWP=608), and R450A (GWP=682), which are well-recognized alternatives for R134a in domestic and commercial settings nowadays, providing a detailed comparison among mid- to low-GWP cooling agents. Finally, a holistic life cycle assessment (LCA) is performed herein to compute the carbon footprint of potential R134a drop-in replacements, covering every stage from raw material extraction to end-of-life disposal, in addition to manufacturing energy consumption, operational leakages, or indirect electricity usage derived from the optimal functioning of the cycle. A prospective 2050 LCA forecast is presented next to project both direct and indirect emission contributions, providing valuable insights into future environmental impacts.

Acknowledgements

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References

[1] M. Schulz, D. Kourkoulas, Off. J. Eur. Union 2014(517) (2014) L150/195-230. https://doi.org/10.4271/1999-01-0874.
[2] C.G. Albà, I.I.I. Alkhatib, F. Llovell, L.F. Vega, Renew. Sustain. Energy Rev. 188 (2023) 113806. 10.1016/j.rser.2023.113806.
[3] C.G. Albà, I.I.I. Alkhatib, F. Llovell, L.F. Vega, ACS Sustain. Chem. Eng. 9(50) (2021) 17034–48. 10.1021/acssuschemeng.1c05985.

Innovative AI Applications in Thermodynamic Modeling of CO_2-based Mixtures

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As Europe enforces mandates [1] to substantially phase down the emission of high global warming potential (GWP) refrigerants, a pressing challenge emerges in the refrigeration and air conditioning industry: the development of environmentally sustainable alternatives [2]. In response, CO_2-based refrigerants are emerging as an optimal choice of consensus, distinguished by its low GWP, in addition to reduced flammability, as opposed to newly formulated hydrofluoroolefins, thus offering a safer and more sustainable solution in the context of next generation drop-ins. Building on this challenge, this study presents a machine-learning-based methodology to estimate the saturation properties of CO_2-based mixtures, thus allowing for the precise fitting of molecular-based coarse-grained models like the polar soft-SAFT without relying on experimental data. The approach departs from the thermodynamic characterization of several pure-components, covering a diverse set of systems, including novel fluorine-based refrigerants and unique formulations like R13I1 and short-chain ether RE170. The parametrization allows an excellent description of the vapor pressure, saturated densities, and latent heat. Next, a constant, temperature-independent binary parameter is used when estimating the solubility profiles of CO_2-derived mixtures in selected refrigerants. The model effectively captures azeotropic and zeotropic behaviors, demonstrating its strength in fine-tuning solubility with minimal deviations from ideality. Subsequently, data from the molecular characterization via SAFT is used as output targets to train a machine learning algorithm based on artificial neural networks, enabling the prediction of mixture saturation properties out of the training dataset's scope. Using COSMO σ-profiles, the developed ANN demonstrates high efficiency in predicting saturation boiling and dew temperatures, with its effectiveness confirmed by key performance indicators like R^2 values and minimal mean deviations in statistical analysis. In summary, this research marks a significant breakthrough in the application of artificial intelligence within the domain of thermodynamics and chemical engineering.

Acknowledgements

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References

[1] M. Schulz, D. Kourkoulas, Off. J. Eur. Union 2014(517) (2014) L150/195-230. https://doi.org/10.4271/1999-01-0874.
[2] C.G. Albà, I.I.I. Alkhatib, F. Llovell, L.F. Vega, Renew. Sustain. Energy Rev. 188 (2023) 113806. 10.1016/j.rser.2023.113806.

Study of the density and thermal conductivity of mixtures of bentonite with saline solutions

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This work presents a study of the density and thermal conductivity of mixtures of bentonite clay with saline solutions of different salinity, for their possible therapeutic and cosmetic applications in thermal centres.

In a previous work [1], specific heat was already studied, and now we expand the study with other properties such as density and thermal conductivity; from those three properties we will also study thermal diffusivity [2].

The measurements were made at 298.15 K and 308.15 K and atmospheric pressure. To determine the density, an Anton Paar DMA 500 mechanical oscillation densimeter for the liquid phase has been used [3], while for the pastes the pycnometric method was used, with a 25 ml Alamo pycnometer described in Caridad et al. 2014 [4]. The thermal conductivity has been determined with a KD2 Pro Thermal Properties Analyzer (Decagon Devices Inc., Pullman, WA, EE. UU) [5].

The bentonite was supplied by the commercial company BENESA (Bentonitas Especiales S.A.) (Alcayna, Murcia), which has its deposits located in Spanish territory and is described in Casas et al. 2011 [6]. The seawater was supplied by the Quintón laboratory, and its properties can be seen in Casas et al. 2011 [6]. The saline solutions were obtained by mixing seawater with tridistilled water with salinities, 1 (S1), 2 (S2), and 3 (S3).

The mixtures were prepared by weighing in proportions of 17% bentonite and 83% S1; 56% bentonite and 44% S2; 28% bentonite and 72% S3.

The results show that the mixtures are suitable for both therapeutic and cosmetic applications.

Acknowledgements

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References

[1] Mato M.M., Casás L., Legido J.L., Gómez C.P., Mourelle L., Bessières D., Plantier F. J. Therm. Anal. Calorim. 2017, 130, 479-484 (2017).

[2] Casás L. M., Pozo M., Gómez C.P., Pozo E., Bessières D., Plantier F., Legido J.L. Applied Clay Science. 72, 18-25 (2013)

[3] Glavaš N., Mourelle M. L., Gómez C. P., Legido J. L., Šmuc N.R., Dolenec M., Kovač N. Applied Clay Science 135, 119–128, (2017).

[4] Caridad V., Ortiz de Zárate J.M., Khayet M., Legido J.L. Applied. Clay Science. 93–94, 23-27, (2014).

[5] Pastoriza-Gallego M.J., Lugo L., Legido J.L., Piñeiro M.M. Nanoscale Research Letters. 6, 560, (2011).

[6] Casás L., Legido J., Pozo M., Mourelle L., Plantier F., Bessières D. Thermochim. Acta, 524, 68–73, (2011).

A novel equation of state for mixtures of cylindrically-symmetric hard-core fluids of different aspect ratios

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Concepts of statistical mechanics associated to a thermodynamic perturbation theory (TPT) have allowed the development of molecular-based equations of state (mEoS) with great potential to predict the thermodynamic behavior of real fluids. The greatest examples of mEoSs are the Statistical Associating Fluid Theory (SAFT) [1] and its semi-empirical extensions, such as SAFT with variable range (SAFT-VR) [2, 3] and Perturbed-Chain SAFT (PC-SAFT) [4]. These SAFT-like EoSs provide an accurate description of the properties of different types of fluid systems, including polar fluids, copolymers and polymers, as well as an accurate correlation of the phase equilibria of multicomponent mixtures at high pressure. Recently, a new mEoS has been developed for cylindrically-symmetric hard bodies (CSHB) [5, 6], such as ellipsoids of revolution (EoR), spherocylinders (SPC), and cylinders (CYL). The CSHB EoS is similar to the SAFT-VR EoS [2] regarding the central square-well (SW) potential used to model the attractive interactions in a perturbation system, described by the Barker-Henderson's second-order TPT. The difference lies in the contributions to the Helmholtz free energy with respect to the hard-sphere repulsive interactions and the hard-sphere chain terms, which are replaced by a single convex reference fluid described according to the Onsager's theory [7] modified by the Parsons-Lee (PL) decoupling approximation, ultimately relating the ratio of the second virial coefficients of hard spheres and hard convex bodies. Although the application of the central SW potential for non-spherical convex fluids seems unusual, it has been recently validated through canonical Monte Carlo simulations [8, 9] by assuming only isotropic fluid phases, in which the excluded-volume expressions are valid. Overall, this sole modification in the SAFT-VR EoS [2] has enhanced the description of some thermodynamic properties and the coexistence curve of a series of pure fluids, such as aliphatic and aromatic hydrocarbons, perfluoroalkanes, and carbon dioxide. Currently, the CSHB EoS is only applicable to pure components. Given that most applications of EoSs in industry are related to mixtures of unlike chemical species, it is somewhat desirable to extend the CSHB EoS approach to mixtures of non-spherical convex fluids. In this case, the mixing and combining rules applied to the perturbation system are consistent with the MX1b rule developed by Galindo *et al.* [10]. For the reference system, the van der Waals one-fluid mixing rule is applied, and the generalized Isihara-Hadwiger theorem [11, 12, 13] is used as the combining rule for the ratio of the second virial coefficients. A comparative analysis is presented for the phase behavior of binary mixtures of CO_2 and *n*-alkanes using the SAFT-VR SW and CSHB EoSs.

References

[1] W. Chapman, K. Gubbins, G. Jackson, M. Radosz, *Fluid Phase Equilibria* **1989**, *52*, 31-38.
[2] A. Gil-Villegas *et al*., *Chemical Physics* **1997**, *106*, 4168-4186.
[3] T. Lafitte *et al*., *Chemical Physics* **2013**, *139*, 154504.
[4] J. Gross, G. Sadowski, *Industrial & Engineering Chemistry Research* **2001**, *40*, 1244-1260.
[5] J. T. Lopes, L. F. M. Franco, *Industrial & Engineering Chemistry Research* **2019**, 58, 6850-6859.
[6] J. T. Lopes, L. F. M. Franco, *Molecular Liquids* **2021**, 330, 115676.
[7] L. Onsager, *Annals of the New York Academy of Sciences* **1949**, 51, 627-659.
[8] N. B. de Souza, J. T. Lopes, L. F. M. Franco, *Fluid Phase Equilibria* **2021**, 549, 113209.
[9] N. B. de Souza, J. T. Lopes, L. F. M. Franco, *Fluid Phase Equilibria* **2022**, 561, 113543.
[10] A. Galindo, L. A. Davies, A. Gil-Villegas, G. Jackson, *Molecular Physics* **1998**, 93, 241-252.
[11] A. Isihara, *Chemical Physics* **1950**, 18, 1446-1449.
[12] H. Hadwiger, *Experientia* **1951**, 7, 395-398.
[13] J. M. Rallison, S. E. Harding, *Colloid and Interface Science* **1985**, 103, 284-289.

Coupling the tc-PR and COSMO-RS approaches to get a purely predictive equation of state: application to the prediction of the phase behavior of +200 complex systems

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Kontogeorgis and co-workers recently conducted a survey on industrial demands for thermodynamic modeling [1]. Their study revealed a growing interest in the COSMO-RS model over the past decade mainly due to its distinct advantages over traditional group contribution methods like UNIFAC. The key advantages of the COSMO-RS model include:

- No need for extensive experimental database to fit Binary Interaction Parameters (BIP's) between functional groups, since COSMO-RS depends only on pure compound information obtained via quantum chemistry calculations like Density functional theory (DFT).
- It is not limited to the availability of predefined functional groups, which increases its scope of application to a wider range of chemical species.
- It can deal with different conformations and structural arrangements, capturing the nuances of geometry variations on the thermodynamic behavior of molecules.

In short, COSMO-RS is of significant interest to industrial practitioners due to its remarkable versatility in handling diverse compounds, with the sole prerequisite being the knowledge of their chemical structure. Despite its remarkable flexibility, challenges persist: it is well-known that COSMO-RS is particularly adept at modeling incompressible liquids that are far from the critical region. This raised an important question: how can pressure effects be appropriately incorporated into the COSMO-RS model? One of the answers found was not to incorporate pressure directly into the model's formalism,but use it as an activity coefficient model (or excess Gibbs energy g^E model) within advanced mixing rules of cubic equations of states (EoS). Few studies in the literature have dealt with this topic, showcasing the potential of this approach, but a more systematic analysis of the performance of this approach is still lacking.

With this in mind, we conducted a comprehensive benchmarking study of this method across 200 binary systems [2]. These systems encompassed a diverse range of phase equilibrium and mixing property data, spanning both low and high-pressure conditions. To achieve this, we integrated the *translated- consistent* Peng-Robinson EoS (*tc*-PR [3]) with one of the published versions of COSMO-RS [4]. It was observed that, the *tc*-PR / COSMO-RS model has been successful in well reproducing the fluid phase behaviors of many systems - at least in a qualitative standpoint. More generally, this study highlights the potential of this approach but also its limitations. We will propose some modifications to the model in order to improve quantitative prediction.

As a concluding remark, we believe that integrating COSMO-RS with a cubic EoS proves to be a valuable strategy for various applications – including screening, product design, and generation and complementation of experimental data. This approach will be further developed and enhanced in the near future.

References

[1] G.M. Kontogeorgis, R. Dohrn, I.G. Economou, J.-C. de Hemptinne, Ind. Eng. Chem. Res. 60 (2021) 4987–5013.

[2] J.-N. Jaubert, Y. Le Guennec, A. Pina-Martinez, N. Ramirez-Velez, S. Lasala, B. Schmid, I.K. Nikolaidis, I.G. Economou, R. Privat, Ind. Eng. Chem. Res. 59 (2020) 14981–15027.

[3] Y. Le Guennec, R. Privat, J.-N. Jaubert, Fluid Phase Equilibria 429 (2016) 301–312.

[4] A. Klamt, F. Eckert, Fluid Phase Equilibria 172 (2000) 43–72.

Combining soft-SAFT and Neural Networks to address the Thermophysical Properties of Choline Chloride DES with Co-solvents

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In the search for environmentally greener solvents, Deep Eutectic Solvents (DESs) have emerged as suitable systems for applications in diverse chemical processes [1]. These compounds consist of mixtures between hydrogen bond donors and acceptors where, due to the strength of these bonds, at a certain proportion, they have a melting point lower than that of their pure components, as well as lower than that of an ideal liquid mixture. However, the hydrogen bonding network may be affected by the presence of water and other cosolvents, strongly affecting their thermophysical properties and future performance in a particular process [2]. Despite ongoing research, the fundamental mechanisms governing their thermophysical behavior remain under investigation. Multiscale simulations serve as a valuable tool, offering additional insights to guide experimental efforts efficiently. In this study, we present a thorough thermodynamic characterization of choline chloride (ChCl)-based DESs and their mixtures with co-solvents using the soft-SAFT equation of state, employing accurate transferable and semi-predictive models. A comprehensive approach treating each entity within the DES as an independent compound is adopted to describe their density, activity coefficients, isentropic compressibility, and speed of sound, comparing with experimental data. To complement the DESs modeling studies, we introduce an Artificial Neural Network (ANN) framework to address the viscosity of ChCl-based DESs and their co-solvent mixtures, leveraging molecular parameters derived from COSMO-SAC [3]. The reliability of the developed ANN is validated using several statistical parameters. The combination of classical molecular-based approached with artificial intelligence tools can serve to facilitate the screening of new solvents, such as DESs, thereby accelerating their industrial-scale implementation across diverse applications.

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References

[1] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R. L. Reis, A. R. C. Duarte, *ACS Sustain Chem Eng* **2014**, *2(5)*, 1063–107.
[2] L.V.T.D. Alencar, S.B. Rodríguez-Reartes, F. Tavares, F. Llovell, *J Chem Eng Chem* **2023**, *132*, 279-290.
[3] L.V.T.D. Alencar, S.B. Rodríguez-Reartes, F. Tavares, F. Llovell, *ACS Sustain Chem Eng.* **2024**, *submitted.*

Poster Communication I-P28: Tuesday, September 10th, 16:40h - 18:00h

Investigation of interfacial tension and minimum miscibility pressure between a Brazilian dead oil and a CO_2:CH_4 mixture

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CO_2 flooding is a commonly applied enhanced oil recovery (EOR) method. In CO_2-EOR processes, the interfacial tension (IFT) affects the capillary number and sweep efficiency, influencing the distribution and displacement of the oil within the reservoir. When the gas injection pressure is above the minimum miscibility pressure (MMP) the injection is miscible, the most favorable condition for increasing the sweep efficiency. In this context, IFT and MMP are essential for understanding CO_2-EOR processes. In the case of the Brazilian Pre-Salt fields, the injected gas is a mixture composed mostly of light gases, mainly CO_2 and CH_4. In this work, the IFT at 60 °C between a gas mixture (CO_2:CH_4 equimolar) and a Brazilian dead oil was measured on a Drop Shape Analyzer using the pendant drop technique. The IFTs measured at different pressures were used to estimate the MMP by the vanishing interfacial tension (VIT) method (mathematical extrapolation of the data to a pressure condition in which the IFT has a zero value) [1]. Furthermore, the experimental data were compared to the predicted IFT and MMP results calculated using the Parachor and Multiple-Mixing-Cell (MMC) methods, respectively. The Peng-Robinson (PR) model was used in both calculations [2,3]. The experimental and calculated IFT results are illustrated in Fig. 1. The IFT decreases linearly with increasing pressure up to a certain point, known as the extraction pressure (15.50 MPa). Above this pressure, the IFT continues to decrease linearly, but the pressure dependence is smaller. The MMP was estimated as (24.76 ± 1.24) MPa by mathematical extrapolation of the experimental IFT from the region below the extraction pressure to the zero value (Fig. 1). The MMP calculated by the MMC method was 29.15 MPa. For both IFT and MMP, the calculated deviations between experimental results and model predictions were higher than the experimental uncertainty. The results from both methods can be improved by tuning PR model parameters (such as the binary interaction parameters, k_{ij}) using the experimental data.

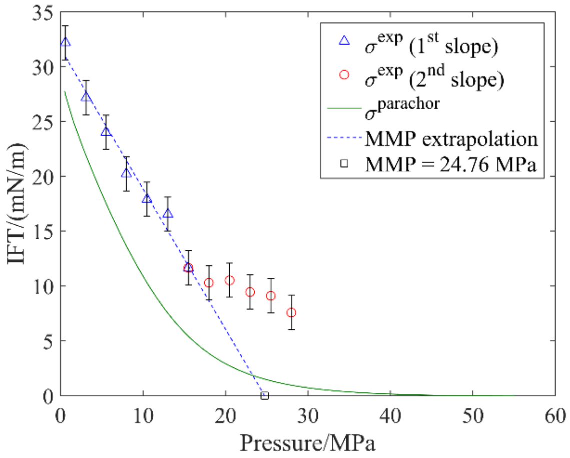

Fig. 1. Experimental results of IFT (σ) and MMP for CO_2:CH_4/dead oil at 60 °C.

References

[1] A. Almeida da Costa, G. Costa, M. Embiruçu, J. B. Soares, J. J. Trivedi, P. S. Rocha, A. Souza, P. Jaeger, *SPE Res Eval & Eng* **2021**, *24*, 45-65.
[2] S. C. Ayirala, D. N. Rao, *Journal of Physics: Condensed Matter* **2004**, *16*, S2177-S2186.
[3] K. Ahmadi, R. T. Johns, *SPE Journal* **2011**, *16*, 733-742.

Vapor-Liquid-Liquid Equilibrium for the Water + Butanol + CPME Mixture

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Oxygenate additives, such as short-chain alcohols or ethers, are commonly blended with gasolines to increase their octane number and reduce their environmental impact through a more effective combustion. Additionally, those additives can be produced from renewable sources reducing dependence on fossil fuels. Promising blends are made with 2,5-Dimethylfurane (2,5-DMF) [1], Cyclopentyl methyl ether (CPME) [2], Ethanol or Butanol, where the latter is particularly attractive due to its lower water miscibility and higher energy density (27 MJ/L) compared to ethanol (21 MJ/L). However, the renewable production of alcohols is based on the fermentation of algae or forestry residues, which yields highly hydrated alcohols. Combining all those additives, the resulting gasoline blend can contain a mixture of hydrocarbons, alcohols, ethers and water.

To design more ecological and efficient fuels, it is critical to evaluate the compatibility and mixture properties (*e.g.,* their VL, LL and VLL equilibria, among others) of all compounds into hypothetical gasoline blends, such as Hexane + Butanol + CPME + Water mixture. From the proposed mixture, equilibrium data for all binary and only two ternary mixtures (Hexane + Butanol + Water by Gomis, *et al.,* [3] and Hexane + Butanol + CPME by Mejía *et al.* [4]) are currently available. To complete the experimental information and provide accurate models to reproduce the behaviour of one of the remaining unexplored mixtures, we have carried out thermodynamically consistent isobaric (101.3 kPa) VLLE measurements of the Water + Butanol + CPME mixture. Its phase equilibrium was excellently modelled by the SAFT-VR-Mie EoS showing two heterogeneous binary azeotropes in the Water + CPME and Water + Butanol mixtures and a homogeneous azeotrope in the Butanol + CPME mixture with no azeotrope in the ternary VLLE region. Finally, we are carrying out Gibbs Ensemble Monte Carlo (GEMC) simulations to validate the accuracy of current force fields to reproduce the phase equilibria of the mixture with the aim of simulating their phase and interfacial properties.

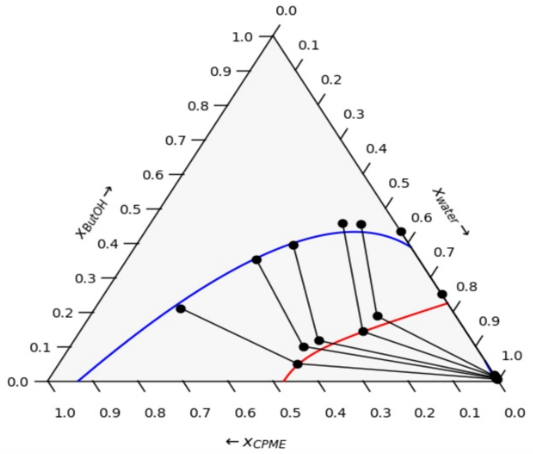

Fig. 1. Water + Butanol + CPME ternary VLL equilibria.

References

[1] A. Hernandez, M. Cartes, A. Mejía, *Fuel* **2018**, *229*, 105−115.
[2] A. Mejía, M. Cartes, G. Chaparro, E. Müller, *J. Mol. Liq* **2024**, *397*, 124087:1-10.
[3] V. Gomis, A. Font, M.D. Saquete, J. García-Cano, *Fluid Phase Equilib.* **2012**, *316*, 135–140.
[4] A. Mejía, M. Cartes, A. Velásquez, G. Chaparro, V. Sanhueza, *Fluid Phase Equilib.* **2022** *558*, 113444:1-15.

Analysis of saponin extraction from beet leaves using the ultrasound-assisted

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Saponins are a biosurfactant that can be found in some plant species such as were quillaja shell (Quillaja saponaria) with 9-10% saponin content, root and leaves of sugar beet (Beta vulgaris) with 5.8%, chinese ginseng (Panax ginseng) with 2-3%, quinoa (Chenopodium quinoa) with 0.14-2.3%[1-2]. Currently, the replacement of synthetic surfactants of low biodegradability and high toxicity by natural surfactants has become more relevant nowadays, making it crucial to study the extraction of these biosurfactants from their sources[3].

In this work, the extraction of saponins from beet leaves was optimized, using ultrasound-assisted extraction by changing the ratios of ethanol/water solutions, ratios of aqueous solution/beet leaves and contact time.

The results were compared with those obtained by the traditional method, maceration with ethanol/water 50%(v/v), followed by n-butanol partition, verifying an improvement of (0.22±0.02)%(m/m) to (1.94±0.12)%(m/m).

In the end, the extracts obtained were applied in the remediation of soils contaminated with hydrocarbons, testing the surfactant capacity resulting from the extracts obtained from both methods. Under the same soil washing conditions, the saponin-rich extracts obtained by the ultrasound-assisted method were (90.40±1.40)%(m/m), instead of (73.3±3.0)%(m/m) obtained by the saponin-rich extracts obtained by traditional method.

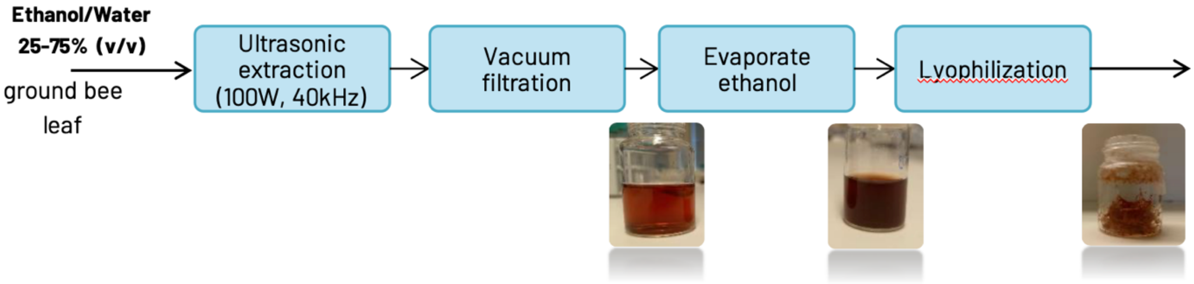

Fig. 1. Flowsheet of saponin extraction using ultrasound-assisted method.

Acknowledgements

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References

[1] M. A. Mir, K. Parihar, U. Tabasum, E. Kumari, A. Mir, and M. Amin Mir, "Estimation of alkaloid, saponin and flavonoid, content in various extracts of Crocus sativa," 2016.

[2] Ö. Guclu-Ustundag and G. Mazza, "Saponins: Properties, Applications and Processing," Crit Rev Food Sci Nutr, 2007, vol. 47, no. 3, pp. 231–258.

[3] A. Karthick, B. Roy, and P. Chattopadhyay, "A review on the application of chemical surfactant and surfactant foam for remediation of petroleum oil contaminated soil," J Environ Manage, 2019, vol. 243, pp. 187–205.

Fast calorimetry scanning for degrading quaternary ammonium compounds

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Accurate measurements of melting properties are crucial for understanding solid-liquid equilibria diagrams, providing insights into the thermodynamic behaviour of substances and their mixtures. However, for some compounds, these properties cannot be measured by traditional methods such as differential scanning calorimetry (DSC) due to the degradation upon melting. Choline chloride and some quaternary ammonium salts are examples of compounds that undergo this phenomenon [1,2].

To avoid this issue, the Fast-Scanning Calorimetry (FSC) poses as a valuable technique for quickly examining phase transitions through controlled heating rates up to 5000 $K \cdot s^{-1}$ [3]. This technique has already been applied to characterize the thermal properties of choline chloride, an important deep eutectic solvents precursor [1].

Tetraalkylammonium salts are versatile compounds which are commonly used as phase-transfer catalysts, electrolytes in electrochemical studies, and in organic synthetic reactions [4]. These salts also are valued for their hydrogen-bonding abilities, making them important as organocatalysts [5]. Extensive research has been conducted on tetraalkylammonium salts, focusing on their equilibrium constants, conductivity, dissociation constants, and catalytic properties, highlighting their significance in chemistry and material science [6–8].

The focus of this work is to study the melting properties of different quaternary alkyl ammonium salts using the FSC technique, complemented by conventional DSC and thermogravimetric analysis (TGA). The mass of the added samples has been assessed in two different ways; either by comparing the specific heat capacity of the solid phase measured by the FSC with specific heat capacities obtained by conventional DSC, or by comparing solid-solid transitions enthalpies measured by the FSC, when present, with the same transitions' enthalpies obtained by conventional DSC. To validate the technique and ensure reproducible results, the measurements were first carried out using compounds such as indium, 4-nitrophenol, benzoic acid and anthracene for which the melting properties are well described in the literature.

References

[1] A. van den Bruinhorst, J. Avila, M. Rosenthal, A. Pellegrino, M. Burghammer, M. Costa Gomes, *Nat Commun* **2023**, *14*, 6684.
[2] A. Xenopoulos, J. Cheng, M. Yasuniwa, B. Wunderlich, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals* **1992**, *214*, 63–79.
[3] N. Bosq, N. Guigo, E. Zhuravlev, N. Sbirrazzuoli, *J Phys Chem B* **2013**, *117*, 3407–3415.
[4] T.J. McNeese, R.D. Pike, *Acta Crystallogr Sect E Struct Rep Online* **2012**, *68*, 2382–2383.
[5] T. Nakamura, K. Okuno, R. Nishiyori, S. Shirakawa, *Chem Asian J* **2020**, *15*, 463–472.
[6] S.T. Goga, A. V. Lebed, N.O. Mchedlov-Petrossyan, *J Chem Eng Data* **2010**, *55*,1887–1892.
[7] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg Chem* **1996**, *35*, 1168–1178.
[8] F. Ren, J. Xian, Z. Jia, Z. Chen, H. Fu, R. Wang, W. Chu, X. Pan, J. Wu, Angewandte, *Chemie International* **2023**, *62*.

A COSMO-RS Based Approach for Predicting the Solubility of Vanillin and Ethyl Vanillin in Mixed Solvents

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The correct description of solid-liquid equilibrium (SLE) and liquid-liquid phase equilibrium (LLE) is crucial in the design and optimization of extractive crystallization, which is widely applied to isolate and purify target compounds in the pharmaceutical, chemical, and food industries [1]. Although SLE and LLE can be experimentally measured, empirical and semi-empirical models are a more direct and less time-consuming approach. In this work, the Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to predict the solubility of vanillin (VA) and ethyl vanillin (EVA) in mixtures of water and organic solvents. Both solutes are used as additives in food, perfume, and commodity industries and present complex phase equilibria in binary solvent mixtures [2]. Two major solute conformers were identified by Raman spectroscopy and confirmed by DFT calculations (Figure 1a). The SLE was predicted using the default conformer distribution of COSMO-RS, resulting in good predictions with an intermediate behaviour between the predictions using each individual conformer (Figure 1b). In a second approach, the conformer degeneracy prefactor was adjusted to fit experimental solubility data of VA and EVA in pure (water or organic) solvents. For the mixed solvents, the degeneracy was calculated using a linear regression considering the prefactors fitted for the pure solvents (Figure 1c). With this approach, the model provided better predictions than the default conformation for solubility calculations, improving the description of the solubility maxima.

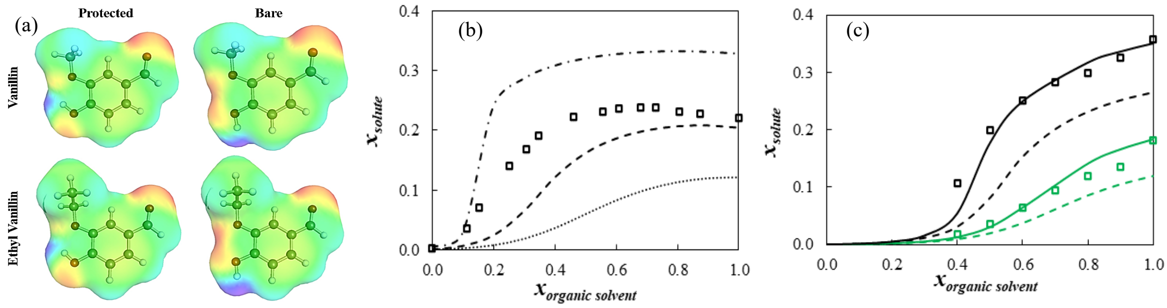

Fig. 1. Solute conformers (a), solubility predictions with bare (dash-dotted line), protected (dotted line), and default COSMO-RS distribution (dashed lines) conformers (b), and using calculated conformer prefactor (solid lines) (c). Squared dots denote experimental data, with distinct colours representing different temperatures.

This work proposes a semi-predictive approach to COSMO-RS for binary solvents that requires experimental solubility values of the target solute in pure solvents. This methodology improves the predictions of solubility in mixed solvents and emphasizes the importance of the distribution of the solute conformers throughout the solvent mixtures and its impact on predictions.

Acknowledgements

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References

[1] D. Duffy, N. Cremin, M. Napier, S. Robinson, M. Barrett, H. Hao, B. Glennon, *Chem Eng Sci* **2012**, *77*, 112-121.
[2] L. Jager, G. Perfetti, G. Diachenko. Journal of Chromatography A 2007, 1145, 83-88.

Prevention of crystallization of copper sulfate in hydrometallurgical plants.

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In copper hydrometallurgical plants, the crystallization of copper sulfate in equipment, pipes and valves causes damage, decreased flows, affects the production line and sometimes causes the process to stop [1,2]. In order to avoid this phenomenon, the conditions under which crystallization occurs in synthetic and industrial solutions are determined. The latter, PLS (Pregnant Leach Solution), lean electrolyte (LE) and rich electrolyte (RE), which were obtained from the industrial plant of Minera Antucoya, Chile.

Copper sulfate saturation tests were carried out in a phase equilibrium equipment with temperature control (± 0.1 ºC) and agitation. Copper concentrations as a function of temperature were determined for different concentrations of sulfuric acid (140 to 200 g/L), iron (0 to 1.5 g/L), Guar gum (20 to 100 ppm) and surfactants FS-101 (5 to 20 ppm) used in this type of industries. In all tests, density, viscosity, pH and oxidation-reduction potential were measured to know the behavior of the physical properties of the solutions. Iron and sulfuric acid decrease the solubility of copper sulfate, facilitating its crystallization (see figure 1). On the other hand, Guar gum and surfactant have no influence.

In addition to the analysis of the main crystallization variables, tests were carried out to determine the effect of the cooling rate of the different solutions on the crystallization of copper sulfate. For this, we worked in a 500 mL reactor, stirred and provided with temperature control at ± 0.1 ºC. Crystallization times, temperature and supersaturation concentrations were determined in each case. At higher cooling rates, supersaturation increases, decreasing the crystallization temperature. The supersaturation curves turned out to be approximately parallel to the saturation curves. The previous study was complemented with measurements of temperature profiles and atmospheric cooling rates in the plant (see figure 1).

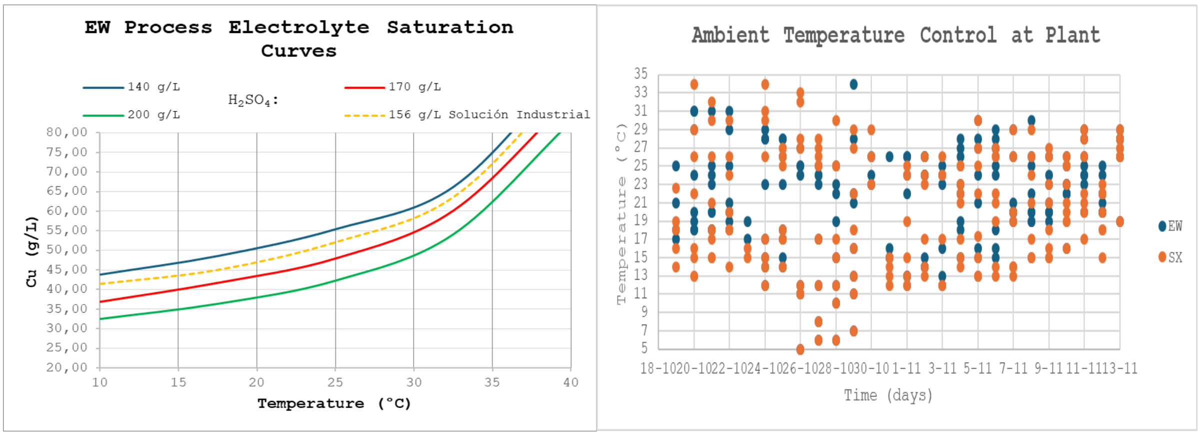

Fig. 1. a) Copper sulfate saturation curves. Influence of H2SO4 concentration. b) ambient temperature at Minera Antucoya plant

References

[1] F. J. Justel, D. M. Camacho, M. E. Taboada and K. J. Roberts, *Journal of Crystal Growth., Crystallisation of copper sulphate pentahydrate from aqueous solution in absence and presence of sodium chloride,* **2019**, *Vol 525*, Pag. 125204

[2] Mohod A. Bangadankar S. A. Deshmukh, S. Singh, M Bagal, P. R. Gogate, *B Improvements in crystallization of copper sulphate using ultrasound and comparison with conventional method, Chemical Engineering and Processing,* **2022**,*178, 109028*

$NaNO_3$ Copper Leaching and NOx Recovery: A Sustainable Process for Metal Extraction.

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This paper presents a study on the impact of the use of nitrate salts on acid oxidative leaching with seawater of a chalcopyrite concentrate produced in Antofagasta region, Chile. The concentrate is mainly composed of chalcopyrite($CuFeS_2$), with small amounts of pyrite, covelite, molybdenite, and quartz.

The treatment of minerals using sulfuric acid with addition of small amounts of nitrogen species have been employed in industrial applications decades ago. Nitric acid or nitrate salts that are available in Antofagasta, Chile (KNO_3, $NaNO_3$, $NaNO_2$) provide great potential, being the subject of study for copper processing [1-2]. They can be used to oxidize the sulfide content partially or totally, the reaction rate is faster, therefore, the reactor volume is smaller, the process does not require the use of high temperatures or pressures and the oxide-reduction potential that occurs in the reaction is high.

Leaching tests were performed at 45 °C and are carried out in cylindrical reactors with salts added in stoichiometric proportions. Copper concentration, metal recovery and the generation of polluting gases are analyzed. Positive results were obtained in the recovery of copper, around 75%, which tends to decrease after 46 hours. This decrease could be due to the formation of a layer of sulphur precipitated on the surface of the particle, difficulted the passage of the solution into the solid. In addition, the results show that the initial reaction rate is controlled by a surface reaction and subsequently by diffusion, due to this sulfur layer being formed as a reaction product [3].

The generation of polluting gases such as nitrogen oxides (NOx) was observed due to the interaction between acid, nitrate, and oxygen. For this reason, a stage of gas absorption and recovery of nitrate salts is incorporated. The absorbent solution, in this case NaOH, was cooled to a temperature of 5 °C ± 2 °C. Higher production of $NaNO_3$ than $NaNO_2$ was achieved in the absorbent solution.

This process allows: reducing the emission of polluting gases into the atmosphere, recovering nitrate and sodium nitrite salts through crystallization, reusing the recovered salts as oxidizers in future leaching. Figure 1 shows the complete system (leaching-absorption).

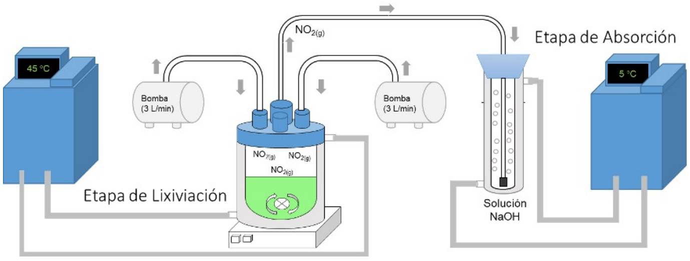

Figure 1. Process Diagram

References

[1] O. Gok. "Oxidative leaching of sulfide ores with the participation of nitrogen species-a review." *Journal of Ore Dressing*, **2010,** *12,24.*
[2] M. D. Sokić, (2011). "Mechanism of chalcopyrite leaching in oxidative sulphuric acid solution." *J. Chem.* **2011**, *5: 37-41.*
[3] Castellón, C. I. and M. E. Taboada (2023). "Leaching of Copper Concentrate with Iodized Salts in a Saline Acid Medium" Part 1 and 2." *Materials* **2023** *16(6): 2312* and *Materials* **2023**, *16(17): 5940.*

Understanding the Thermophysical Behavior of Phosphonium Ionic Liquids in Carbon Capture Applications through a Multiscale Modelling Approach

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The progress of effective separation systems for CO_2 capture is crucial in combating greenhouse gas emissions. Nowadays, the most common solvents employed in industrial absorption circuits are amines, whose degradation and evaporation during operation provoke major economic and environmental concerns. In addition to these challenges, there is currently a pressing need to discover alternative solvents capable of functioning across a spectrum of CO_2 concentrations found in treated streams, ranging from 15% in flue gases to parts per million (ppm) levels in air.

Among many alternatives, ionic liquids (ILs) represent an atractive option due to their low vapor pressure and tuneable solvent power achieved by combining different cations and anions. Specifically, certain combinations of phosphonium cations and anions have been explored in the literature, showing promising performance. However, comprehensive characterization is still necessary to identify the most suitable CO_2 absorber, considering the specific streams composition and conditions for absorption.

This study adopts a multiscale approach to investigate CO_2 gas absorption in phosphonium-based ILs with different anions. New molecular models are developed using the soft-Statistical Association Fluid Theory (soft-SAFT) [1] methodology, which builds upon existing soft-SAFT coarse-grain models for this ILs family. The study includes analyzing molecule charge distribution obtained by means of Turbomole-COSMO software for new ILs and approximating association parameters through DFT calculations. Subsequently, soft-SAFT is employed to accurately simulate and predict the thermodynamic and absorption properties [2] of these ILs across a wide range of conditions. The molecular models account for specific CO_2-IL cross-association interactions to accommodate chemisorption phenomena, if present. The analysis considers diverse CO_2 compositions and is completed by estimations of Henry's law constants, solvation enthalpies, and entropies, ultimately proposing the most promising solvents. A preliminary capture unit is finally proposed to address the CO_2 capture in a flue gas, establishing a comparison with the benchmark amine absorption process.

Acknowledgments

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References

[1] F.J. Blas, L.F. Vega, *Mol. Phys.* **1997** 92 135-150 (1997).
[2] G. Alonso, P. Gamallo; R. Sayós, F. Llovell, *J. Mol. Liq.* **2020**, 297, 111795.

Interactions of COVID virus with Different Surfaces

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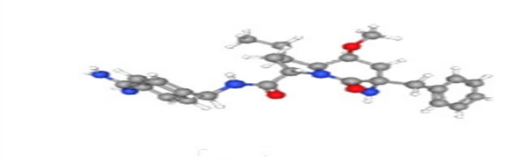
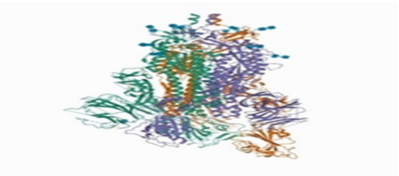
This study presents a comprehensive investigation into the half-lives of SARS-CoV-2 on an array of diverse surfaces. Current methods for finding virus half-lives on surfaces are mostly experimental. A recent study by Neeltje van Doremalen [1] compared the aerosol and surface stability of two COVID. His experimental observations of virus decay rates in aerosol and virus titer calculations show that the areas of interface between the air-liquid phase are similar to the solid-liquid phase. We make an alternative calculation through a theoretical study of virus – surface interactions. We present an approach to calculating SARS-CoV-2 half-lives by using binding energies of virus surface particles with different surfaces. The binding energies are calculated by using different molecular modelling software and theoretical energy distributions. The binding energies are estimated from the interactions of spike proteins of the virus with surface molecules of the solid interface. Figure1 shows Stainless Steel 3D structure and spike protein of COVID2 virus is shown in Figure 2





Statistical surface renovation in the liquid phase and first order chemical deactivation (unfolding rates) at the air/solution interface. The energy values are then substituted into mathematically derived equations using simple decay rate equations to find the final half-life values. The study reveals that polystyrene exhibits the most extended half life among the examined surfaces at approximately 0.74hr, signifying its crucial role in virus persistence and potential transmission within practical, real-world contexts. The research methodology employs molecular docking software to calculate binding energies, providing valuable insights into the intricate interactions between the virus and different surface materials. However, it is essential to acknowledge that the limited variations in binding energies introduce a degree of uncertainty into the results, necessitating a prudent approach in their interpretation. These findings carry substantial implications for our understanding of SARS-CoV-2's persistence on surfaces. The extended half-life of the virus on polystyrene becomes a focal point, underscoring the significant role of material surfaces in the transmission of infectious diseases.

References

[1] N.van Doremalen, New England Journal of Medicine 2020;382:1564-1567

PVT analysis of the exotic phase behavior of systems composed of hexadecane (n-$C_{16}H_{34}$) with high CO_2 content

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The study of the phase behavior of systems rich in carbon dioxide (CO_2) is an area with great scope for research applied to the oil and gas industry, especially because of the Brazilian pre-salt, which has oil reserves with a high gas-oil ratio (GOR) and a high concentration of CO_2 in the associated gas. This chemical compound has specific properties that can lead oil-containing mixtures to exhibit exotic phase behavior under certain conditions. The challenges for production in such pre-salt reservoir conditions include understanding the unusual phase behavior observed in the laboratory from field samples. In this paper, experimental data on the high-pressure phase equilibrium of a model system containing CO_2 and n-$C_{16}H_{34}$ will be presented. The n-hexadecane is selected to represent petroleum, as this chemical compound has a molar mass similar to those found in oil samples produced in Brazilian basins. The equipment used to obtain the data was a Schlumberger® visual PVT cell with a maximum volume of 80 cm^3, within the extreme operating conditions of 100 MPa and -10 to 180 °C. The equipment was also used to determine the phase transition pressures and measure the specific masses of the fluids in equilibrium. The n-hexadecane was mixed in increasing molar contents with CO2 of analytical purity (57.14%; 83.06%; 86.53% and 94.18% - percentage gas in the total mixture). The transitions observed during this study were liquid-liquid (LL), vapor-liquid (VL) and vapor-liquid-liquid (VLL). The phase behavior investigated includes equilibrium conditions observed at a constant temperature of 293.15 K and at pressures of up to 80 MPa. With great temperature control of the equipment, it was possible to map the miscibility window of this binary mixture of n-C16H34 and CO_2, as shown in Figure 1, which highlights the region of two liquid phases at high pressures and high CO_2 contents, in this case it was only possible to observe this behavior at 86.53% and 94.18%. This region of the graph is characterized by two dense phases and has been little investigated in the literature. The separation of the phases in the upper region is slow due to the low interfacial tension between them and the small difference in specific mass.

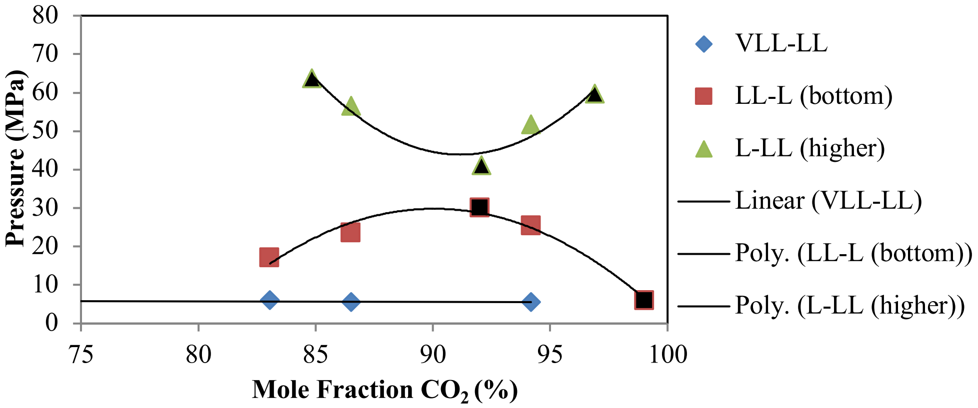

Figure 1. P-x diagram of CO_2 and n-C16H34 system at 298 K

References

[1] Simoncelli, A. P., Goméz, W., Charin, R. M., Fleming, F. P., Ndiaye, P. M., & Tavares, F. W. Phase behavior of systems with high CO_2 content: Experiments and thermodynamic modeling. *Fluid Phase Equilibria*, **2020**, *515*, 112574.
[2] Schneider, G., et al. Hasengleichgewichte und kritische Erscheinungen in binären Mischsystemen bis 1500 bar, CO_2 mit n-Octan, n-Undecan, n-Tridecan und n-Hexadecan. *Chemie Ingenieur Technik*, **1967**, *39* (11), 649-656.

Poster Communication I-P38: Tuesday, September 10th, 16:40h - 18:00h

Immobilization of different types of lipase on activated carbon

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Enzyme immobilization is a widely recognized and employed strategy in the biotechnological industry to improve the stability, reusability, and efficiency of enzymes in various processes. Among immobilization techniques, the use of solid supports such as activated carbon has sparked interest due to its high surface area, porosity, and ability to interact with biomolecules [1]. Lipases, a group of enzymes widely studied due to their versatility and applicability in different fields, have been the subject of numerous immobilization studies aiming to optimize their catalytic properties. Immobilization of lipases on activated carbon offers significant advantages, such as protection against inhibitors and adverse reaction conditions, as well as the possibility of biocatalyst reuse [2]. In this context, this study aimed to investigate the immobilization of different lipases in activated carbon functionalized with genipin, without functionalization and functionalized with iron particles and chelator. The activated carbon used as support was synthesized from licuri coconut shells and submitted to an optimization process using phosphoric acid as an activating agent according to the methodology described by Santos et al. [3]. The lipases used in the immobilization process were lipase from Candida type VII, lipase from porcine pancreas, lipase from Rhizopus oryzae and Amano lipase from Mucor javanicus following methodology by Brito et al. [4]. The hydrolytic activity of the free enzyme and immobilized in the support was determined using the method of hydrolysis of the olive oil emulsion [4].

In this study, three lipases of microbial origin were used and one of animal origin, was observed that lipases of microbial origin obtained good performance in immobilization and enzymatic activity in all whereas animal lipase obtained better results only in the functionalized support (Fig. 1). This fact can be attributed to the fact that microbial enzymes have a more compact, simplified, and stable structure that facilitates penetration and effective interaction with the support. The difference in size and molecular structure between different types of lipases can directly influence the efficiency and stability of immobilization in activated carbon, making it necessary to consider these aspects in the selection and optimization of the enzymatic immobilization process [2,4].

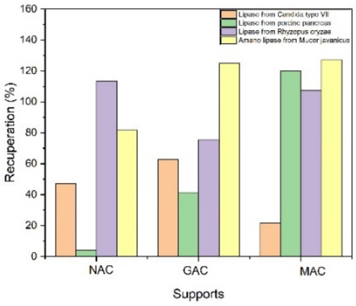

Fig. 1. Recuperation (%) of lipase immobilized on activated carbon non-functionalized (NAC), genipin-functionalized carbon (GAC), metalized activated carbon (MAC) on different types of lipases.

References

[1] A. B. Silva, C. D. Smith, E. F. Johnson, G. H. Brown, J. K. Lee, *Journal of Biotechnology* **2022**, 45, 210-225.
[2] S.A. Khan, H. Saleem, S. Khan, H. Ali, *Bioprocess and Biosystems Engineering* **2023**, 68, 451-468.
[3] M.P.F. Santos, J.F. da Silva, R. C. I. Fontan, R.C.F. Bonomo, L.S. Santos, C.M. Veloso, Journal Chemical Engineering **2020**, 98, 1501–1511.
[4] M. J. P. Brito, M P. F. Santos, E. C. S. Júnior, L. S. Santos, R. C. F. Bonomo, R. C. I. Fontan, Journal of Environmental Chemical Engineering **2020**,8, 104391.

Feynman-Hibbs quantum corrections for hydrogen; effect on VLE and confinement

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Energy consumption has been rapidly increasing over the last years, where the main source corresponds to fossil fuels. Despite being the primary source of energy, these fuels are limited and produce a significant amount of greenhouse gases. Among the alternatives available to find new sources and diminish the damage to the environment, hydrogen is considered a clean energy carrier and a reliable source for energy.

There are different routes to obtain hydrogen, however, how to store it and transport it with efficiency is the issue that remains unsolved. At room temperature, hydrogen is a gas that occupies a significant volume. The most common options are storing the hydrogen as a high-pressure gas up to 200 bar, as liquid hydrogen (~21K), adsorption into a nanomaterial (77K) and employing hydrates [1]. To understand the behaviour of hydrogen under storage conditions, it can be studied through experiments, theoretical models, and molecular simulations. For the last two, it is important to have an accurate and realistic description of the fluid molecules. Due to the cryogenic temperature and the small size of hydrogen molecules, the quantum effects might be noticeable and relevant in the description of fluid behaviour. The Feynman-Hibbs (FH) [2] correction applied over the intermolecular potential is an alternative to take into account the quantum effects.

The present work employs Monte Carlo simulations to study the VLE (Gibbs ensemble) and the confinement in carbon nanotubes (Grand Canonical ensemble) of hydrogen at both cryogenic and room temperature. Moreover, several models for hydrogen are tested for temperature-density, temperature-pressure, and isochoric curves for the VLE case, covering classical and quantum approximations. For the confinement into carbon nanotubes, the same models are compared against each other to predict adsorption isotherms in the range of pressure between 0 and 60 bar. In addition, the effect of considering FH quantum corrections for the fluid-solid potential is studied to see its effect on the adsorption isotherms at different temperatures and pore sizes. Preliminary results are illustrated in Figure 1.

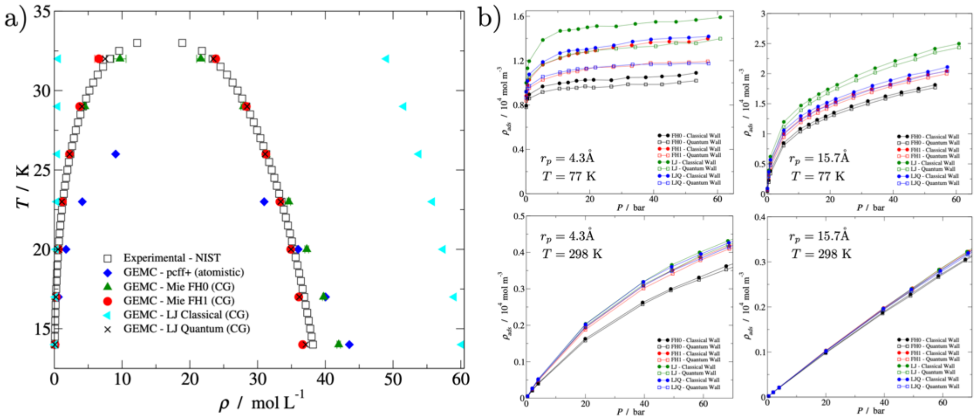

Fig. 1. Effect of FH quantum corrections for hydrogen in (a) VLE and (b) confinement in carbon nanotubes for two different pore sizes at two temperatures, employing different models for hydrogen.

References

[1] L. Schlapbach and A. Züttel, *Nature* **2001**, 414 353-358.
[2] R.P. Feynman and A.R. Hibbs, *Quantum Mechanics and Path integral*, Dover publications, New York (2010).

Surfing the Molecular Sea with Stochastic Machine Learning: Sigma Profiles as a Digital Chemical Space

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This work establishes a new paradigm on digital molecular spaces and their efficient navigation by exploiting sigma profiles. To do so, the remarkable capability of Gaussian processes (GPs), a type of stochastic machine learning model, to correlate and predict physicochemical properties from sigma profiles is demonstrated, outperforming state-of-the-art neural networks previously published. The amount of chemical information encoded in sigma profiles eases the learning burden of machine learning models, permitting the training of GPs on small datasets which, due to their negligible computational cost and ease of implementation, are ideal models to be combined with optimization tools such as gradient search or Bayesian optimization.

Gradient search is used to efficiently navigate the sigma profile digital space, quickly converging to local extrema of target physicochemical properties. While this requires the availability of pre-trained GP models on existing datasets, such limitations are eliminated with the implementation of Bayesian optimization, which can find global extrema with a limited number of iterations. A remarkable example of this is that of Bayesian optimization towards boiling temperature optimization. Holding no knowledge of chemistry except for the sigma profile and boiling temperature of carbon monoxide (the worst possible initial guess), Bayesian optimization finds the global maximum of the available boiling temperature dataset (over 1000 molecules encompassing more than 40 families of organic and inorganic compounds) in just fifteen iterations (i.e., fifteen property measurements), cementing sigma profiles as a powerful digital chemical space for molecular optimization and discovery, particularly when little to no experimental data is initially available.

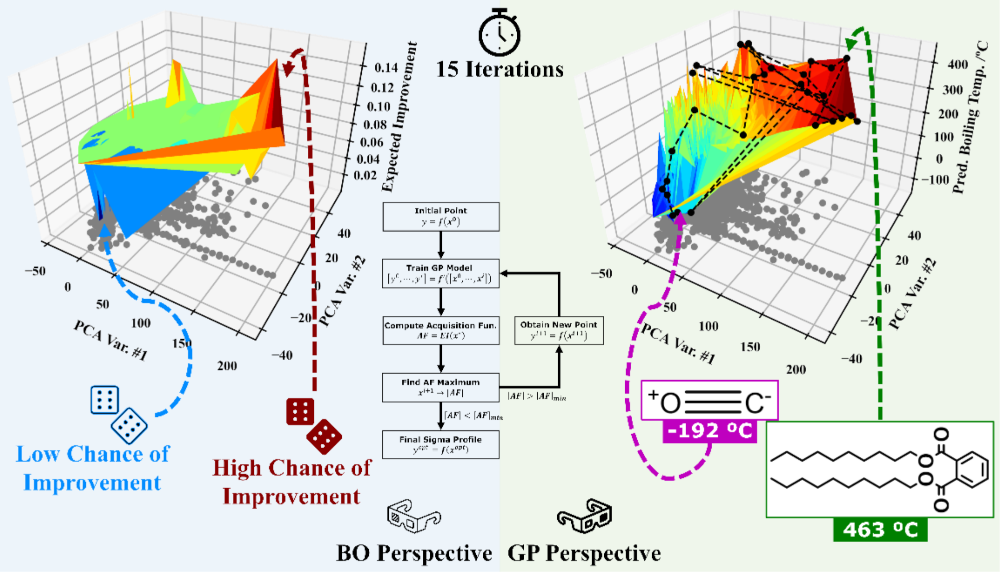

Fig. 1. Illustration of the Bayesian optimization (BO) algorithm used in this work for molecular optimization towards boiling temperature maximization, including the BO perspective (left) where the space is seen in terms of expected improvement (related to the probability of finding a molecule with a larger boiling temperature than that of the current iteration) and the goal is to find global extrema, and the GP perspective (right) where the space is seen in terms of predicted boiling temperature values and the goal is to minimize the uncertainty of the model in its full domain.

Incorporation of constant thermodynamic yield lines into reactive phase diagrams at set initial global composition

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For a multicomponent system of set initial global composition $\boldsymbol{z_0}$, where a number of simultaneous chemical reactions take place, the reaction thermodynamic yield for product l (Υ_l), is defined in this work as the ratio of the equilibrium amount of product l (n_l^{eq}) to the maximum amount of product l (n_l^*) calculable on the basis of stoichiometry only, i.e., $\Upsilon_l = n_l^{eq}/n_l^*$. There are reactive systems for which the computation of n_l^* is not trivial. For instance, for the two-reaction system $\{\boldsymbol{R_1}: CO(1) + 2H_2(3) \leftrightarrow CH_3OH(5),\ \boldsymbol{R_2}: CO_2(2) + H_2(3) \leftrightarrow CO(1) + H_2O(4)\}$, reaction $\boldsymbol{R_2}$ consumes the H_2 , i.e., one of the reactants of $\boldsymbol{R_1}$, but $\boldsymbol{R_2}$ simultaneously produces $CO(1)$, i.e., the other reactant of $\boldsymbol{R_1}$. Hence, it might not obvious at first sight how to obtain n_l^*. This problem is solved in this work through linear programming (LP) rather than in the straightforward way applicable to systems of reactions of simpler stoichiometry. The found value of n_l^* is used as input in an equation that makes possible to specify the value for Υ_l. Such equation is incorporated into a system of equations that describes a multicomponent multiphase multi-reaction flash. Such system is solved, in a range of conditions, keeping constant the Υ_l specification, by using a robust numerical continuation method, thus generating a constant Υ_l curve. Several such curves are computed at set $\boldsymbol{z_0}$ (=initial global composition), and such set of curves is then added to a computed reactive isopleth (R-IP), which in the simplest case is made of a reactive dew point line and a reactive bubble point line, both at $\boldsymbol{z_0}$. Fig. 1 shows, for the case of methanol production (reactions $\boldsymbol{R_1}$ and $\boldsymbol{R_2}$) a computed R-IP, for $z_{CO}^0 = 0.244$, $z_{CO2}^0 = 0.035$, $z_{H2}^0 = 0.67$, $z_{H20}^0 = 0.00$, $z_{CH3OH}^0 = 0.00$, $z_{CH4}^0 = 0.051$, which presents both, a set of curves of constant H_2 conversion (χ_{H_2}), and also a set of constant Υ_{CH_3OH} curves. Fig.1 makes possible to see at a glance the behavior of the reactive system over wide ranges of conditions. We observe that, for this system, the conversion χ_{H_2} and the thermodynamic yield Υ_{CH_3OH} tend to vary in tandem. This would not necessarily be the case for other reactive systems, e.g., when unwanted side reactions are present. At, e.g., 100 bar, Fig. 1 indicates that a significant increase in yield is obtained when going from the homogeneous to the heterogeneous region.

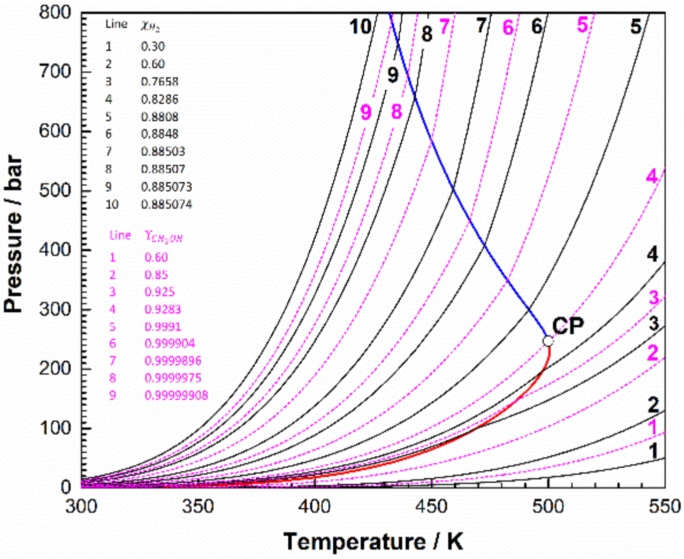

Fig. 1. P vs. T projection of a computed reactive isopleth. System of reactions: $\boldsymbol{R_1}$ and $\boldsymbol{R_2}$ (methanol synthesis). Inert component: methane. Red: reactive dew points curve. Blue: reactive bubble points curve. Black: constant χ_{H_2} curves. Orchid: constant Υ_{CH_3OH} curves. Model: SRK EoS + quadratic mixing rules. Interaction parameters from Pankaj et al (Chem. Eng. Commun., vol. 102, no. 1, pp. 35–46, Apr. 1991). Information on standard state properties of formation and on ideal gas specific heats taken from DIPPR 2003 database

Strategies to increase the solubility of organic redox active materials using thermodynamic principles

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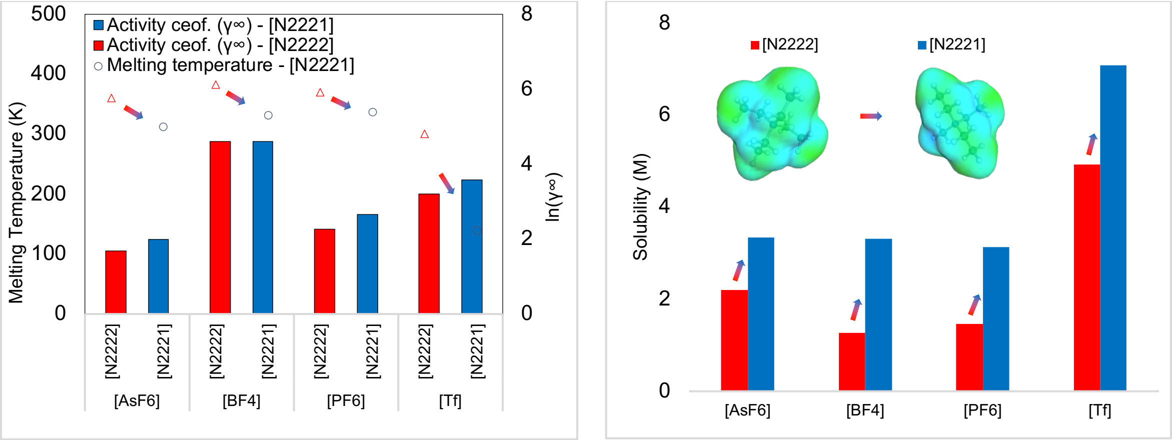
Enhancing the solubility of redox-active organic molecules (ROM) in electrolyte solutions is crucial to increase the energy density of redox flow batteries and avoid unwanted precipitation. This work discusses how the thermophysical properties and interactions control ROMs' solubility, and describes thermodynamic strategies to increase their solubility in electrolyte solutions. In particular, it shows how introduction of molecular asymmetry and rearrangement of functional groups can decrease the melting temperature and enthalpy, therefore, increasing ROMs' solubility. Furthermore, the ROMs' structural optimization, and addition of co-solvent or additives can improve the solute-solvent interactions, therefore reducing the activity coefficients, and increasing the ROMs' solubility. Employing tools like COSMO-RS for activity coefficient estimation, this study provides a deeper thermodynamic understanding to guide strategies for solubility enhancement of redox active species in electrolyte solutions, crucial for the design of these species for enhancing the battery performance.
Fig. 1 shows one example of asymmetric alkylation strategy applied on quaternary ammonium salts [1], that could can be used to increase ROMs' solubilities. By reducing their melting properties (using Carnelley's rule) without significantly affecting the activity coefficient, this strategy allows a solubility increase to most ROMs on any solvent.



(a) (b)

Fig. 1. Comparison of (a) Melting temperature & activity coefficients, and (b) solubilities in EC/DMC solvent (normal conditions) of salts formed with triethylmethylammonium [N_{2221}] (red) and tetraethylammonium [N_{2222}] (blue) cations, coupled with trifluoromethanesulfonate [Tf], hexafluorophosphate [PF6], tetrafluoroborate [BF4], and hexafluoroarsenate [AsF6] anions [1].

Acknowledgements

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References

[1] Xu, K., M.S. Ding, and T.R. Jow, *Quaternary Onium Salts as Nonaqueous Electrolytes for Electrochemical Capacitors*, **2001**, *148(3),* A267.

Technological potential of aqueous extract from artichoke *(Cynara cardunculus* subsp. *scolymus*) on milk-clotting properties

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Milk coagulation properties provide important parameters for the cheese making process. The coagulation step using chymosin as a rennet is the most used procedure. However, the worldwide increase in the production, encouraging the search for alternative sources. Among the plant-derived enzymes used as coagulants are the aspartic proteases obtained from the extract of cardoon flowers (*Cynara cardunculus* L.). They can also be found in artichoke flowers (*Cynara cardunculus* subsp. *scolymus*), and have a high potential for industrial application. Thus, this study evaluated the technological potential of artichoke flowers (*Cynara cardunculus* subsp. *scolymus*) as milk coagulant. Artichoke flower extracts were obtained and thistle flower extract was used as a reference. The crude extracts were analyzed for protein concentration, proteolytic activity (PA), specificity ratio (SR) and milk clotting activity (MCA) using raw and pasteurized cow milk. The protein content and the PA of the crude thistle extract (3.24 mg mL^{-1}; 58.21 µg mg^{-1}) was higher than that of the crude artichoke extract (2.82 mg mL^{-1}; 47.87 µg mg^{-1}). It should be considered that the artichoke and thistle flowers are of different varieties, which may influence the proteases present [1]. The extract of artichoke flower showed high MCA and SR for raw and pasteurized milk (Table 1). This can be explained possibly by the high concentration of enzymes in the artichoke flower extract. The quantity/concentration of enzymes is one of the decisive factors during the milk coagulation and directly influences the characteristics of the cheese [2]. The properties of the extract can be interfered by variety of flowers, geographical location, stage of ripeness at harvest, or even differences in the enzyme profile, influencing the concentration of coagulation enzymes and, consequently, the coagulation properties of the milk [3]. The specificity ratio is used as an index to evaluate the suitability of an enzyme extract for use as a coagulant in cheese making [4]. In the present study the SR of crude artichoke flower extract for raw milk was higher than the value found by Jesus et al. (2023) [1] for microbial chymosin (26.51) in the study of chemical characterization of aspartic protease from artichoke flower. Thus, the high specificity ratio exhibited by the crude artichoke flower extract, along with its ability to produce milk curd (MCA), make this coagulant an alternative for cheese market, resulting in cheeses with high added value.

	Artichoke extract		Thistle extract	
	MCA / (SU mL^{-1})	SR	MCA / (SU mL^{-1})	SR
Raw Milk	$150,26^{aA} \pm 0,1$	$37,72^{aA} \pm 1,0$	$75,42^{bA} \pm 0,2$	$16,84^{aA} \pm 0,1$
Pasteurized Milk	$92,74^{bB} \pm 0,08$	$20,88^{bB} \pm 1,1$	$85,15^{aB} \pm 0,3$	$18,96^{aB} \pm 0,3$

Table. 1. Milk clotting activity (MCA) and specificity ratio (SR) for artichoke and thistle (mean ± standard deviation).

References

[1] J. C. de Jesus, L. C. C. Reis, M. P. F. Santos, L. S. Santos, S. P. B. Ferrão. Chemical Characterization of Aspartic Protease from Artichoke Flower (Cynara cardunculus L. var scolymus) Using MIR Spectroscopy and Analytical Measurements**.** *Journal of the Brazilian Chemical Society* **2023**, *34*, 1520-1530.

[2] M. Fresno, A. Argüello, A. Torres, N. Castro, S. Álvarez, L. Sepe. Invited review. Milk clotting enzymes: A transcendental decision in goat´s milk cheese quality. *Small Ruminant Research* **2023**, *229*, 107-147.

[3] A. I. Gostin, V. Y. Waisundara. Edible flowers as functional food: A review on artichoke (*Cynara cardunculus* L.). *Trends Food Sci. Technol.* **2019**, *86*, 381-391.

[4] X. Liu, Y. Wu, R. Guan, G. Jia, Y. C. Ma, Y. Zhang. Advances in research on calf rennet substitutes and their effects on cheese quality. *Food Res. Int.* **2021**, *149*, 110704.

Evaluation of clotting properties of crude extracts from cardoon (*Cynara cardunculus* L.) and artichoke (*Cynara cardunculus* subsp. *scolymus*) in sheep and buffalo milk's

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Milk coagulation is a crucial step in cheese-making process and the choice of the coagulating enzyme is fundamental to the yield, texture and flavour. Several enzymes derived from plants are currently available on the market and can be used as coagulants in this process. Vegetable proteases have been studied as milk coagulants and artichoke flower (*Cynara cardunculus* subsp. *scolymus*) has potential coagulant action as a substitute for microbial chymosin [1]. Thus, this study evaluated the coagulation efficiency of crude artichoke flowers extract as a coagulant using raw and pasteurized sheep and buffalo milk. The crude extract was analyzed for protein concentration, and proteolytic activity (PA) as well as the milk-clotting activity (MCA) were determined considering aqueous extracts of thistle flowers (*Cynara cardunculus* L.), as a reference coagulant. The protein content and the PA of the crude thistle extract (3.24 mg mL^{-1}; 58.21 µg mg^{-1}) was higher than that of the crude artichoke extract (2.82 mg mL^{-1}; 47.87 µg mg^{-1}). It should be considered that the artichoke and thistle flowers are of different varieties, which may influence the proteases present [1]. For a protease to be considered ideal for cheese production, it must have low PA and high MCA [2], which was found in the present study both extracts. In general, it was possible to observe that the milk clotting activity was influenced by the type and heat treatment of the milk (Table 1). The extract of thistle flower showed high MCA for raw sheep milk and the artichoke flower extract presented high MCA for both pasteurized samples. It was also possible to observe that regardless the type of extract, there was no statistically significant difference ($p < 0.05$) for raw buffalo milk. The type of protease present in crude plant extracts affects the determination of milk coagulation activity [3] and, consequently, its potential as a substitute for rennet. Several authors have reported on how the type ad composition of milk influence coagulum development and how they affect yield and cheese quality. Significant effects were observed for the type of milk (bovine, ovine and caprine) when cardoon extract was used for milk coagulation [4]. These results demonstrate that artichoke flower may be a alternative as a coagulant with active enzymes for artisanal and industrial cheese production with a consistent clotting efficiency.

	Sheep Milk		Buffalo Milk	
	Raw	Pasteurized	Raw	Pasteurized
Artichoke extract	$759,24^{aA} \pm 0,7$	$622,92^{bA} \pm 0,05$	$286,12^{cA} \pm 0,07$	$244,58^{dA} \pm 0,1$
Thistle extract	$1072,72^{aB} \pm 0,9$	$342,89^{bB} \pm 0,8$	$289,76^{cA} \pm 0,08$	$198,50^{dB} \pm 0,2$

Table. 1. Milk clotting activity (SU mL^{-1}) for artichoke and thistle (mean ± standard deviation).

References

[1] J. C. de Jesus, L. C. C. Reis, M. P. F. Santos, L. S. Santos, S. P. B. Ferrão. Chemical Characterization of Aspartic Protease from Artichoke Flower (Cynara cardunculus L. var scolymus) Using MIR Spectroscopy and Analytical Measurements**.** *Journal of the Brazilian Chemical Society* **2023**, *34*, 1520-1530.

[2] X. Liu, Y. Wu, R. Guan, G. Jia, Y. C. Ma, Y. Zhang. Advances in research on calf rennet substitutes and their effects on cheese quality. *Res. Int.* **2021**, *149*, 110704.

[3] M. A. Mazorra-Manzano, J. M. Moreno-Hernández, J. C. Ramírez-Suarez, M. J. Torres-Llanez, A. F. González-Córdova, B. Vallejo-Córdoba. Sour orange Citrus aurantium L. flowers: A new vegetable source of milk-clotting proteases. *LWT - Food Science and Technology*, **2013**, *54*, 325-330.

[4] M.J. Sousa, F.X. Malcata. Advances in the role of a plant coagulant (*Cynara cardunculus*) in vitro and during ripening of cheeses from several milk species. *Le Lait*, **2002**, *82*, 151–170.

Verifying the authenticity of the ripening time of artisanal Minas cheese using mid-infrared spectroscopy

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Minas Artesanal cheese, typically Brazilian, has been internationally recognized for its sensorial qualities. Recognition of its quality has motivated efforts to ensure safety. However, some producers fail to comply with legislation and sell cheese with a maturation period shorter than that established by law. Determining the maturation time for artisanal Minas cheese is essential, as there is the possibility of microbiological contamination that could pose risks to consumer health [1]. The objective was to verify the authenticity of the ripening time of artisanal Minas cheese using mid-infrared spectroscopy (MIR) combined with multivariate analysis. As a standard, cheeses were collected from 8 producers, matured in their own cheese factories on days 1, 7, 14 and 21 (semi-cured cheese) and 28, 45 and 20 days (cured cheeses), and commercial samples were acquired to evaluate the time of maturation. The samples were analyzed by MIR and the spectra were analyzed by Discriminant Analysis (DA). The spectral profile was similar for both types of cheese, but with different intensities in some bands in the wavenumber ranges between 3500-2800 cm^{-1} (region marked by the presence of hydroxyl and methyl groups) and 1700-800 cm^{-1} (carbonyl), methyl and nitrogen groups, such as amides) (Fig. 1). In DA, the classification percentage was 87.50% (medium matured) and 75% (ripened). In the case of commercial cheese samples, it was found that the ripening time mentioned on the label did not correspond to the actual ripening time in 58% of cases. This indicates that labels are not a reliable indicator of the actual ripening time of these cheeses. The methods used for the tests were effective in distinguishing and categorizing the samples, leading to the conclusion that the commercial samples were probably not authentic with regard to their maturation time.

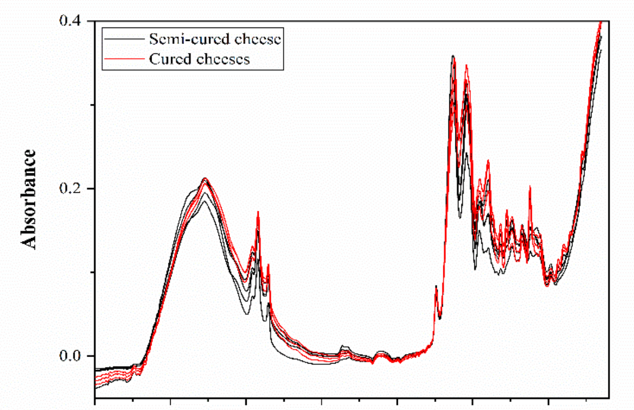

Fig. 1 Spectra of semi-cured and cured cheeses obtained by MIR.

References

[1] J. C. de Jesus, G. J. Silva, B. R. F. Gonçalves, M. R. de Souza, L. S. Santos, S. P. B. Ferrão, *Journal of the Brazilian Chemical Society,* **2020**, *31*, 2000-2011.

Fraud detection in licuri oil by adding soybean oil using thermophysical properties

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The licuri (*Syagrus coronata*) is a fruit native to the Brazilian semi-arid region. It has great socioeconomic and cultural importance for the population. Almonds have a high oil content, about 54% of the almond weight, and are rich in saturated fatty acids [1]. It has been increasingly used for culinary purposes, becoming an important economic product for local extractive communities, presenting high commercial value. Licuri oil can be adulterated with the addition of other oils of lesser commercial value, such as soybean oil, as this mixture is difficult to visually perceive, favoring the fraud process. In this context, the objective was to detect fraud in licuri oil through the addition of soybean oil using thermophysical properties. For this, three repetitions of licuri oil were adulterated with soybean oil at concentrations of 5%, 10%, 20%, 30%, 40% and 50% at different temperatures. To detect fraud, the thermophysical properties of density and viscosity were measured, in addition to the refractive index. Data were analyzed using analysis of variance and factor regression. The results indicated that there was no interaction between the temperature used during the analysis of thermophysical properties and the increase in the concentration of soybean oil ($p>0.05$) in the licuri oil. The changes in density and viscosity in the different concentrations of the adulterant soybean oil were caused by the increase in temperature ($p<0.05$) (Fig. 1), that is, as the temperature range increased, the mixture began to present lower density and viscosity for all concentrations. This variation may have occurred due to the characteristics of the lipids present, the size of the carbon chains and the degree of unsaturation of the fatty acids that differentiate soybean oil from licuri oil. This study indicated that the thermophysical properties and the refractive index did not indicate the adulteration of licuri oil by the addition of other lipid matrices such as soybean oil.

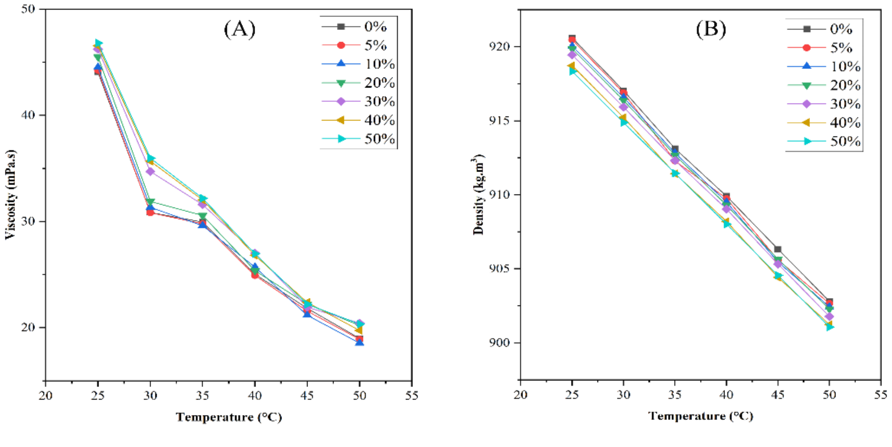

Fig. 1. Dynamic viscosity (A) and density profile (B) of licuri oil prepared with different concentrations of soybean oil.

References

[1] C. P. L. Cavalcanti, T. J. Si. and Macedo, Glayciane C. Gois, V. G. Menezes, A. P. O. do Monte, A. D. da Silva, D. J. M. da Silva, E. O. da Silva, G. G. L. de Araújo, R. T. S. Rodrigues, Á. Wischral, M. H. T. de Matos, M. A. Ávila. *Livestock Science*, **2022**, *256*, 1-6.

Extraction and separation of bioactive peptides from cheeses made with artichoke flower and thistle flower

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Peptides are specific fragments of proteins, which may have bioactive characteristics, including antioxidant properties. In cheese, peptides are formed mainly during ripening, but can be generated in the first few days (10 days) after manufacturing from the residual coagulant in the cheese mass. The objective was to extract, separate and evaluate the functionality of water-soluble peptides (WSP) extracted from cheese produced with artichoke flower and thistle flower coagulants. Cow's milk cheeses were produced using extracts from the artichoke flower and thistle flower as milk coagulants. 10 days after manufacturing the cheese, the WSP extraction process was carried out, where water was used as a solvent and the peptide solution was freeze-dried. The separation was carried out by high-performance liquid chromatography and the compounds present in the WSP were evaluated by mid-infrared spectroscopy (MIR). The functionality of the peptides was performed using the DPPH radical scavenging assay [2].

In Fig. 1A, the chromatograms demonstrate a clear separation between hydrophilic and hydrophobic peptides. The peptides that eluted in the first 30 min are characterized as hydrophilic, and between 35 and 55 min of elution the effective presence of hydrophobic peptides derived mainly from the degradation of α- and β-caseins can be seen [1]. PSA extracted from cheese made with artichoke flowers showed more intense peaks, indicating a higher concentration. In the DPPH test, WSP extracted from cheeses produced with both extracts showed antioxidant action. In MIR (Fig. 1B) it was possible to verify the presence of bands (1641 cm^{-1}, 1546 cm^{-1} and 1444 cm^{-1}) more intense for WSP extracted from cheese produced with artichoke flowers, with bands characterized by Amides I, II and III. All these bands can be useful to study the proteolysis in cheese caused by residual cogulant. The extraction process was efficient in obtaining WSP from cheeses and its separation indicated the presence of hydrophobic and hydrophilic peptides with bioactive capacity.

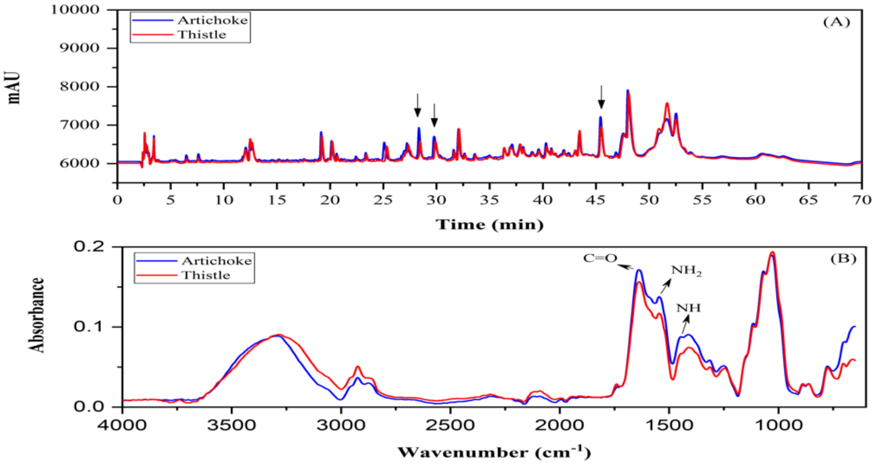

Fig. 1. Chromatograms (A) and MIR spectra (B) of WSP extracted from cheeses.

References

[1] M. Soltani, O.S. Boran, A.A. Hayaloglu. *LWT - Food Science and Technology*, **2016**, *68*, 724-728.
[2] M. L.Timón, A. I. Andrés, J. Otte, M. J. Petrón. *Food Research International*, **2018**, *120*, 643-649.

Study of aspartic proteases from the artichoke flower (*Cynara cardunculus L. var scolymus*) in the formation of buffalo milk curd

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The artichoke (*Cynara cardunculus L. var scolymus*) is native to southern Europe in the Mediterranean region and belongs to the same species as the thistle (*Cynara cardunculus L.*). Studies show that artichoke flower extract is effective as a milk coagulant [1]. These extracts contain aspartic proteases (EC 3.4.23) also known as cardosins/cyprosins or cinnarases, with activities similar to those of animal origin. This study aimed to evaluate the behavior of proteases from artichoke flower extract on the coagulation activity of buffalo milk (MCA).

The effect of pH and temperature on the MCA of artichoke extract and microbial chymosin (as control) was determined following the method of [2]. The pH of the buffalo milk was adjusted by adding lactic acid or sodium chloride, adjusting pH values of 5.8, 6.3, 6.8 and 7.3. The effect of temperature was determined by varying the incubation temperature (30, 40, 50, 60 and 70°C). It can be seen that both chymosin and artichoke extract showed a decreasing linear effect on the MCA in relation to pH (Figure 1a), and as the pH of the milk increased, the MCA decreased. Both showed maximum MCA at pH 5.8, and at pH close to 5.5 the casein micelles tend to come closer together, due to the reduction in their stability by the neutralization of negative charges [3]. The coagulants showed quadratic behavior with temperature variation (Figure 1b), and microbial chymosin showed maximum MCA at 48.5°C and artichoke extract at 50.3°C. The artichoke extract showed MCA results similar to chymosin, an important characteristic to be considered a potential buffalo milk coagulant for cheese production [3].

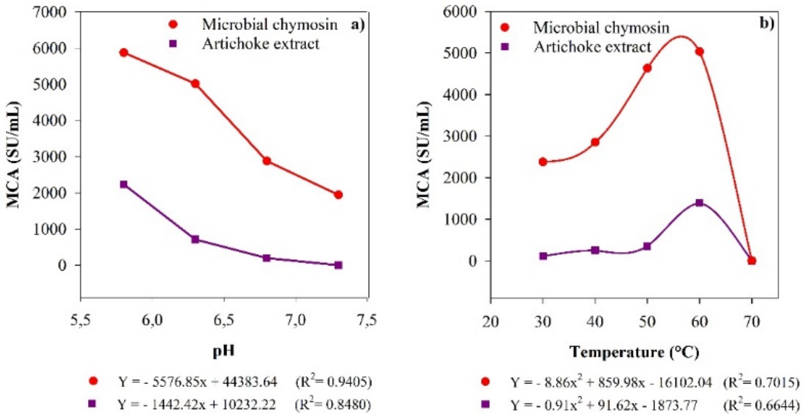

Figure 1. Effect of the change in pH (a) and temperature (b) on the MCA for the coagulants: (•)Microbial chymosin and (■)Artichoke extract, regression model and coefficient of determination (R^2).

References

[1] J. C. Jesus, L. C. C. Reis, M. P. F. Santos; L. S. Santos, S. P. B. Ferrão. *Journal Brazilian Chemical Society*, **2023**, *v. 34*, p. 1520-1530.

[2] N. Bey, H. Debbebi, F. Abidi, M. N. Marzouki, A. B. Salah. *Industrial Crops and Products*, **2018**, *v. 112*, p. 181-187.

[3] M. Britten, H. J. *Giroux. International Dairy Journal*, **2022**, *v. 124*, p 1-12.

Effect of the type of cation on obtaining buffalo milk curd using aspartic proteases from artichoke flowers (*Cynara cardunculus L. var scolymus*)

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Studies carried out on artichoke extract (*Cynara cardunculus L. var scolymus*) describe its technological application in the dairy industry for coagulating milk in cheese production. The extract is made up of aspartic proteases called cardosins, which have activities similar to those of animal origin, chymosin and pepsin [1]. Crude extracts are generally used, making it important to evaluate the milk clotting activity (MCA) under different conditions. This study aimed to evaluate the behavior of proteases from artichoke flower extract in MCA using buffalo milk and different concentrations of NaCl and $CaCl_2$. The effect of the concentrations of NaCl (0, 500, 1000, 1500 and 2000 mmol) and $CaCl_2$ (0, 20, 60, 100 and 140 mmol) on the MCA of the artichoke extract was determined following the method of [2]. Table 1 shows that the samples differed significantly ($P < 0.05$) according to Tukey's test for the salt concentrations used in the MCA. For NaCl concentrations there was an increase in MCA with increasing concentration and in concentrations above 1000 mmol there was no difference. For $CaCl_2$ there was no significant difference at lower concentrations, but there was an increase in MCA at concentrations above 60 mmol. The addition of NaCl to milk promotes the dissociation of calcium and phosphate from the casein micelles, affecting the colloidal state of the milk and also the coagulating action. NaCl contributes to lowering the pH of the milk, increasing the hydration of the casein and reducing the zeta potential of the milk, decreasing the coagulation time, resulting in a higher MCA. The addition of $CaCl_2$ to milk increases the concentration of calcium in its ionic form (Ca^{2+}) and also of colloidal calcium phosphate, also causing a decrease in pH due to the reaction of Ca^{2+} ions with sodium phosphate salts, releasing H^+, resulting in an increase in MCA with an increase in $CaCl_2$ concentration. [3]. It can be concluded that the use of adequate concentrations of NaCl and $CaCl_2$ favors the formation of buffalo milk curd by proteases from the artichoke extract.

Table 2. Mean values and standard deviations of the effect of different concentrations of NaCl and $CaCl_2$ on the coagulation activity of buffalo milk (MCA) with artichoke extract.

	NaCl (mmol)				
	0	**500**	**1000**	**1500**	**2000**
MCA (SU/mL)	165.3±10.4^{a}	209.6±1.2^{b}	240.21±6.1^{c}	239.9±2.4^{c}	244.3 ±14.2^{c}
	$CaCl_2$ (mmol)				
	0	**20**	**60**	**100**	**140**
MCA (SU/mL)	162.8±9.2^{a}	185.0±11.6^{a}	231.1±20.0^{ab}	289.9±50.9^{b}	408.9±19.0^{c}

^{a,b} Results followed by the same letter in line do not differ ($P > 0.05$) by the Tukey test.

References

[1] M. Esposito, P. Di Pierro, W. Dejonghe, L. Mariniello, R. Porta. *Food Chemistry*, **2016**, *v. 204*, p. 115-121.
[2] N. Bey, H. Debbebi, F. Abidi, M. N. Marzouki, A. B. Salah. *Industrial Crops and Products*, **2018**, *v. 112*, p. 181-187.
[3] J. C. Jesus, L. C. C. Reis, M. P. F. Santos; L. S. Santos, S. P. B. Ferrão. *Journal Brazilian Chemical Society*, **2023***, v. 34*, p. 1520-1530.

Poster Communication I-P50: Tuesday, September 10th, 16:40h - 18:00h

Effect of the presence of hydrocolloids on the thermal properties of yogurt

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Starches are hydrocolloids commonly added to yogurts, acting as a thickener and stabilizer of colloidal suspensions to increase the strength and viscosity of the gel [1]. The aim was to apply Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) to identify the influence of the addition of starch on thermal events in yogurts. Five yogurt formulations were produced with different concentrations (0%, 0.5%, 1.0%, 1.5% and 2.0%) of two types of corn starch (AM1 and AM2) with different amylose content and analyzed on the day of production. The DTA curves showed the formation of two endothermic peaks for AM1 (72.45 °C and 91.48 °C) and AM2 (61.04 °C and 83.28 °C), which can be related to the order-disorder phase transition related to gelatinization and the nucleation process of the amylose crystals [2,3]. For the yogurts produced without added starch, an endothermic peak was observed at 106.50 °C, with behavior similar to that shown by the curves of the treatments using the addition of AM2. However, the intensity of the peaks increased as the AM2 content increased. The TGA curves showed the occurrence of three stages of mass loss in the yogurts produced with different concentrations of starch, where the second stage was more intense and may be associated with the removal of water from the casein micelles [2]. It was possible to distinguish the two types of starch and their different concentrations, indicating that thermal analysis is an efficient tool for detecting the presence of starch in yogurts.

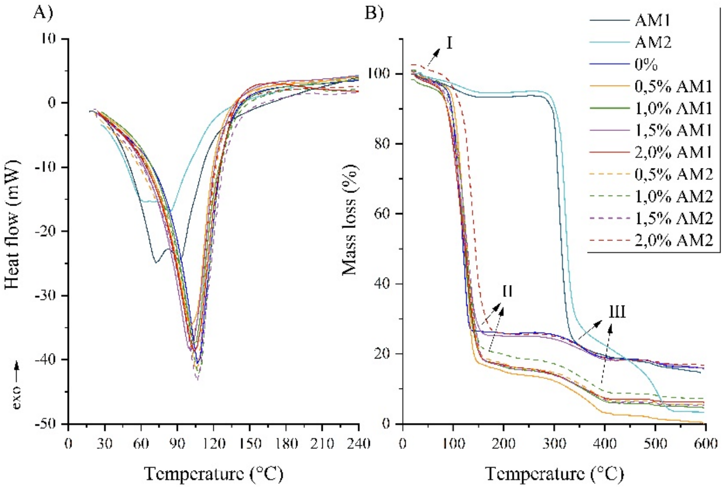

Fig. 1. DTA (A) and TGA (B) curves of pure starches (AM1 and AM2) and yogurts produced with different concentrations of starch.

References

[1] Wong S. S., Wicklund R., Bridges J., Whaley J., Koh Y. B. Starch swelling behavior and texture development in stirred yogurt. *Food Hydrocolloids* **2020**, *98*.
[2] Kaletunç G. *Calorimetry in Food Processing Analysis and Desing of Food Systems*, Wiley-Blackwell and the Institute of Food Technologists. Iowa, USA (2009).
[3] Zhao Y., Khalesi H., He J., Fang Y. Application of different hydrocolloids as fat replacer in low-fat dairy products: Ice cream, yogurt and cheese. *Food Hydrocolloids* **2023**, *138*.

Isothermal liquid – vapor equilibria in ternary systems of (2,2,2 – trifluoroethanol + ethanol) and (2,2,2 – trifluoroethanol + 1-propanol) at 323.15K.

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Experimental liquid – vapor equilibria for binary systems consisting in (2,2,2-trifluoroethanol + ethanol) and (2,2,2-trifluoroethanol + 1-Propanol) were determined at 323.15 K. The experimental liquid – vapor data were correlated together with available activity coefficients at infinite dilution γ_i^∞ using the NRTL, Wilson, Van Laar , Margules and UNIQUAC models and the relative van der Waals volume and surface area parameters r and q estimated by the Bondi method. Parameters of several g^E-models were fitted to the experimental data and the reproducibility of the data with the g^E-models was checked. New UNIQUAC -parameters for the alcohol - 2,2,2-trifluoroethanol interaction are reported.Trifluoroethanol is a better proton donor and it have strong electronegative inductive effects of the fluorine atoms which reduces the ability of the oxygen atom to act as a potential acceptor for hydrogen bonding with other solvents, and makes the hydrolytic hydrogen atom considerably more acidic than the corresponding hydrogen atom in the hydrocarbon alcohols. The minimum values of excess Gibbs energy for alcohols + 2,2,2-trifluoroethanol binary systems are in the following order: 1-Propanol >TFE >Ethanol.The standard deviations obtained from correlations in binary systems agree well with those used for the data reduction .[1-3] This means the binary data are thermodynamically consistent.

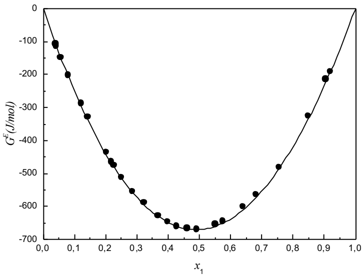

Fig 1. Molar excess Gibbs function diagram: ●,(TFE (1) + Ethanol (2)); ─,Van Laar equation

References

[1] Atik, Z., Densities and Excess Molar Volumes of Binary and Ternary Mixtures ofaqueous solutions of 2,2,2-trifluoroethanol with acetone and alcohols at a temperature of 298.15 K and pressure of 101 kPa., J. Solut. Chem., **2004**,33, 1447.

[2] Atik, Z.;Lourdani, K., Volumetric Properties of Binary and Ternary Mixtures of DiisopropylEther,α,α,α– Trifluorotoluene, 2,2,2 – Trifluoroethanol and Ethanol at aTemperature 298.15 K and Pressure 101 kPa.,J. Chem. Thermodyn. **2007,** 39, 576-582.

[3] Atik, Z.,Experimental Isobaric Vapor-Liquid Equilibria of Binary Mixtures of 2,2,2Trifluoroethanol with Benzene or Toluene. J. Chem. Eng. Data, **2007**, 52, 1086- 1088

Ionic liquids and eutectic solvents for the extraction of gelatine from fish skin: fundamental studies

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As the demand for seafood rises globally, so does the production of associated residues, which are rich in valuable components such as proteins, minerals, and bioactive compounds. The valorisation of these by-products represents a primary challenge facing the fishery and aquaculture industry, addressing both environmental and economic challenges. Specifically, the extraction of gelatine represents a significant opportunity for the valorisation of fish skin, since it is a versatile material with numerous applications in different fields.

Conventional methods to obtain gelatine have several disadvantages such as the use of harsh chemicals, elevated energy requirements, environmental concerns, and low-quality products. In this context, ionic liquids (ILs) and eutectic solvents are emerging as promising alternatives to overcome these problems. One of the main advantages of these solvents is their tunability. It is possible to select either the cations or anions in the ILs, or the constituent compounds in the case of eutectic mixtures, based on the desired application. In this work, three ILs (1-ethyl-3-methylimidazodium acetate, 1-hexyl-3methylimidazolium acetate, and 1-ethyl-3-methylimidazodium propionate) and the eutectic solvent constituted by urea and sodium acetate trihydrate, have been proposed for the recovery of gelatine from the skin of yellowfin tuna. All of them were selected because the basic character of the anion makes them suitable for breaking the hydrogen bonds of the target molecule and thus enhancing the process of extraction [1]. In the case of the eutectic mixture, the solid-liquid equilibrium was determined by differential scanning calorimetry (DSC) in order to select the correct composition (eutectic) of the solvent to be used in the application.

As preliminary studies, the solubility of the most representative gelatine-forming amino acids was determined in [C_2mim][OAc], [C_6mim][OAc], [C_2mim][OPr] and in the eutectic mixture (constituted by urea and sodium acetate trihydrate in a 60:40 molar ratio), as well as in their 50 wt% mixtures with water [2,3]. The classic van't Hoff model was satisfactorily applied to model the solubility data at different temperatures, and a thermodynamic analysis was performed to obtain the apparent properties of dissolution. In all cases, the dissolution of amino acids was endothermic and enthalpy-driven. Furthermore, the results showed encouraging values of solubility for glycine, L-proline and *trans*-4-hydroxy-L-proline, which are the main constituting amino acids of gelatine.

Due to these promising results, the aforementioned solvents were tested as pretreatment agents for the extraction of gelatine from yellowfin tuna skin, yielding different products with a wide spectrum of properties. These findings point to the consideration of these solvents as an alternative and more sustainable approach for the revalorisation of fish by-products.

References

[1] K. Dong, S. Zhang, *Chemistry-A European Journal* **2012**, *18*, 2748–2761.
[2] C. Gallego, H. Rodríguez, A. Soto, *International Journal of Molecular Sciences* **2023**, *24*, 1550.
[3] P. Souto-Montero, E. Rodil, A. Soto, *Fluid Phase Equilibria* **2024**, *582*, 114075.

Physicochemical and rheological characterization of different compositions of deep natural eutectic solvents for application in biomolecule extraction

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Natural deep solvents (NADES) have currently attracted a lot of attention as a promising green technology in the food sector, as they present several advantages when compared with conventional solvents. They are usually liquids with adjustable viscosity when mixed in a certain molar ratio. The objective of the work was to characterize 5 different types of NADES with the purpose of exploring their parameters physical chemistry and rheological to optimize the extraction of biomolecules and bioactive compounds. 5 types of NADES were prepared, their compositions and molar proportions are, respectively: (A) betaine, citric acid, glucose and water (1:1:1:5); (B) choline chloride, citric acid, glucose, water (2:1:1:2); (C) citric acid, glucose, water (1:1:5); (D) choline chloride, lactic acid, glucose (1:1:1); (E) choline chloride, glucose (2:1). Density analyzes were carried out (Anton Paar DMA 5000), viscosity (Brookfield DV-II+ Pro), refractive index (Quimis ABBE digital refractometer), both analyzes were carried out at 5 different temperatures (20, 25, 30, 35, 40 °C). The activation energy values (E_a) were obtained using equation Arrhenius-Guzman. Finally, Fourier Transform Infrared Spectroscopy (FTIR) (Agilent Cary® 630), using the spectral range of 4000 to 500 cm^{-1}. The solvent samples presented density values that varied from 1272.04 kg/m^3 to 1401.91 kg/m^3 according to the applied temperature. The solvents showed the behavior of the Newtonian fluid and presented viscosity values dependent on the temperature observed, decreasing considerably with the increase of the same. The most viscous solvent (C) presented values of 16397 cP at 20°C and the least viscous (B) 854.31 cP at 40°C. The refractive index of the samples varied between 1.456 (40°C) and 1.498 (20°C). The behavior of solvents confirms the influence of temperature on physical-chemical and rheological parameters, which is already scientifically known and reported by works such as [1]. E_a values decreased with increasing temperature, varying from 13.704 kJ.mol^{-1} (40°C) for solvent A and 23.653 kJ.mol^{-1} (20°C) for sample C, with correlation coefficient R^2 >0.99 for all solvents. Increasing temperature increases the kinetic energy of particles, increasing the number of effective shocks and the speed of reactions. In the FTIR analysis, the spectral behavior of four main peaks was noted, located in the regions of 3291.21; 2896.97; 1696.41 and 1061.57 as shown in figure 1, representing vibrations of functional groups (O-H), (C-H), (C=O) and (C-O) respectively. From this study, it was founded that the properties physical and rheological properties of solvents depend on temperature and this information, together with FTIR results, can contribute to subsequent extraction processes.

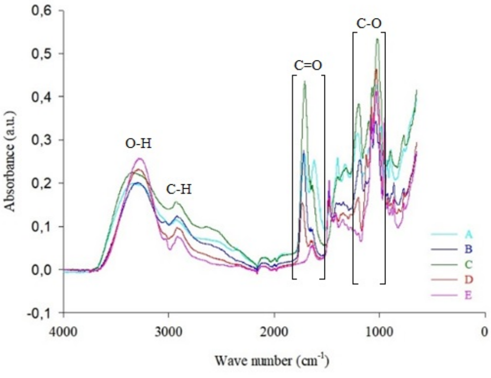

Fig. 1. FTIR solvent spectra

References

[1] T. Raj, V. Singh. Natural deep eutectic solvents (NADES) assisted deconstruction of oilcane bagasse for high lipid and sugar recovery. Industrial Crops and Products, v. 210, p. 118-127, 2024.

Liquid-liquid and liquid-vapor modeling for fuel fractionation from pyrolysis-derived bio-oil

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The bio-oil from biomass pyrolysis is a multicomponent complex system, containing carboxylic acids, aldehydes, alcohols, ketones, esters, furans, phenols, guaiacols, syringols and other lignin derivatives. The effective bio-oil fractionation is decisive to obtain fractions and compounds with high added-value and industrial application. The separation process involves generally liquid-liquid and liquid-vapor equilibrium. This work presents a study of the modeling and simulation of the fractionation process of a slow pyrolysis bio-oil resolved by inert atmosphere distillation and solvent extraction operations. The bio-oil fractions show upgraded properties and high added value in relation to the original bio-oil. The kinematic viscosities were 2.16 $mm^2 \cdot s^{-1}$ for extract fraction from n-butanol extraction, 0.36 $mm^2 \cdot s^{-1}$ for the extract fraction from chloroform extraction, 0.60 $mm^2 \cdot s^{-1}$ for the extract fraction from n-heptane extraction, and 0.81 $mm^2.s^{-1}$ for the raffinate fraction from n-heptane extraction, all measured at 40 ºC. A process simulation was built using Aspen Plus. The model simulation allows describe the non-ideal phase separation and the main fuel properties of bio-oil fractions. The high heat values of bio-oil fractions were ranging from 25 to 55 $kJ \cdot g^{-1}$. The properties of the final bio-oil fractions enable them to be used as an alternative replacing for conventional fuels. A single mixture rule was applied to determine the fuel properties of blends of fractions. The adequate blending of the bio-oil fractions can result in a stable fuel for application in combustion devices.

Interactions of metamizole and polyethylene glycol (PEG 200) in water: A thermodynamic study

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In order to verify possible effects of the interactions of painkiller with polyethylene glycols, experimental data for density and speed of sound of metamizole (dipyrone) in polyethylene glycol solutions (PEG200) were determined at different temperatures and concentrations and at atmospheric pressure ($p = 92{,}3$ kPa). Densities and sound velocities of the solutions were obtained using a Density and Sound Velocity Analyzer, manufactured by Anton Paar (Model DAS 5000). The solutions were prepared at concentrations of $m \approx (0.1 - 0.7)\ \mathrm{mol{\cdot}kg^{-1}}$ in pure water and in solutions of polyethylene glycols with a concentration of $m = (0.025;\ 0.050;\ 0.075 \text{ and } 0.100)\ \mathrm{mol{\cdot}kg^{-1}}$. Data were determined at temperatures $T = (283.15;\ 288.15;\ 293.15;\ 298.15 \text{ and } 303.15)$ K. From the experimental results of density and speed of sound, the following thermodynamic properties were calculated: the apparent molar volume, the partial molar volume at infinite dilution, the partial molar volume of transfer of dipyrone from water to the PEG solutions, the apparent molar isentropic compressibility, the partial molar isentropic compressibility at infinite dilution and the partial molar transfer isentropic compressibility of dipyrone from water to the PEG solutions. The behavior of the volumetric and acoustic properties at infinite dilution leads to the assumption of weak solute-solute interactions and strong solute-solvent interactions.

Establishing the foundation for the description of aqueous polyether systems: temperature dependent hydrogen bond energies

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Polyethers are versatile compounds used in various industries, including cosmetics and pharmaceuticals [1]. However, their application in aqueous systems, such as lubricants and biphasic systems, rely heavily on a precise understanding of their thermodynamic behavior and phase equilibria [2-3]. Traditional models like UNIFAC, commonly applied in such analyses, lack the capability to adequately account for the complex interactions between water and ethers. More recently, significant advances were achieved by using realistic polymer conformers derived from molecular dynamics simulations in conjunction with COSMO-RS [4]. Despite these results, challenges persist. One notable limitation of COSMO-based models is their inability to accurately predict the Gibbs excess temperature dependence for ether-water systems [5], which is particularly important for liquid-liquid equilibrium (LLE) predictions. In this work, the specific interactions between ethers and water are investigated. It is found that infinite dilution activity coefficient (IDAC) data of ether/water systems can only be described with specific hydrogen bond parameters as a function of temperature. A total of 214 experimental IDAC data points, of different ethers diluted in water, were used to fit the parameters in a COSMO-SAC implementation. The results show significant improvements in describing the temperature dependance of the Gibbs excess energy in the water-rich region, but this parametrization still fails in precisely describe the LLE for these systems. Hence there are still open questions to be answered for the prediction of aqueous polyether systems.

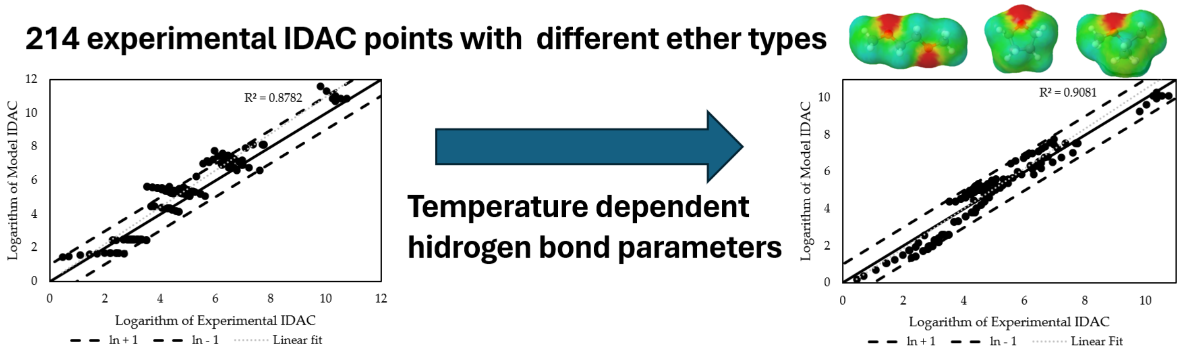

Fig. 1. Impact of Temperature-Dependent Hydrogen Bonding Parameters on ether/water IDAC.

Acknowledgments

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References

[1] A. A. D'souza, R. Shegokar, *Expert Opinion on Drug Delivery* **2016**, 13, 1257-1275
[2] A. Gangopadhyay, J. Cuthbert, *Lubricants* **2018**, 6, 72.
[3] H. Bakhshi, P. Mobalegholeslam, S. A. Mosavi, *Chemical Thermodynamics and Thermal Analysis* **2023**, 10, 100113
[4] G. M. C. Silva, D. A. Pantano, S. Loehlé, J. A. P. Coutinho, *Industrial & Engineering Chemistry Research* **2023**, 62, 20936-20944.
[5] R. P. Soares, P. B. Staudt, *Fluid Phase Equilibria* **2024,** 114113.

Effect of the addition of activated carbon in green plantain starch bioplastic water resistance properties

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The bioplastic produced from starch is a packaging alternative for food known for its advantages, such as being renewable, biodegradable, non-toxic, and aligned with new sustainability trends. However, its high hygroscopicity and sensitivity to water limit its use, requiring processes and additives to make it viable [1]. To this end, bioplastics were developed from green plantain starch, both native and modified by hydrothermal treatment (HMT), with the addition of activated carbon (AC) derived from corn cob, activated with phosphoric acid, executed according to Santos et al. (2020) [2]. Starch was extracted from green plantain in a 0.03 mol L^{-1} ammonia hydroxide solution at a ratio of 1:7 (pulp/solution) [3]. The starch was subjected to HMT under two modification conditions (M1 - 19% moisture, 19.5 hours, 88°C; M2 - 25% moisture, 23.92 hours, 100°C) [4]. Bioplastics were produced by the casting method, where 250 mL of solution containing 3% native and HMT-modified starch, 40% glycerol (w/w), and AC varying from 0.2 to 0.5% (w/w), were prepared and poured into glass containers measuring 22.5 cm x 32.5 cm, and dried in a forced air circulation oven at 40°C for 40 hours [4]. The bioplastics were evaluated for solubility (S) according to Gontard et al. (1994) and water vapor permeability (WVP) according to method E96/ ASTM (2016) [5-6], and the results were subjected to regression analysis and analysis of variance (Tukey), considering $p < 0.05$, which are presented in Table 1.

	N	**N 0,2**	**N 0,3**	**N 0,4**	**N 0,5**	**M1**	**M1 0,2**	**M1 0,3**	**M1 0,4**	**M1 0,5**	**M2**	**M2 0,2**	**M2 0,3**	**M2 0,4**	**M2 0,5**
WVP	0,81 ±0,07 **a**	0,77 ±0,05 **a**	0,67 ±0,06 **ab**	0,56 ±0,04 **bc**	0,45 ±0,05 **cd**	0,45 ±0,06 **cd**	0,37 ±0,03 **cd**	0,44 ±0,02 **cd**	0,41 ±0,05 **cd**	0,45 ±0,02 **cd**	0,36 ±0,01 **d**	0,43 ±0,07 **cd**	0,55 ±0,03 **bc**	0,46 ±0,07 **cd**	0,49 ±0,01 **cd**
S	17,67±0,92 **a**	16,77±1,58 **a**	15,28±0,50 **a**	17,72±1,24 **a**	15,25±1,88 **a**	18,40±1,45 **a**	16,09±0,73 **a**	17,82±3,08 **a**	14,78±3,08 **a**	14,79±0,36 **a**	14,13±1,39 **a**	15,95±1,28 **a**	14,59±1,13 **a**	15,95±0,46 **a**	13,24±2,87 **a**

Table 1 – Water vapor permeability and solubility results expressed as WVP (g water. mm·day^{-1}m^{-2}·kPa^{-1}) and S = Solubility (%), respectively.

The solubility of the films did not show significant differences, ranging from 13.24%±2.87^{a} in the film with M2 starch and 0.5% AC to 18.40±1.45^{a} in the film with M1 starch without AC. The WVP showed significant differences, from 0.81±0.07^{a} g water.mm.day^{-1}m^{-2}·kPa^{-1} for the native starch film without AC to 0.45±0.05^{cd} g water.mm.day^{-1}m^{-2}·kPa^{-1} with the addition of 0.5% AC. Films produced with modified starch had reduced WVP compared to native starch but without a direct correlation with AC addition (M1 0.2% AC 0.37±0.03^{cd}; M2 0.36±0.03^{d}). Therefore, the addition of AC in native starch films significantly decreased WVP, and the M2-modified starch without AC had the lowest value found. It can be taken from this work that for bioplastics produced from native starch, AC could contribute to decreasing WVP. For bioplastics that require higher WVP barrier properties, it is recommended to perform hydrothermal modification, especially with M2 parameters, which have already demonstrated efficiency in increasing the WVP barrier [4]. These findings were relevant for future study foundations.

References

[1] Z Lin et al., *Food Hydrocolloids* **2024**, *151*, 109860.
[2] M. P. F. Santos et al., *The Canadian Journal of Chemical Engineering* **2020**, *98*, 1501-1511.
[3] M. J. M. Cordeiro et al., *Food Technology and Biotechnology* **2018**, *56*, 506-515.
[4] E. B. M. Viana et al., *Food Packaging and Shelf Life* **2022**, *31*, 100776.
[5] N. Gontard et al., *International Journal of Food Science & Technology* **1994,** *29*, 39-50.
[6] ASTM, Standard Test Method for Water Vapor Transmission of Materials, ASTM International, West Conshohocken PA (2016).

Poster Communication II-P8: Wednesday, September 11th, 16:40h - 18:00h

Study of cholinium chloride-based ABS through phase separation hydrodynamics

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Aqueous Biphasic Systems (ABS) have been extensively studied as an efficient extraction platform for distinct (bio)molecules [1]. Despite all their advantages, the industrial use of ABS is still limited due to the poor understanding of the partition/separation mechanisms, few predictive models, incompatibility with current extraction equipment/facilities, and lack of large-scale studies [2]. For that purpose, the phase separation hydrodynamics of three ABS composed of PPG-400/[Ch]Cl, [Ch]Cl/K_3PO_4 and [Ch]Cl/K_2HPO_4 was studied by correlating the mixing time (T_m) and the phase settling time (T_s), at 25 ºC and 50 ºC. The results showed that T_s is independent of T_m, being very long for the polymer/salt ABS ($T_s > 6$ h) and very fast for salt/salt ABS ($T_s < 150$ s). The enhanced separation hydrodynamics of the salt/salt ABS is directly related with the salting-out effect of the inorganic salt. The phases' density was the most important physicochemical property in ABS' formation. A best biphasic region of operation was defined for [Ch]Cl/salt-based ABS, where the LLE should be designed if aimed the industrial implementation of these types of systems using conventional mixer-settler units.

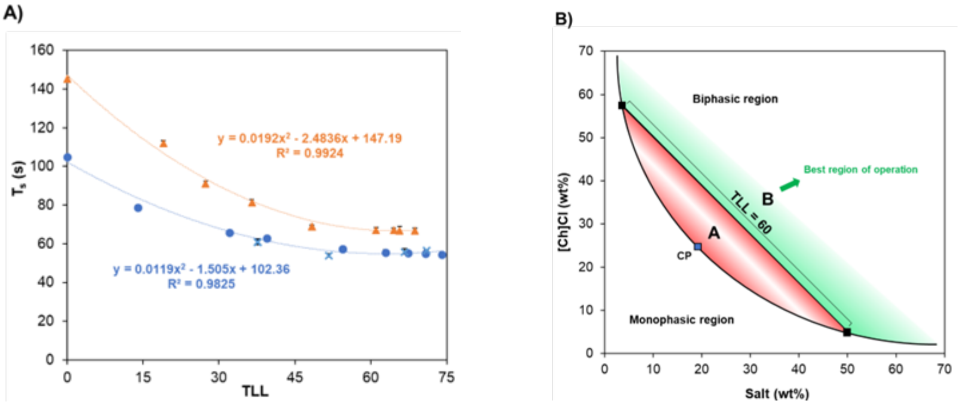

Figure 1. *T_s values as a function of TLL at 25 ºC (A) (● – mixture points of [Ch]Cl/K_3PO_4; (▲– mixture points of [Ch]Cl/K_2HPO_4; × – mixture points from Shahrihari et al. [3]; and generic best region of operation for the studied [Ch]Cl-based ABS. Adapted from [4].*

Acknowledgements

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References

[1] J. F. B. Pereira and J. A. P. Coutinho, Aqueous Two-Phase Systems, in Liquid-Phase Extraction, Elsevier, 2020, pp. 157–182, https://doi.org/10.1016/B978-0-12-816911-7.00005-0
[2] J. F. B. Pereira, M. G. Freire, and J. A. P. Coutinho, Aqueous two-phase systems: Towards novel and more disruptive applications, Fluid Phase Equilib., vol. 505, p. 112341, Feb. 2020, https://doi.org/10.1016/j.fluid.2019.112341
[3] S. Shahriari, L. C. Tomé, J. M. M. Araújo, L. P. N. Rebelo, J. A. P. Coutinho, I. M. Marrucho and M. G. Freire, Aqueous biphasic systems: a benign route using cholinium-based ionic liquids, RSC Adv., vol. 3, no. 6, pp. 1835–1843, 2013, https://doi.org/10.1039/C2RA22972B
[4] A. M. S. Jorge, J. A. P. Coutinho, J. F. B. Pereira, Hydrodynamics of cholinium chloride-based aqueous biphasic systems (ABS): A key study for their industrial implementation, Sep. Purif. Technol., vol. 320, p. 124183, https://doi.org/10.1016/j.seppur.2023.124183

Density and Speed-of-Sound Data by Experimental and Molecular Simulation Measurements of Propionate-Based Protic Ionic Liquids: [DEA][Pr] and [BA][Pr]

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Due to their unique properties, the research about synthesis and utilization of protic ionic liquids (PIL) have received significant attention. However, the number almost illimited of possible PIL leads to a difficult to synthetize and measure all the thermophysical properties. As an alternative, it is desirable to obtain these properties previously the synthesis. The molecular simulation is a powerful tool to accomplish that task. However, the accuracy is attached to the quality of the force field used to represent the fluids involved in the phenomena. Unfortunately, there is not available yet general force fields to describe the protic ionic liquids. The development of force field relies in the validation through experimental data comparison. Therefore, this work realized measurements of density and speed-of-sound of two PILs: diethylammonium propionate [DEA][Pr] and n-butylammonium propionate [BA][Pr] in temperature range from 293-323K, in order to evaluate a general force field that has being under development by the group. Density and speed-of-sound of gravimetric aqueous solutions in the entire composition range were acquired in an Anton Paar DSA5000. The results obtained by molecular simulation using the developed force field for the PILs are in very good agreement with experimental data obtained in this work for [BA][Pr] and also with previous experimental data reported in literature [1]. Good results were also found for [DEA][Pr]. The molecular simulation density predictions for this PIL are closer from those values reported in literature (~0.5%) while present an average deviation of 3.3% related to experimental data obtained in this work. Some results are presented in Figure 1.

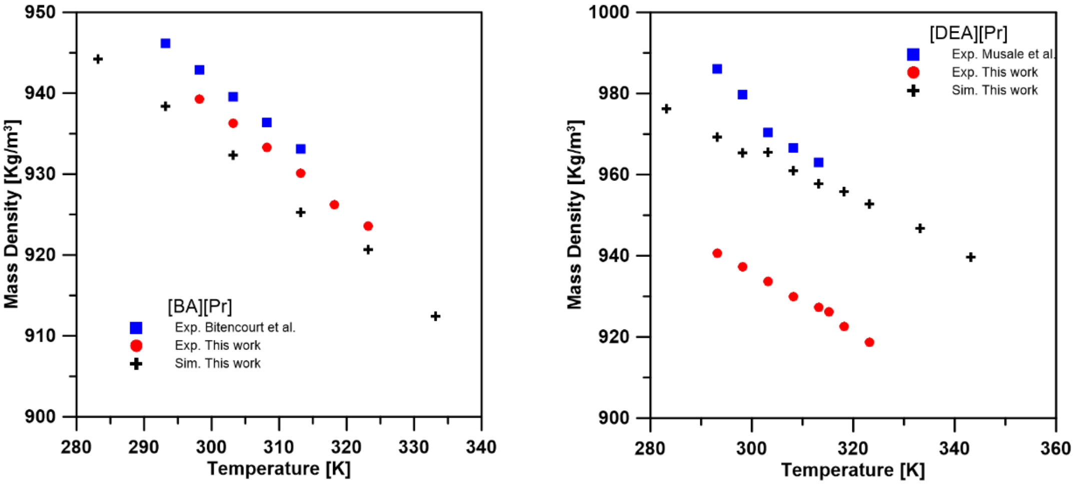

Figure 1. Density of [BA][Pr] and [DEA][Pr] versus temperature.

References

[1] Musale et al. J..Chem..Eng..Data, 2018, 63, 1859−1876
[2] Bittencourt et al, *J Therm Anal Calorim, 2019,* 135, 2519–2539.

Thermodynamic Principles Applied to Energy Industry Climate Effects

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Using the Gibbs concept of state functions to define the first and second laws of thermodynamics, we analyse the effects of changes in atmospheric average temperatures and pressures arising from anthropogenic emissions of enthalpy and water, besides CO_2, into the atmosphere. An application of the Hess-Gibbs 1st law of thermodynamic equilibrium (H is a state function) shows that the enthalpy (H) output from fossil fuel consumption is seven times greater than the H-increase of the global warming index (GWI) of 0.0175K/year that has given rise to the greenhouse gas hypothesis (GGH).

The Joule-Mayer 1st law of irreversible thermodynamics (conservation of energy) shows there is a level of inherent uncertainty, in any multivariate computer model of the global energy budget, which is more than 1000 times the experimental enthalpy flux associated with the GGH. The Carnot-Gibbs 2nd law of thermodynamic equilibrium: entropy and Gibbs energy of water are state functions if its concentration is a well-defined state variable. Here, this concept is used to assess the effect of water vapour output from fossil fuels on climate-change hypotheses (CCH): we report that is not negligible.

We assess the global effects of endothermic photosynthesis processes in the biospheres land and ocean sinks which, in accord with Le Chatellier principle of Gibbs chemical equilibrium, are enhanced by the anthropogenic increases in both $[CO_2]$ and $[H_2O]$ in the atmosphere. Whereas the long-term effect of the ocean sink may be negligible due to its massive heat capacity, we report evidence of an endothermic effect upon biosphere land areas, which offsets the enthalpy output from the energy industry to a significant extent.

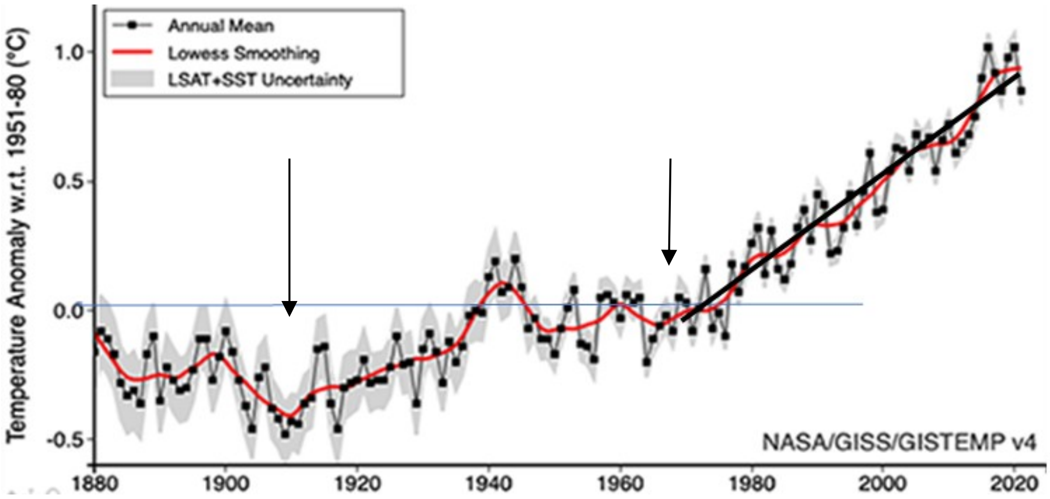

Fig.1 Global warming index (GWI) from 1850 to 2023: the present annual rate of increase average temperature <ΔT> (GWI) per year is 0.0175 ± 0.0005 K. The smoothed fluctuations with a periodicity of 4-5 years arise from solar system planetary insolation effects; the present total warming effect, since zero, in 1970 is 0.875 K. The arrows mark the timeline changes from coal to oil to gas. https://data.giss.nasa.gov/gistemp/

Reference

[1] I. Khmelinskii and L. V. Woodcock, On earth system dynamics hypothetical "greenhouse effect", Global Journal of Ecology, 2024, 9 (1) 042-050 https://dx.doi.org/10.17352/gje.000095/

Vapor-Liquid Equilibrium Measurements and Cubic-Plus-Association (CPA) Modeling of Triethylene Glycol Systems

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Triethylene glycol (TEG) is a very relevant chemical in the oil and gas industry nowadays as it is used in about 95% of the natural gas dehydration units [1]. However, despite the importance of measurements of physical and thermodynamic properties for the process design of these facilities, there is still a lack of TEG-related data sets available in the open literature and some of the published data are questionable. For the binary TEG + Methane, for example, the TEG concentration in the methane vapor phase reported by Jerinić et al. [2] and in our previous work [3] is in considerable disagreement. It is important to note that the experimental mole fractions of TEG in the vapor phase for this binary system are extremely low, with measurements in the order of ppm. These concentrations pose a significant challenge in the experimental procedure, requiring a meticulously designed setup and procedure for accurate sampling and analysis. Nevertheless, another possible cause for the discrepancies found between Jerinić's dataset and ours is the presence of water in our system. Burgass et al. [4] have shown that even low concentrations of water cause great interference in TEG + Methane phase equilibria. In this context, we have measured new vapor-liquid-equilibrium (VLE) data for the binary TEG-Methane using pure glycol at 323.15 K and pressure ranging from 5.0 to 18.0 MPa. We have also measured new VLE data for TEG-Ethane using pure TEG and a TEG aqueous solution (95.2 wt.% or 70.1% in molar basis) at 3.0 and 4.0 MPa from 293.17 K to 303.19 K. The solubility of a gas mixture rich in ethane, propane, and CO_2 in pure TEG was also studied in the 303.15 K to 333.15 K temperature range at 14.0 and 18.0 MPa. From the thermodynamic modeling point of view, the Cubic-Plus-Association (CPA) equation of state has been showing good performance for natural gas dehydration applications. In essence, the model keeps the relative simplicity of the Cubic's, ideally suitable to describe interactions between alkanes, while specific interactions between molecules such as water and glycols, are accounted for by the association term. In our recent works, we have also discussed different association schemes for TEG within the CPA framework. It was concluded that the assumption of TEG as a self-associating fluid by the well-known 4C association scheme (where two proton donors and two proton acceptors are assumed on every molecule) previously estimated by Derawi et al. [5] is the best option when applying CPA. This set of parameters is, therefore, the one used for correlating the experimental data generated in this work.

References

[1] A.K. Mostafazadeh, M.R. Rahimpour, A. Shariati. J. Chem. Eng. Data. 54 (2009) 876–881. https://doi.org/10.1021/je800675u.
[2] D. Jerinić, J. Schmidt, K. Fischer, L. Friedel. Fluid Phase Equilib. 264 (2008) 253–258. https://doi.org/10.1016/j.fluid.2007.11.017.
[3] J. Trancoso, D. Qvistgaard, M. V. Danielsen, E. Panteli, E. Solbraa, G.M. Kontogeorgis, N. von Solms. J. Chem. Eng. Data. 68 (2023) 127–137. https://doi.org/10.1021/acs.jced.2c00597.
[4] R. Burgass, A. Reid, A. Chapoy, B. Tohidi. GPA Midstream Conv. (2017) 12.
[5] S.O. Derawi, M.L. Michelsen, G.M. Kontogeorgis, E.H. Stenby. Fluid Phase Equilib. 209 (2003) 163–184. https://doi.org/10.1016/S0378-3812(03)00056-6.

Monitoring Natural Gas Properties Using Near-Infrared Spectroscopy in Pressurized Systems

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The monitoring of natural gas properties, such as density, viscosity, and composition in pressurized systems, faces several technical constraints, particularly in offshore production and distribution operations. This study aims to develop and validate a method based on Near-Infrared Spectroscopy (NIR), renowned for its capability to provide rapid, precise, and non-destructive analyses without the need for chemical reagents and sampling, suitable for application in gaseous systems [1]. During this research, a Near-Infrared spectrophotometer with Fourier Transform (FT-NIR) was employed. Spectra were collected using an NIR probe (Series 650, Transflectance mode, from Precision Sensing Devices INC.) with a 10 mm optical path, attached to a high-pressure cell with a useful volume of 600 ml. The spectra were gathered over 16 scans with a resolution of 8 cm^{-1}, varying the temperature from 25 to 75 °C and pressure from 100 to 300 bar. Calibration of NIR spectroscopy monitoring models (OPUS QUANT2®) was conducted following the characterization of the samples and the acquisition of reference spectra, comprising pure gases and mixtures (30, 50 and 73%) of CO_2 in CH_4. Spectral analysis commenced with a data pre-treatment in OPUS, utilizing techniques such as Standard Normal Variate (SNV) normalization and the application of first and second order derivatives to optimize the quality of spectral data. The data were organized into three main sets: calibration or training, validation, and testing, with the OPUS PLS algorithm integrating the calibration and validation phases. The calibrated model was tested on independent samples to confirm its accuracy in predicting spectral properties. The results indicate a strong correlation in both the calibration and validation phases (Figure 1), achieving linear determinations coefficients (R^2) greater than 0.99 for the composition, density, and viscosity models of gases. The methodology applied can contribute to the advancement of real-time monitoring techniques for natural gas, offering a process that can be applied to enhance operational efficiency in the natural gas production chain.

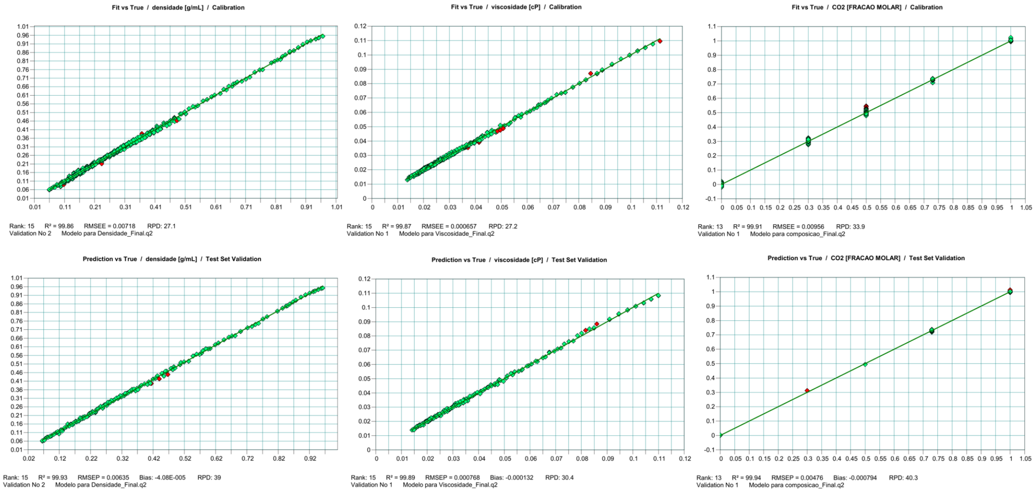

Fig. 1. Calibration and Validation Results for NIR Spectroscopy Models in Gas Monitoring.

References

[1] PASQUINI, C. Near Infrared Spectroscopy: A mature analytical technique with new perspectives. Analytica Chimica Acta, 2018, 1026, p. 8 – 36.

Thermophysical Properties of High CO_2 Mixtures: Experiments and Theory

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In oil fields, the utilization of Multiphase Flow Meters (MPFMs) is crucial for reservoir management and maximizing oil and gas production (Meribout et al., 2020). MPFMs play a significant role in accurately measuring the flow rates of oil, gas, and water simultaneously within a production well. By providing real-time data on the composition and flow rates of the multiphase fluids, MPFMs enable operators to make informed decisions regarding reservoir management strategies, production optimization, and allocation of resources. Besides that, the use of MPFMs reduces hardware needed for onshore and offshore applications due to the removal of a dedicated test separator for well testing applications (Falcone et al., 2002).

The recent discoveries of pre-salt reservoirs, known for their high carbon dioxide (CO2) content (de Freitas et al., 2022) have prompted the need to evaluate the performance of modern flow meter technologies in the presence of such elevated CO2 levels. Therefore, there is currently significant attention being given to investigating the influence of carbon dioxide content on the thermophysical properties of multiphase mixtures, as well as its subsequent impact on flow meter performance.

The aim of this study is to conduct an experimental and theoretical investigation into the influence of dissolved CO2 quantity in the liquid phase of a CO2 and dodecane mixture. The focus is on understanding how this affects the thermophysical and electrical properties of the mixture, with the ultimate goal of exploring the impact of these property variations on Multiphase Flow Meters (MPFM) measurements.

The experiments were carried out by varying pressure (1 to 170 bar) and temperature (5 to 80°C), which in turn influenced the solubility of CO2 (ranging from 0 to 100%). This allowed for the analysis of the latter parameter's influence on the viscosity, density, and electrical permittivity of the liquid phase in the mixture.

A thermodynamic model, employing the Cubic Plus Association (CPA) equation of state, was applied and implemented for comparison with the experimental results obtained.

References

[1] de Freitas, V. A., Vital, J. C. dos S., Rodrigues, B. R., & Rodrigues, R. (2022). Source rock potential, main depocenters, and CO2 occurrence in the pre-salt section of Santos Basin, southeast Brazil. *Journal of South American Earth Sciences*, *115*, 103760. https://doi.org/10.1016/j.jsames.2022.103760

[2] Falcone, G., Hewitt, G. F., Alimonti, C., & Harrison, B. (2002). Multiphase Flow Metering: Current Trends and Future Developments. *Journal of Petroleum Technology*, *54*(04), 77–84. https://doi.org/10.2118/74689-JPT

[3] Azzi, A., Ghendour, N., Kharoua, N., Khezzar, L., & AlHosani, E. (2020). Multiphase Flow Meters Targeting Oil & Gas Industries. *Measurement*, *165*, 108111. https://doi.org/10.1016/j.measurement.2020.108111

Effect of quadrupole moment on the ethene adsorption on zeolites

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Ethene also named ethylene is a very important raw-material in several industrial applications. Their separation/purification is a energy consumption step by traditional distillation. The adsorption process arises as a less energy demand operation in order to promote the separation of olefins from parafins. The molecular simulation appears as an important tool on the screening materials such as adsorbents. However, the efficiency of this approach is attached to the accuracy on the models used to describe the interatomic interactions. The goal of this work is evaluate the impact of the inclusion of ethene quadrupole moment on its force field over the prediction of adsorption on zeolites. Three different force field to describe ethene were selected. The TraPPE-UA force field, developed by [1] with neglect the ethene quadrupole moment; the three-site force field (3S) proposed by [2] which included the quadrupole moment by adding a dumb atom in the center of mass with a negative point charge and a four site force field (TraPPE-UA2) proposed by [3] which added two dumb atoms with negative charge located on the perpendicular bisector of C-C bond. The zeolites were evaluated by two different force fields: The TraPPE-zeo [] and a not yet published force field proposed by the group. The combination of these force fields were evaluated on the predicting of ethene adsorption on MFI and 13X. The results indicate that the inclusion of quadrupole moment promote higher differences on the adsorption prediction on zeolites with low Si/Al ratio, such as the 13X. On the purely siliceous zeolite (MFI) the differences on the values predicted are within the variability of experimental data reported by several groups. However, the TraPPE-UA force field, with contains only Lennard-Jones interaction sites, and therefore do not include the quadrupole moment are not able to describe the ethene adsorption on 13X neither using the TraPPE-Zeo or the force field proposed by group to describe the zeolite. The results also indicate the the general zeolite force field proposed by the group presents similar performance compared to the TraPPE-Zeo, using less framework interaction sites.

References

[1] Wick, C. D.; Martin, M. G.; J. ILJA Siepmann. Transferable Potentials for Phase Equilibria. 4. United-Atom Description of Linear and Branched Alkenes and Alkylbenzenes. The journal of physical chemistry. B, v. 104, n. 33, p. 8008–8016, 2000.

[2] Weitz, S. L.; Potoff, J. J. Effect of quadrupole moment on the phase behavior of binary mixtures containing ethene. Fluid phase equilibria, v. 234, n. 1-2, p. 144–150, 2005.

[3] Shah, M. S.; J. Ilja Siepmann; Tsapatsis, M. Transferable potentials for phase equilibria. Improvedunited-atom description of ethaneand ethylene. AIChE journal, v. 63, n. 11, p. 5098–5110, 2017.

[4] Bai, P.; Tsaptasis, M.; J. Ilja Siepmann. TraPPE-zeo: Transferable Potentials for Phase Equilibria Force Field for All-Silica Zeolites. Journal of physical chemistry. C./Journal of physical chemistry. C, v. 117, n. 46, p. 24375–24387, 2013.

Catalytic Thermochemical Conversion of Animal Fats into Advanced Biofuels

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Statistical data on global jet fuel consumption has estimated an increase from 4 quadrillion energy units (Btu) in 2010 to 16 quadrillion Btus in 2050. This scenario suggests a steady increase in levels of carbon dioxide (CO2) emissions into the atmosphere [1]. The HEFA (hydroprocessed esters and fatty acids) isan approved technology to produce sustainable aviation fuel (SAF), which represents a promising alternative for reducing the dependence on fossil fuels and greenhouse gas emissions. Over time, economic and life-cycle assessments of HEFA from vegetable oil have been published in the literature. However, there are few studies on the composition and the potential of the catalytic thermochemical conversion of animal fats to bio-jet fuels [2]. Hence, this study aims to investigate a catalytic thermochemical process for converting chicken and pork fats into SAF. For this purposed, a continuous lab scale unit was developed to study the conversion of oils and fat residues of frigorific industry. Experiments were conducted at constant pressure, using niobium-based catalysts in a fixed bed placed inside a chromatographic oven. Hydrogen and oil were continuously displaced through the catalytic reactor by means of HPLC and syringe pumps, respectively. Effects of pressure (100 to 200 bar), reactants flow rate (up to 1 ml/min) and their proportion (1:1 to 1:10 considering molar ratio between oil to hydrogen), and temperature (300 to 400oC) were investigated on the content of fatty acids converted into biofuels. The conversions were monitored by gas chromatography coupled to a mass spectrometer detector (GC-MS). The results indicated that the catalytic process investigated was capable to promote the hydrotreatment reactions of the fatty acids. The temperature was the principal variable that controlled the fatty acid conversion. Also, in situ transesterification reactions were conducted prior the catalytic fixed bed, indicating a promising strategy to improve the fatty acid conversion process.

References

[1] E. I. Fitriasari, W. Won, J. Jay Liu, Sustainable energy & fuels **2023**, 7, 3625–3636.
[2] P. H. Chen, U. Lee, X. Liu, H. Cai, M. Wang, Biofuels, Bioproducts and Biorefining 2024, 18, 42-5.

Paraffin precipitation modelling in waxy multicomponent synthetic systems

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Paraffin precipitation in reservoir fluids represents a significant challenge in oil and gas production. Accurate modelling of paraffin precipitation is essential to avoid or minimize operational problems in oil production or transportation and to reduce the associated economic losses. This involves considering a number of factors, such as fluid composition, pressure and temperature conditions.

The phenomenon of paraffin precipitation in reservoir fluids is modelled through two main approaches in the literature. The "multi-solid model" considers the precipitation of the compounds as pure solids, leading to the occurrence of multiple solid phases, whereas the "solid solution model" considers the solid phase as a solution consisting of all the components of the mixture. Although the description of solid-fluid equilibrium assuming that solid phases precipitate in a pure state has been widely implemented, it is strictly inconsistent when applied to pseudo-components in reservoir fluids [1].

Among the solid solution models, the simplest one considers the solid phase as an ideal solid solution and uses different approaches to describe the fluid phase. Regarding the description of the behaviour of mixtures in fluid phases, the Redlich-Kwong-Peng-Robinson (RKPR) equation of state (EoS) with its third parameter (δ_1), succeeded in overcoming the limitations of typical two-parameter cubic EoS, such as Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR), and demonstrated clear superiority in highly asymmetric hydrocarbon mixtures, especially at high pressures [2] and in its predictions of deviations from ideality [3].

Recently, we employed the ideal solid solution model (ISSM) approach coupled to RKPR-EoS for the first time to account for fluid phases, and demonstrated improved predictions of paraffin precipitation phenomena in multicomponent fluids compared to the PR-EoS + ISSM approach. However, important limitations remain due to the consideration of the ideality of the solid phase, which become more significant as the asymmetry of the paraffin composition increases [4].

In this work, the non-ideality of the solid phase will be considered by means of a simple model for multicomponent mixtures using a single parameter per binary. Since in such mixtures the non-ideality is due only to the difference in molecular size, it is possible to maintain adequate mathematical simplicity and engineering practicality. We calculate complete phase envelopes through numerical continuations methods. Additionally, paraffin precipitation curves are obtained from flash calculations, which are compared to experimental data when available.

References

[1] K.S. Pedersen, M.L. Michelsen, Letters to the editor, AIChE J. 43 (1997) 1372– 1374.

[2] N.G. Tassin, V.A. Mascietti, M. Cismondi-Duarte, Phase behavior of multicomponent alkane mixtures and evaluation of predictive capacity for the PR and RKPR EoS's. Fluid Phase Equilib, 480 (2019), 53-65.

[3] M.J. Quinzio, S.B. Rodriguez-Reartes, M. Cismondi-Duarte, Phase behavior and type of non-ideality in n-alkanes mixtures predicted from equations of state: The role of a third parameter, Fluid Phase Equilib. 577 (2024) 113963.

[4] M.J. Quinzio, S.B. Rodriguez-Reartes, M. Cismondi-Duarte, Solid precipitation modelling in waxy multicomponent synthetic systems using an ideal solid solution model and the RKPR EoS, XII Brazilian conference on applied thermodynamics (CBTermo), Book of Abstract, Abstract R240-2.

Thermocharacterization of coconut fiber biomass by TG-MS

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One of the agro-industrial residues with the greatest potential to be explored as an energy source in Brazil is coconut (Cocos nucifera L.), mainly due to its high availability, high lignin content, low density and high energy potential due to its average calorific value of around 20 MJ/kg, significantly higher than most biomasses [1]. Coconut fiber biomass samples were dried, crushed and ground to facilitate the required heat transfer rates during pyrolysis and analyzed by TG, DTG and TG-MS. The results demonstrate the existence of four stages, with evaporation of water with slight loss of mass due to drying and release of volatiles, decomposition of hemicellulose with a significant decrease in mass, degradation of cellulose and decomposition of lignin and high weight components molecular [2-4]. Analysis of evolved gases by TG-MS suggests that the gaseous products were mainly composed of light volatiles such as H_2 (m/z=2) and H_2O (m/z=18), hydrocarbons such as CH_4 (m/z=16) and C_2H_{4+} (m/z=28), carbon oxides (C-O) such as CO (m/z=28) and CO_2 (m/z=44), as well as nitrogen compounds such as NO_2 (m/z=46) and sulfur compounds such as H_2S (m/z=34) and SO_2 (m/z=66). The activation energy value was 66.8 kJ mol^{-1}, and is in agreement with other works [5-7]. These findings are important for understanding the combustion characteristics of biomass and can provide important insights for the development of biomass-based sustainable energy technologies.

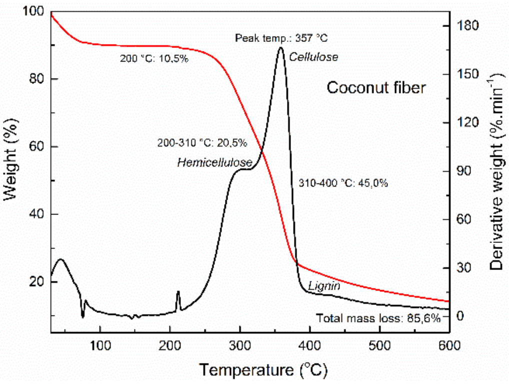

Fig. 1. TG-DTG of coconut fiber biomass at a heating rate of 10 °C.min^{-1}.

References

[1] E. C. S. Paz, M. M. Pedroza, L. R. A. Oliveira, Alternativa de exploração sustentável dos resíduos do coco verde para a produção de energia. *Revista Brasileira de Energias Renováveis* **2017**, 6 (2), 1-28.

[2] Y. Luo, Z. Li, X. Li, J. Fan, J. H. Carrk, C. Hu, The production of furfural directly from hemicellulose in lignocellulosic biomass: A review, *Catalysis Today* **2019**, 319, p. 14-24.

[3] A. C. Opia, M. K. B. A. Hamid, S. Syahrullail, A. B. A. Rahim, C. A. N. Johnson, Biomass as a potential source of sustainable fuel, chemical and tribological materials - Overview. Materials Today: Proceedings **2020**, 30, 922-928.

[4] Y. B. Andrade, A. dos Santos Polidoro, J. K. Schneider, L. dos Santos Freitas, E. B. Caramão & R. de Oliveira Farrapeira, Influence of residual biomass deposition time of green coconut on the quality of bio-oil generated by pyrolysis. *Journal of Analytical and Applied Pyrolysis* **2024**, 106436.

[5] Z. Li, W. Zhao, B. Meng, C. Liu, Q. Zhu, G. Zhao, Kinetic study of corn straw pyrolysis: comparison of two different three-pseudocomponent models. *Bioresource technology* **2008**, 99(16), 7616-7622.

[6] D. K. Seo, S. S. Park, J. Hwang, T. U. Yu, Study of the pyrolysis of biomass using thermo-gravimetric analysis (TGA) and concentration measurements of the evolved species. *Journal of Analytical and Applied Pyrolysis* **2010**, 89(1), 66-73.

[7] T. Mani, P. Murugan, J. Abedi, N. Mahinpey, Pyrolysis of wheat straw in a thermogravimetric analyzer: effect of particle size and heating rate on devolatilization and estimation of global kinetics. *Chemical engineering research and design* **2010**, 88(8), 952-958.

The complex phase behavior of CO2 + Brazilian crude oils

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This study explores the complex phase behaviour of two Brazilian oils, particularly focusing on the effect of carbon dioxide dissolution in the phase transitions. Constant Mass Expansion (CME) assays were performed in a full visibility PVT cell (400/1000 FV, Sanchez Technologies). Additionally, a Solid Detection System (SDS 40/1000) equipped with a Navitar 12x microscopic camera was used to detect and monitor wax precipitation during isobaric cooling cycles. The cooling process, controlled by a thermostatic bath (Presto A40 – Julabo), ranged from the reservoir temperature of 337.15 K to 288.15 K at a nominal rate of 15 K/min. The same SDS system worked as a chamber for the isolation and sampling to analyze the phases' density and composition. Samples of oil/CH_4/CO_2 with carbon dioxide molar compositions up to 80% were recombined at reservoir pressure and temperature (600 bar and 337.15 K, respectively). The CCE results highlighted the occurrence of phase splitting between an oil-rich phase and a CO_2-rich one in a liquid-liquid equilibrium (LLE) for both oils at temperatures under 303.15 K and a CO_2 composition of 80%. The LLE pressure and temperature wereinfluenced by the content of methane. Also, the wax appearance temperatures changed from ~303 to 292 K when pressure was reduced from 600 to 60 bar. Furthermore, there was a direct correlation between the amount of dissolved carbon dioxide and the precipitation of wax. Hosseinipour et al. (2016) [1] confirm that CO_2 typically reduces the oil WAT, but the current study shows that the morphological characteristics of the precipitated wax showed higher opacity and aggregation magnitude when carbon dioxide was present. It is worth highlighting that the formed wax aggregates during the sample depressurization were redissolved into the oil matrix once the carbon dioxide-rich phase migrated out of the solution to the gas phase. Such phase was collected and analyzed regarding its density and composition via gas chromatography with a flame ionization detector. The phase was composed of hydrocarbons ranging from C_1 to C_{10} and CO_2. Above all, the mixture complexity resulted in the occurrence of mass density inversion - the mass barotropic effect. The barotropic pressure, as well as the total relative volume of the CO_2-rich phase, decreases according to temperature reduction. Finally, the occurrence of liquid-liquid phase splitting, wax precipitationfollowed by redissolution, and density inversion for the same mixture reinforce the indispensablesolid understanding of the thermodynamic conditions in which they occur. The efficiency of several operational processes relies on it [2] and the obtained results are useful guidelines for developing flowassurance strategies for CO_2-rich oil reservoirs as well as CO_2-based EOR techniques.

References

[1] Hosseinipour A., Japper-Jaafar A. B., Yusup S. Procedia Engineering, **2016**, 148, 1022-1029.
[2] de Souza A. F. F., Secchi A. R., de Souza M. B. IFAC PapersonLine, **2019**, 52, 790-795.

Evaluation of derivative properties by different thermodynamic models for non-polar compounds

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Thermodynamic models have been developed for many decades, while a pervasive challenge exists in identifying the most effective model for a given system. In this study, a wide range of thermodynamic models have been analyzed at different ranges of pressure and temperature to end up with this idea of which model is an accurate estimator of thermophysical properties for derivative properties including liquid density, saturation pressure, isobaric and isochoric heat capacity, speed of sound, and Joule-Thomson coefficient. The Clapeyron package [1] was used to analyze the advantages and weaknesses of thermodynamics models for different compounds including Alkanes (C_1-C_{10}), nitrogen, and carbon dioxide. The SAFT-γ-Mie and SAFT-VR-Mie [2] models are the best estimators of thermophysical properties among the other existing models. However, none of the models could estimate isochoric heat capacity precisely. It also concluded that the results of isochoric heat capacity are more deviated for CO_2 (linear structure with net dipole moment zero act as quadrupolar molecules) and N_2 (Linear structure and diatomic molecule) than simple alkanes (Tetrahedral geometry around each carbon atom) due to higher-order electric multiple moments rather than alkanes. Therefore, the temperature dependency of Helmholtz energy of these models still needs to be improved. To understand the reasons for the deviation of the results, derivatives such as *dP/dT* and *dP/dV* have been analyzed for different EOS in the liquid region. The results show that *dP/dT* exhibits the most deviation compared to the other properties to calculate second-order properties.

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References

[1] Walker (P.J. Walker, H.-W. Yew, A. Riedemann), Clapeyron. jl: an extensible, open-source fluid thermodynamics toolkit, Ind Eng Chem Res 61 (2022) 7130–7153.

[2] Lafitte (T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C.S. Adjiman, E.A. Müller, G. Jackson), Journal of Chemical Physics 139 (2013).

A pleyade of molecular simulation methods (DFT, COSMO-RS and Molecular Dynamics) for understanding the catalytic conversion of CO2 to cyclic carbonates based on ionic liquids

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Ionic Liquids (IL) have become promising catalysts in cylic carbonates production from epoxides base reactants by CO_2 cycloaddition. This reaction scheme effectively converts CO_2 into a valuable product which is important today from the environmental perspective due to global warming mitigation by CO_2 capture and utilization. Literature evaluation on this reaction is composed of experiments difficult to compare because of the variety of conditions (pressure, temperature, and catalyst dosage), making also challenging to evaluate the effect of tuning the IL structure (anion, cation, and substituents) and therefore selecting best ILs for specific conditions. The application of molecular smilation tools may contribute to obtain a deeper insight on the catalytic behavior of these systems, but it is scarce in the literature and mainly focus on describing the reaction mechanism for a limited number of systems.

In this work, different computational approaches will be applied for trying to understand, from a molecular point of view, the recently reported experimental results from systematic catalytic tests performed with 24 ILs based on halide anions (Cl^-, Br^- and I^-) and different cation families (phosphonium, ammonium and imidazolium) in the synthesis of hexylene carbonate and styrene carbonate, which stand as representative cyclic carbonates from the most conventional ones. Thus, DFT calculations will be used to describe the reaction pathways by considering the effect of anion and cation on the stability of reaction intermediates and activation barriers. Then, COSMO-RS method will allow predicting the solubility of the different IL catalysts in reaction media, also providing predictions of the dissociation degree of the IL in the epoxide, as thermodynamic parameter of cation-anio interaction to be related to the catalytic activity. Finally, to check in detail the chemical information about the microstructure of the reactive systems, molecular dynamics (MD) simulations were performed over the variety of reactants, products, and ILs at different concentrations, to analyse transport properties, aggregate formation, solubilities of these systems, and solvation effects of reactant, intermediates and products of CO2 conversion to cyclic carbonates based on ILs.

Enantioselective liquid-liquid extraction of ofloxacin using hydrophobic eutectic solvents and β-cyclodextrin derivatives

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The separation of enantiomers in chiral drugs is a major challenge for the pharmaceutical industry, as the pharmacological effects of enantiomers can be different, which can lead to serious side effects in the treatment of diseases. The aim of this study is to develop a platform for the enantioseparation of ofloxacin (R/S-OFX) using enantioselective liquid-liquid extraction (ELLE) based on hydrophobic eutectic solvent (HES) in combination with β-cyclodextrin (β-CD) derivatives as chiral selectors. The β-CD derivatives investigated for the enantioseparation of R/S-OFX included β-CD, hydroxypropyl-β-cyclodextrin (HP-β-CD), carboxymethyl-β-cyclodextrin sodium salt (CM-β-CD) and sulfated-β-cyclodextrin sodium salt (S-β-CD). Among these, CM-β-CD proved to be the most effective. Then, the efficacy of the HES-based ELLE system was evaluated using a total of fourteen HES-based ELLE systems from four HES groups: L-menthol with fatty acids, L-menthol with fatty alcohols, fatty acid with fatty acid, and fatty acid with fatty alcohols. The combination of decanoic acid and dodecanoic acid (C10 acid: C12 acid) in a molar ratio of 2:1 was identified as the optimal HES-based ELLE system for the enantioseparation of R/S-OFX. This system was subsequently used to refine the enantioseparation conditions, including pH, HES-water ratio (v/v), and the amount of chiral selector (CM-β-CD), using response surface methodology (RSM). Under the optimal conditions, which included a pH of 3.6, a HES-water ratio of 1:2, and a 77-fold molar excess of the chiral selector, the achieved OFX selectivity (α) was 3.8 ± 0.3 in a single-step.

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Evaluating zwitterionic compounds analogous to ionic liquids for solubility enhancement of hydrophobic compounds

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The limited water solubility of drugs poses a significant challenge for the pharmaceutical industry. Although conventional hydrotropes have been used to address this issue, there is an urgent need for new, highly efficient hydrotropes with low toxicity. Recent research suggests that zwitterionic compounds analogous to ionic liquids (ZILs) are promising candidates for enhancing the solubility of poorly water-soluble compounds due to their lower cytotoxicity [1] and ecotoxicity [2].

In this study, we investigate the use of (i) sulfonate-based ZILs, (ii) carboxylate-based ZILs, and (iii) ILs analogous to ZILs to improve the solubility of two model molecules: syringic acid and ibuprofen. The results show three main points: (i) ZILs with longer alkyl chains and spacers show higher hydrotropic activity, especially for carboxylate-based ZILs; (ii) the hydrotropic effect is more pronounced for solutes with greater hydrophobicity; and (iii) ZILs exhibit lower hydrotropic behaviour compared to their analogous ILs. These results are particularly important for pharmaceutical formulations, as while ZILs exhibit slightly lower hydrotropic behaviour than the ZIL/IL pairs studied, their low toxicity profile makes them a highly desirable option.

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References

[1] K. Kuroda, T. Komori, K. Ishibashi, T. Uto, I. Kobayashi, R. Kadokawa, Y. Kato, K. Ninomiya, K. Takahashi and E. Hirata, *Commun. Chem.,* **2020,** *3*, 163.
[2] F. Jesus, H. Passos, A. M. Ferreira, K. Kuroda, J. L. Pereira, F. J. M. Gonçalves, J. A. P. Coutinho and S. P. M. Ventura, *Green Chem*., **2021**, *23*, 3683–3692.

Enhancing the energy density by controlling the solubility of redox species to develop more efficient redox flow batteries

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Renewable energy sources, such as solar and wind technologies, face challenges related to intermittency, requiring the use of Energy Storage Systems (ESS) to store excess energy during peak generation and release it during periods of low power. While significant advancements have been made in battery technology, particularly in lithium-ion batteries, their widespread deployment is limited by metal scarcity and high costs. In contrast, Redox-Flow Batteries (RFBs) are highly regarded for their cost-effective storage capabilities, especially for extended discharges and storage periods. RFBs utilize liquid-state species dissolved in electrolyte solutions, offering prolonged operational lifespan and cost benefits. Although Vanadium RFBs are primarily employed in such systems, they encounter issues such as high expenses and susceptibility to corrosion. Alternatively, organic redox compounds present a cost-effective option with varied structures and easy availability. Regarding electrolyte solutions, non-aqueous flow batteries face challenges like high costs and flammability, while aqueous RFBs provide advantages due to their non-flammable nature, high dielectric constant, and superior ionic conductivity. Enhancing the solubility of redox-active species in aqueous RFBs is crucial for improving energy density and decreasing the formation of solid precipitates. Redox organic species pose unique challenges for solubility optimization, often requiring complex organic synthesis. Following a different approach, battery additives offer an economically viable solution, widely used in various energy storage systems such as vanadium flow batteries, lead-acid batteries, and lithium-ion batteries. These additives boost battery performance without impacting battery reactions. Solubilizing additives create a link between the aqueous solution and the compound, eliminating the need for intricate molecular synthesis and serving as a supporting electrolyte. Therefore, this work proposes enhancing the solubility of redox-active species through the incorporation of additives in the solution, namely inorganic salts. First, a screening of the solubility of redox active species, namely ferrocene, methyl viologen derivatives, and TEMPO, in the selected salt solutions were performed using the predictive model COSMO-RS. Then, the systems with most relevant results were studied experimentally. Addressing these challenges can lead to the development of scalable and sustainable energy storage solutions, facilitating the integration of renewable energy sources into the power grid.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC). This work has received funding from the European Innovation Council (EIC) under grant agreement 101046742. The EIC receives support from the European Union's Horizon Europe research and innovation program.

Study of the saline effect of lithium salts on the phase equilibrium of the water + 1- and 2-propanol systems

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Certain materials mined in Europe (like lithium) currently have to leave Europe for processing because there is not capacity for extraction, processing, recycling, refining and separation, reflecting a high dependency on supply from other parts of the world. The technologies, capabilities and skills in refining and metallurgy are a crucial link in the value chain. Through the European Battery Alliance, public and private investment has been mobilised at scale and should, for example, lead to 80% of Europe's lithium demand being supplied from European sources by 2025 [1]. Due to the importance of this process, different methods for the lithium enrichment in brines have been studied in the literature [2], including liquid-liquid extraction, which has been investigated due to its efficient and economical application. Because the effects of the presence of an electrolyte in a water + solvent mixture are very varied and of great industrial interest, the study of systems is important in which water, electrolytes and organic solvents of different nature intervene, such as 1- and 2-propanol. To carry out the simulation and process design of lithium separation, it is necessary to have accurate, reliable and thermodynamically consistent experimental LL, SL, SLL equilibrium data to study the extraction process. The thermodynamic models that could be applied to correlate experimental data and that, therefore, could later be used for simulation and process design, are also in need of experimental equilibrium data.

In order to expand the limited liquid-solid equilibrium database available, it has been decided to analyse the effect of different anions (Cl^-, SO_4^{2-} and NO_3^-) on the ability to split the phases of the water + 1-propanol + salt and water + 2-propanol + salt systems.

For this purpose, mixtures of known composition have been prepared covering the whole ternary composition diagram in order to analyse the different phases presented by each system. The mixtures were kept in the bath at a constant temperature of 313.15K until the phase equilibrium was reached. The water and alcohol composition were analysed by gas chromatography using a TCD detector, while the salt composition was analysed by gravimetry.

The results show that both lithium chloride and lithium sulphate produce phase splitting in 1-propanol and 2-propanol, with appearing regions of immiscibility with (LLSE) and without solid (LLE). However, no amount of lithium nitrate has been found to cause the appearance of more than two phases.

References

[1] COM/2020/474. *Communication from the commission to the european parliament, the council, the european economic and social committee and the committee of the regions. Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability*. Brussels (2020).

[2] J. Li, M. Wang, Z. Youjing, H. Yang, Y. Zhong,. *Royal Society Open Science* **2018**, *5*. 180965

The effect of temperature in liquid-solid equilibrium data of water + propanol + lithium chloride ternary systems

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The effects of the presence of an electrolyte in a mixture of water + solvent are very varied and of great industrial interest. The presence of an electrolyte causes a significant change in the composition of the water + solvent equilibrium by altering the structure of hydrogen bonds and other intermolecular forces. Especially sensitive to this effect are the liquid-liquid equilibrium due to the change in the mutual solubilities of water + solvent caused by the salt. For all water + electrolyte + solvent systems, there is a considerable need to have accurate, reliable and thermodynamically consistent experimental equilibrium data, as well as more versatile models to reproduce accurately the phase equilibrium. Experimental data are needed not only to be able to understand the behaviour of the system, but also to guide the development of new models and to verify their correctness. In fact, the improvement of the lithium obtention processes efficiency makes interesting the experimental determination and data correlation of systems were this metal is involved.

In the present communication, the effect of temperature in the equilibrium phases present at three different temperatures (298.15, 313.15 and 333.15 K) have been analysed for the ternary systems water + 1-propanol + LiCl and water + 2-propanol + LiCl. The experimental determination was carried out by preparing known mixtures of water, 1- and 2- propanol and lithium chloride covering the all the phase equilibria regions of the diagrams. The phase composition determination is specially challenging due to the experimental difficulties that arose. All liquid samples were taken and analysed by gas chromatography (Shimadzu GC-14A), equipped with thermal conductivity detector (TCD), to determine water and propanol concentration. The lithium chloride content was analysed gravimetrically. The experimental data obtained have been checked against previously published literature [1, 2].

In the same way as systems with other inorganic salts, lithium chloride illustrates the salting out effect of a water miscible component such as propanol, causing the phase split of the mixture. Nevertheless, the possible presence of two different solid phases changes the shape of the equilibrium diagrams. Both systems present two liquid-solid regions (close to the binaries water + LiCl and 1- and 2-propanol + LiCl), one liquid-liquid region and two regions with three phases: one liquid-liquid-solid and one solid-solid-liquid (anhydrous and monohydrate salt). However, in spite of the similar characteristics of 1- and 2-propanol, the phase equilibrium diagrams differ qualitatively. In fact, the heterogeneous liquid-liquid region is smaller for 2-propanol, so the degree of salting out is bigger with 1-propanol.

However, in the temperature range studied, the effect of temperature does not change the number of regions involved, although it does change the extent of the regions. Therefore, it can be concluded that temperature has a moderate effect on the liquid-solid equilibrium of this type of diagrams.

References

[1] Authors (M. T. Nguyen-Kim, T. A. Smith), *Journal title* **Year**, *Volume*, Pages.

[2] Seidell. *Solubilities of inorganic and metal compounds: a compilation of quantitative solubility data from the periodical literature*. UMI, Ann Arbor (1995)

Equilibrium Diagrams of Water + LiCl + 1- Propanol at the Boiling Temperature at 101.3 kPa

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The fundamental role of lithium-ion batterie as a substitute energy source for fossil fuels has led to an increase in global demand for lithium, driven primarily by new electric mobility models. These batteries accomplished annual growth rates of 24% from 2015 to 2018 [1], with global lithium demand predicted to be around 16% annually beyond 2025. This work contributes to obtaining experimental data on SLLV, SLV, SSLV, LLV and LV equilibrium of aqueous mixtures with lithium salts, which will permit the study of lithium purification and production processes. On the other hand, equilibrium data for mixtures with electrolytes become important because they are scarce in the literature. In this sense, "Working Party on Thermodynamic and Transport Properties" of the European Federation of Chemical Engineering (EFCE) published an article [2] some years ago highlighting that mixtures with electrolytes are one of the research areas where additional data is needed the most. One of the conclusions reached by the article is the need for improving the thermodynamic characterization of water + solvent + electrolyte systems, so that all types of phase behaviour can be reproduced (including wide ranges of temperature and pressure, as well as high salt concentrations).

In this work, experimental equilibrium data of the systems water + LiCl + 1-propanol are determined experimentally at boiling conditions and 101.3 kPa. The lithium chloride salt has been chosen because it is one of the salts obtained in the production process of lithium compounds. And the alcohol, short chain and of renewable origin, has been chosen due to the growing environmental concern that forces us to redesign processes and find new alternatives that significantly reduce impacts on the environment. The results obtained permit a study of the shape and different regions of the equilibrium diagram. It should be noted that the curve corresponding to the organic phases has an S shape, as shown in the next figure.

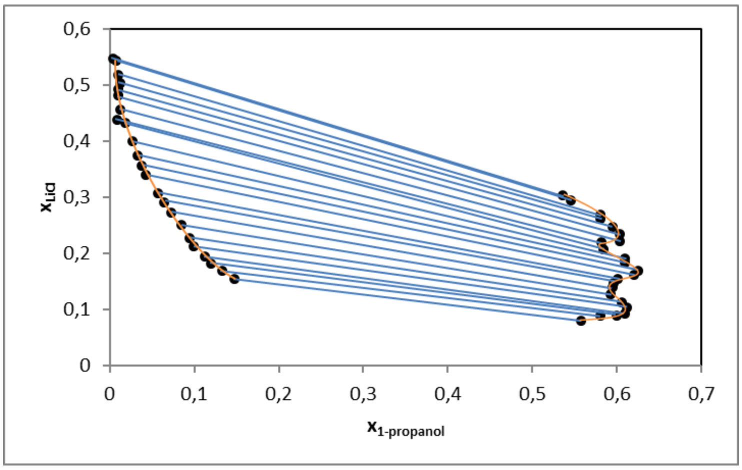

Fig. 1. Experimental LL region where the S shape is observed for the SLLVE of water–1-propanol–LiCl system, P = 1.013.

References

[1] A. Yáñez-Fernández, M.J. Inestrosa-Izurieta, J.I. Urzúa, Desalination **2021**, 517, 115269.

Poster Communication II-P27: Wednesday, September 11th, 16:40h - 18:00h

On the Hydrophobicity of Hydrophobic Eutectic Solvents

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Separation procedures are fundamental in a vast array of industries such as pharmaceuticals, biorefinery and petrochemistry. In this field liquid-liquid extraction is a very appealing technique due to its high efficiency, selectivity, robustness, flexibility and easiness of operation. [1] Simple procedures using volatile organic solvents (VOCs) and aqueous solutions were employed for many decades to perform extractions and separations. However, alternative solvents such as thermotropic systems, switchable solvents and aqueous two-phase systems have been slowly emerging. More recently, ionic liquids and eutectic solvents started to replace conventional VOCs due to their lower vapor pressure and toxicity. Additionally, the capacity to design task specific solvents led to high specificity and process efficiency. The use of these solvents enabled to widen the properties of alternative solvents and shift from the very interesting aqueous biphasic systems to a more hydrophobic domain. [2,3]

In this work, binary one phase mixtures of n-hexane and hydrophobic ES, D,L-menthol:dodecanoic acid (2:1), were separated by adding low molecular glycols (ethylene glycol, diethylene glycol, triethylene glycol, PEG 200, PEG 400). The liquid-liquid phase equilibria diagram of these 6 ternary systems was measured through the turbidimetry method (Fig. 1) and 3 tie-lines for each system were determined by GC-FID, allowing to conclude about the ESs stability. Finally, these systems were used to extract carotenoids and chlorophyll from microalgae (Spirulina and Chlorella).

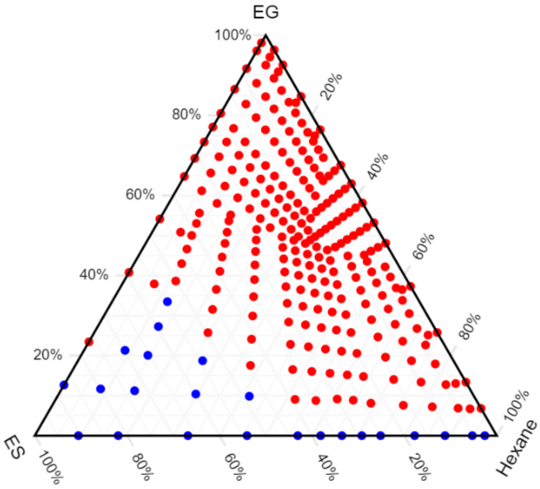

Fig. 1. Simplified liquid-liquid phase equilibria diagram (in molar percentage) for the ethylene glycol, hexane and D,L-menthol:dodecanoic acid (2:1) system. Monophasic behaviour (blue) and biphasic behaviour (red).

Acknowledgments

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References

[1] S. H. Chang, Environmental Science and Pollution Research **2020**, 27, 32371–32388.
[2] Bezold, F.; Minceva, M.; Journal of Chromatography A **2019**, 1587, 166-171.
[3] Xu, D.; Meng, X.; Liu, Z.; Zhang, L.; Wang, Y.; Gao, J.; Brazilian Journal of Chemical Engineering **2020**, 37, 569–576.

Green Electrolytes for Supercapacitors: Exploring Eutectic Systems for Sustainable Energy Storage

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The population growth and technological progress have increased the global demand for energy and intensified dependence on fossil fuels. Therefore, it is essential to integrate renewable energy sources into the worldwide energy supply. However, the inherent intermittency of most of these sources requires the use of energy storage devices. Among these devices, supercapacitors (SC) stand out for their high-power density and high cyclability [1]. However, the main challenge lies in their low energy density. Furthermore, commercially available SCs use organic electrolytes to achieve wider potential windows [2]. These electrolytes have a harmful impact on the environment and generally exhibit high levels of toxicity and flammability, creating safety risks. Therefore, it is desirable for the materials used in these devices to be not only high-performance but also as environmentally friendly and safe as possible. Eutectic Systems (ES) are a new emerging class of electrolytes defined as a mixture of at least two compounds that have a lower melting point than each of its individual compounds [3]. There is a high number of possible combinations between compounds to form an ES, thus enabling the search for environmentally compatible and economically feasible compounds with promising performance. Additionally, they exhibit attractive characteristics at the electrolyte/electrode interfaces, increasing the potential window and inhibiting dendrite growth on the electrodes. The use of ES as electrolytes has only gained prominence in the last 5 years, with Choline Chloride (ChCl)-based ES being the most studied. Lithium (Li)-based ES have also received a lot of attention; however, the scarcity of Li requires alternatives. Sodium (Na) and potassium (K)-based ES electrolytes benefit from higher natural abundance and lower cost. However, research on these systems is still very limited and generally does not focus on the safety and sustainability issues of ES. In this work, hydrophobic potassium and sodium electrolytes are presented using non-toxic compounds. Namely, the combination of sodium hexanoate (NaC6) or sodium octanoate (NaC8) with hexanoic acid (C6) or octanoic acid (C8) and potassium hexanoate (KC6) or potassium octanoate (KC8) with hexanoic acid (C6) or octanoic acid (C8). The initial results were obtained using electrodes with graphene as the active material, and it has been possible so far to achieve potential windows close to 2 volts, which is a first possible indication that the structured network established between the ES compounds allows delaying or preventing the electrochemical decomposition of water present in the electrolyte.

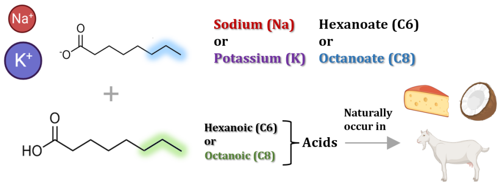

Fig. 1. Studied Eutectic Systems (ES) as electrolytes for supercapacitors.

Acknowledgments

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References

[1] G. Navarro, J. Torres, M. Blanco, J. Nájera, M. Santos-Herran, M. Lafoz, Energies (Basel). 14 (2021).
[2] C. Zhong, Y. Deng, W. Hu, D. Sun, X. Han, J. Qiao, J. Zhang, 2016.
[3] J. Wu, Q. Liang, X. Yu, L. Qiu-Feng, L. Ma, X. Qin, G. Chen, B. Li, Adv Funct Mater. 31 (2021).

Sustainable Solutions for Purification of Platinum Group Metals from Aluminum Salt Leachates

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Increasing demand for Platinum Group Metals (PGM) mainly resulting from their expanding utilization in autocatalytic converters and low recycling rates, underscores the importance of sustainable recycling solutions of these metals [1]. The recovery of PGMs is achievable through a hydrometallurgical process of three main stages including leaching, purification, and refining. Recent studies showed the possibility of substituting conventional lixiviants by using the water-in-salt solutions such as concentrated aqueous electrolyte solutions of aluminum salts [2]. Current study focuses on a purification method of PGMs from aluminum salts leachates using ionic liquid-based aqueous biphasic systems (ABS). For this purpose, formation of two immiscible aqueous phases in the systems containing phosphonium cations, including tetrabutylphosphonium chloride ($[P_{4444}]Cl$) and tributyltetradecylphosphonium chloride ($[P_{44414}]Cl$) with aluminum salts present in the leachate is investigated. ABS phase diagrams of each IL with mixture of Al salts and water were studied. Finally, the PGM extraction efficiency of ILs from leachates obtained from the leaching of the autocatalytic converters by Al salts solutions demonstrated remarkable results with extraction of platinum among other metals.

Acknowledgments

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References

[1] H. Tang, Z. Peng, R. Tian, L. Ye , J. Zhang , M. Rao. Platinum-group metals: Demand, supply, applications and their recycling from spent automotive catalysts. Journal of Environmental Chemical Engineering 2023; 11:110237. doi:10.1016/j.jece.2023.110237

[2] F. Forte, S. Riaño, K. Binnemans. Dissolution of noble metals in highly concentrated acidic salt solutions. Chemical Communications 2020; 56:8230–2. doi:10.1039/d0cc02298e

Exploring Green Solvent for Lupin Debittering via In Silico COSMO-RS Predictive Screening

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Andean lupins have been widely cultivated in the Andean highlands for the enrichment of the soil, animal feeding and as a food crop. Their seeds are nutrient-rich in terms of their high content of protein (about 50%) and oil (about 20%). However, the presence of toxic quinolizidine alkaloids, including sparteine, lupanine, and 13-OH-lupanine, in the seeds limits their industrial applications.
Several ionic liquids (ILs) and eutectic systems (ESs) have been reported in the literature to extract alkaloids from plant materials with the advantages of sustainability, biodegradability as well as adjustable polarity to dissolve polar and non-polar compounds. However, identifying an optimal IL or ES from the large number of possible combinations is quite challenging. To address this issue, the COSMO-RS (COnductor-like Screening MOdel for Real Solvents) model has emerged as a reliable computational tool that can screen numerous compounds or mixtures based on different thermodynamic properties.

The current study demonstrates the dissolution behavior of quinolizidine alkaloids in ILs and ES using the COSMO-RS model. Several combinations were attempted and evaluated by predicting the logarithmic activity coefficient ($\ln \gamma$) of typical quinolizidine alkaloids (sparteine, lupanine, and 13-OH-lupanine) in conventional solvents, ionic liquids and natural-based eutectic solvents.
Through this research, we aim to develop a novel separation method based on the use of green solvents, to debitter the Andean lupin beans, i.e., to remove the toxic alkaloids, and to unveil efficient and environmentally conscious strategies for maximizing their use in the food industry.

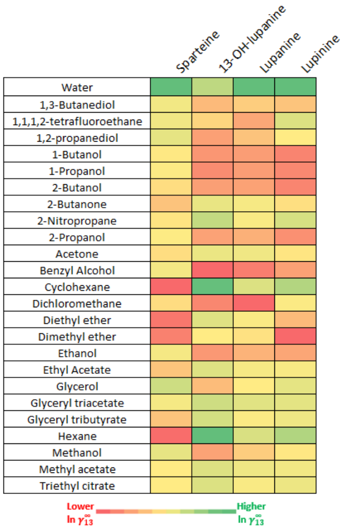

Fig. 1. Preliminar results on the $\ln \gamma_{13}^{\infty}$ of quinolizidine alkaloids in different pure solvents at 298.15 K.

References

[1] M. Yu, K. Kniepkamp, J. P. Thie, G. J. Witkamp and R. J. F. van Haren, J. Food Process Eng., 2023, 46, e14289.
[2] Y. E. Rosas-Quina and F. C. Mejía-Nova, J. Food Process Eng., 2021, 44, e13657.
[3] J. Pavón-Pérez, A. Vallejos-Almirall, C. Agurto-Muñoz and O. Galarce-Bustos, Green Chem., 2022, 24, 9450–9474.

Encapsulated Ionic Liquids in PEBAX® membranes for gas separation

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Over recent decades, greenhouse gas (GHG) emissions have risen, leading to a substantial increase in their atmospheric concentrations. This increase has intensified the natural greenhouse effect, which have negative impacts on life on Earth.[1] The total annual emissions of GHG are approximately 50 billion tons of CO_2 equivalents, of which 71.6% is carbon dioxide (CO_2), 21% is methane (CH_4), 4.8% is nitrous oxide (N_2O), and 2.6% is fluorinated gases (HFCs, PFCs, SF_6, NF_3).[2] In order to mitigate these pollutants many technologies, such as absorption, adsorption, and electrochemical reduction, have been used. However traditional abatement technologies present several drawbacks, including high energy demand, low efficacy and solvent toxicity.[3] To address these challenges, non-volatile solvents, particularly Ionic Liquids (ILs), have been proposed due to their attractive properties including negligible vapor pressure, high thermal and chemical stability, and tunable properties.[4] However, the direct implementation of ILs in conventional separation units confronts obstacles, including the need for large separation units and significant energy demands for solvent recovery.[5] To enhance absorption kinetics, we proposed encapsulating ILs in carbon sub-microcapsules (ENILs). Despite advancements, the direct application of this technology is limited by morphological characteristics such as size and weight. To address this, a synergistic approach combining encapsulation within membrane matrices has been proposed. This approach aims to reconcile the solvent's sorption capacity and selectivity with the modularity, compactness, and scalability inherent in membrane technology. Here, we propose the development of ENILs supported in polymeric membranes of PEBAX® as a novel technology to address the aforementioned challenges. The polymeric selective thin layer containing ENILs enhances absorption kinetics due to improved gas transport properties related to the increased surface area, tunable permeability, and selectivity of ILs while eliminating the need for energy-demanding regeneration steps and units.

Acknowledgments

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References

[1] European Commission, EDGAR - The Emissions Database for Global Atmospheric Research, https://edgar.jrc.ec.europa.eu/report_2023, (accessed July 2024)
[2] Our world, Greenhouse gas emissions, https://ourworldindata.org/greenhouse-gas-emissions, (accessed July 2024)
[3] N. Islam, H. Warsi Khan, A. A. Gari, M. Yusuf, and K. Irshad, *Fuel*, **2022**, *330*, 125540.
[4] Y. Xu, R. Zhang, Y. Zhou, D. Hu, C. Ge, W. Fan, B. Chen, Y. Chen, W. Zhang, H. Liu, G. Cui and H. Lu, *Chemical Engineering Journal*, **2023**, *463*, 142298.
[5] M. T. Mota-Martinez, P. Brandl, J. P. Hallett and N. Mac Dowell, *Mol Syst Des Eng*, **2018**, *3*, 560–571

Partition Coefficients of Terpenoids for Countercurrent and Centrifugal Partition Chromatography Applications

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The primary natural sources of monoterpenes and monoterpenoids are essential oils (EOs). These complex mixtures can be produced by all parts of a plant, such as flowers, leaves, stems, seeds, and fruits. The extraction and purification of EOs are crucial steps to obtain high-value monoterpenes since EO profiles might contain over 80% of monoterpenes. Among the various separation methods available, chromatographic techniques such as countercurrent chromatography (CCC) and centrifugal partition chromatography (CPC) have been used to separate monoterpenes from different EOs.

In this study, we used the analytical shake-flask method to measure the partition coefficients of three monoterpenoids, carvone, eucalyptol, and thymol, in 11 biphasic solvent systems at 298.2 K. These data present the first available partition data in the literature for thymol and eucalyptol. The COSMO-RS model successfully represented the partition coefficients, incorporating both data measured in this work and retrieved from the literature. The obtained RMSDs between the experimental and predicted partition coefficients (on a log basis) ranged between 0.28 and 0.49. Subsequently, COSMO-RS was employed to describe the solute's partition coefficients in three solvent families suitable for CCC/CPC separations: Arizona, Modified Arizona, and Green Arizona. The most promising solvent systems for performing the separations were identified from these predicted profiles, as shown in Figure 1 for the Green Arizona solvents.

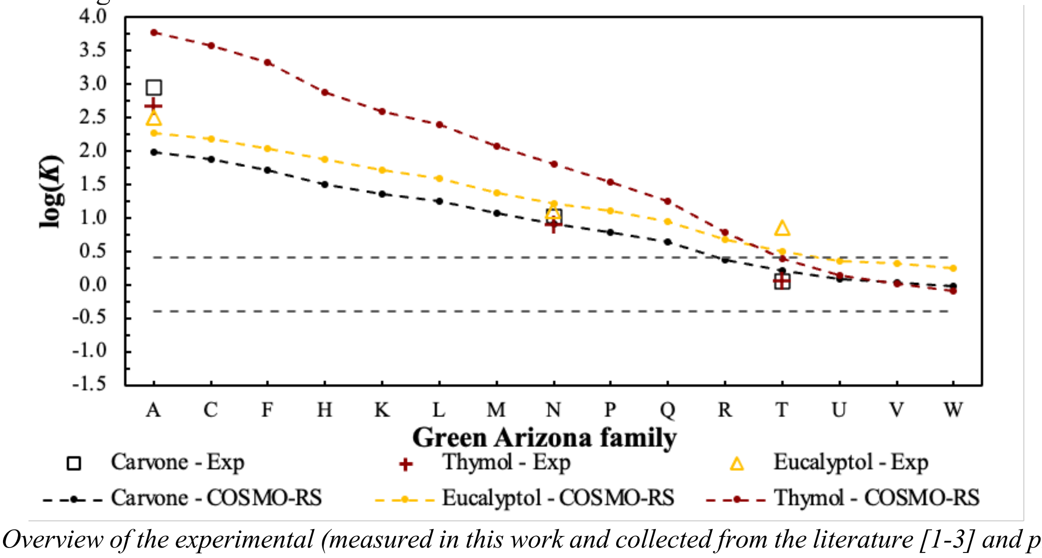

Fig. 1. Overview of the experimental (measured in this work and collected from the literature [1-3] and predicted Log(K) values as a function of the solvent systems for the Green Arizona family. The horizontal grey dashed lines correspond to the sweet-pot polarity region (-0.4 < Log(K) < 0.4) [4].

References

[1] A. Berthod, S. Ignatova, I. A. Sutherland, *J. Chromatogr. A* **2009**, *1216*, 4169–4175.
[2] N. Fumat, A. Berthod, K. Faure, *J. Chromatogr. A* **2016**, *1474*, 47–58.
[3] Y. Lu, A. Berthod, R. Hu, W. Ma, Y. Pan, *Anal. Chem.* **2009**, *81*, 4048–4059.
[4] J. B. Friesen, G. F. Pauli, *J. Chromatogr. A* **2007**, *1151*, 51–59.

Optimization of Artemisinin Extraction from *Artemisia annua* L.: Using Accelerated Solvent Extraction and Biobased Solvents

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Artemisinin, a sesquiterpenoid lactone peroxide found in the leaves of sweet wormwood (*Artemisia annua* L.), is an essential component of artemisinin-based combination therapies (ACTs), which are recognized by the World Health Organization as the one of most successful treatments against chloroquine-resistant malaria [1]. Although there are ongoing efforts to synthesize artemisinin and its precursors, extraction from the plants remains the most economical method [2]. However, the extraction method for artemisinin from plants needs to be more sustainable while preserving its bioactivity. The aim of this study is to develop a more efficient and environmentally friendly extraction process using aqueous mixtures of alternative biobased solvents with accelerated solvent extraction (ASE), a technique that employs high pressures and elevated temperatures to enhance the solubility of the target compounds and the diffusion of the solvent in natural matrix. First, a selection of the most suitable hydrated biobased solvent for the extraction of artemisinin was made, evaluating solvents such as ethyl acetate, gamma-valerolactone (GVL), cyrene and polyols. The selection of the most promising bio-based solvent was supported by COSMO-RS (Conductor-like Screening Model for Real Solvents), a quantum chemistry-based thermodynamic model, trough the relative solubility analysis of artemisinin in these solvents. To further enhance the extraction process, a response surface methodology (RSM) based on a central composite rotatable design (CCRD) was applied to optimize key variables such as extraction time, solvent concentration, and temperature using the most suitable solvent. Under optimized conditions, the hydrated biobased solvent mixture yielded up to 12.4 mg of artemisinin per gram of plant in a single extraction step, outperforming the conventional organic solvents used. In summary, the use of innovative solvents and advanced extraction techniques could significantly increase the yield and efficiency of artemisinin extraction from *Artemisia annua* L., while making the process more sustainable and potentially more cost-effective.

Acknowledgements

The authors are grateful to FCT for financial support through FCT/MCTES (PIDDAC) to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2020) and CICECO, (UIDB/50011/2020, DOI: 10.54499/UIDB/50011/2020; UIDP/50011/2020, DOI: 10.54499/UIDP/50011/2020; & LA/P/0006/2020, DOI 10.54499/LA/P/0006/2020). I. W. Cordova and A. M. Ferreira are grateful to FCT for their contracts 2022.12407.BD and CEECIND/00361/2022 (DOI: 10.54499/2022.00361.CEECIND/CP1720/CT0020), respectively.

References

[1] World Health Organization. World Malaria Report, Geneva (2021).
[2] N. Ikram and H. Simonsen. Frontiers in Plant Science **2017**, *8*, 303099.

Recovery and fractionation of pigments from *Saccharina latissima* using eutectic solvents

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Saccharina latissima, a prolific marine alga, is a rich source of important natural pigments, namely fucoxanthin and chlorophylls. This work used *Saccharina latissima* as a source of pigments to develop an integrated platform to promote the extraction and separation of chlorophyll and fucoxanthin using eutectic solvents (ES). Hydrophobic ES were investigated in the extraction of these pigments, and operational conditions were optimised. After selecting the best ES, considering its capacity to maximize the extraction of fucoxanthin (more than 137 $\mu g_{fucoxanthin} \cdot g_{biomass}^{-1}$), a unique ES-ES biphasic system was applied to selectively separate chlorophylls from fucoxanthin. Using this ES-ES biphasic system the chlorophyll predominantly remained in the hydrophobic phase, while 95% of fucoxanthin migrated to the hydrophilic. To further refine the quality of the extracted fucoxanthin, a subsequent purification step using water was implemented successfully, resulting in a concentrated pigment product. This work [1] highlights ES as potential biocompatible solvents for the recovery of value-added compounds from marine biomass.

Acknowledgments

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References

[1] M. Kholany, W. Reynaga-Navarro, R. Wijffels, J. A. P. Coutinho, S. P. M. Ventura, A. Kazbar, *Separation and Purification* Technology **2024**, *nd*, nd (submitted).

Poster Communication II-P35: Wednesday, September 11th, 16:40h - 18:00h

The Impact of Temperature on Hydrotropy: A Machine-Learning-Enabled Thermodynamics Study

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The aqueous solubility of hydrophobic solutes can be greatly enhanced through hydrotropy, where an amphiphilic molecule (i.e., the hydrotrope) aggregates around the apolar moieties of the solute, boosting its solubility. Although this solubilization mechanism is well understood, little is known about the impact of temperature on it, particularly on how temperature swings can boost or reduce the extent of solute-hydrotrope aggregation and, thus, solute solubility.

To probe the impact of temperature on hydrotropy, the solubility of syringic acid, a model solute frequently employed in hydrotropic studies, was measured in aqueous solutions of different bio-based hydrotropes, namely 1,2-propanediol, 1,3-butanediol, 1,2-pentanediol, 3-methoxypropan-1,2-diol, 2-ethoxyethanol, and dihydrolevoglucosenone (Cyrene). Solubility curves were obtained at temperatures ranging from 278 K to 343 K and each dataset was fitted and modelled using Gaussian processes (GPs), a powerful machine learning interpolator. This allowed for a careful thermodynamic analysis of the experimental data, including the computation of excess solvation properties (enthalpies, entropies, and Gibbs energies) and solute activity coefficients.

As expected, the solubility of syringic acid increased with temperature for all systems and compositions studied. However, at low hydrotrope concentrations, this increase was driven only by the Gibbs energy of the solid solute and not by interactions in the liquid phase. In other words, there were no significant changes in the activity coefficients of the solute across different temperatures, revealing that solute-hydrotrope microheterogeneities remain unchanged by temperature swings. On the other hand, at large hydrotrope concentrations, increasing temperature had a profound effect on the thermodynamic behavior of the solute, greatly decreasing its activity coefficient. These different effects were interpreted considering different solubilization mechanisms, namely hydrotropy and co-solvency, and different clustering behavior. All in all. the results and insights obtained have a profound impact on how hydrotropic systems should be designed and shed light on their resilience to temperature changes.

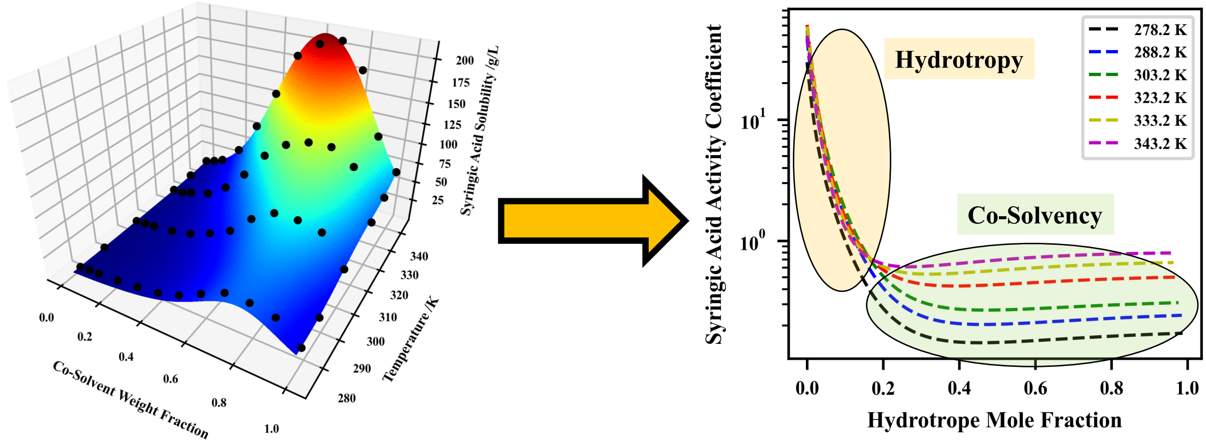

Fig. 1. GP-regressed three-dimensional surface of the solubility of syringic acid in aqueous mixtures of Cyrene (left), and example of derived thermodynamic information (activity coefficients) displaying two solubility mechanism regimes (right). Note how activity coefficients remain constant across different temperatures in the hydrotropy region while changing drastically in the co-solvency regime.

Sustainable valorisation of kiwifruit waste: optimizing phenolic compound extraction using biobased solvents and alternative techniques

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Kiwifruit is rich in bioactive compounds such as phenolic compounds which exhibit biological activity with potential health benefits [1]. Despite this, approximately 30% of kiwifruit production is discarded due to commercial standards [2]. This wastage represents a missed opportunity to utilize a rich source of valuable compounds, particularly in the context of sustainable resource valorisation. Research into extracting phenolic compounds from food waste is limited, and traditional methods predominantly use volatile organic solvents [3]. With the aim of developing a green approach for the valorization of kiwifruit waste, a study combining biobased solvents and alternative extraction techniques for the recovery of phenolic compounds from kiwifruits (*Actinidia deliciosa*) 'Hayward' by-products are presented.

First, a pre-selection of the most suitable by-product for the recovery of phenolic compounds from kiwifruits was done, with kiwifruit peels being the most promising. After a screening of the most suitable biobased solvents to be used as mixtures along with ethanol and/or water was carried out. Gamma-valerolactone (GVL) mixtures yielded the highest phenolic compounds and antioxidant activity levels. The composition of GVL mixtures was optimized to GVL:ethanol in a ratio of 7:3 (wt/wt). Response surface methodology was used to optimize the operating conditions of different extraction techniques, namely, conventional extraction (CE) and the alternative techniques of ultrasound-assisted extraction (UAE) and microwave-assisted extraction (MAE), with MAE being identified as the most promising technique to obtain an extract with high levels of phenolic compounds (mainly epicatechin, caffeic acid and quercetin derivates) and antioxidant activity, in a shorter extraction time. Nevertheless, UAE demonstrated to be the preferable extraction technique, considering the estimated costs of the studied extraction processes. This study demonstrated for the first time the potential of using GVL mixtures for extracting phenolic compounds from biomass. Combining GVL with alternative extraction techniques could form the basis for developing more efficient extraction methods [4].

Acknowledgments

AMF acknowledges the FCT for the research contract CEECIND/00361/2022. This work was partly developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, and UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), and LA/P/0045/2020 (ALiCE), funded by national funds through FCT/MCTES (PIDDAC).

References

[1] A. Wojdyło et al., *J. Funct. Foods*, **2017**, 30, 194–202.
[2] M. Oliveira et al., *Cultivo,* **2007**, 97, 43-44.
[3] V. Sanz et al., *Trends Food Sci. Technol.,* **2021**, 107, 401–414.
[4] S. Silva et al., *Sep. Purif. Technol.*, **2023**, 304, 122344

Unveiling the Nanostructure of Aqueous Hydrotrope Clusters using Molecular Probes

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Hydrotropes are amphiphilic molecules that can greatly enhance the aqueous solubility of hydrophobic solutes. The molecular mechanism of this phenomenon involves the aggregation of apolar hydrotrope moieties around solute molecules driven by the well-known hydrophobic effect. The structure of these aggregates (or clusters) at the nanoscale is still poorly understood, with the general agreement being that they display a highly disorganized arrangement of hydrotrope and solute molecules, unlike, for example, the organized assembly of surfactants into micellular structures.
The objective of this work is to study the nanostructure of hydrotrope-solute clusters using molecular probes as solutes, namely pyrene and N,N-diethyl-4-nitroaniline, and alkanediols as hydrotropes. Note that pyrene is the probe molecule of the Py polarity scale while N,N-diethyl-4-nitroaniline is the probe molecule for the popular Kamlet–Taft solvatochromic parameter π^*. Being both hydrophobic molecules with poor aqueous solubility, alkanediols are expected to aggregate around these molecular probes, forming disorganized structures akin to those seen for other hydrophobic solutes. Thus, the usage of pyrene and N,N-diethyl-4-nitroaniline permits the assessment of the contributions of the various interactions (dipolarity/polarizability, hydrogen bonding, etc.) that promote solute solubilization, and allows for the estimation of the local composition of hydrotrope around solute molecules.
A detailed experimental protocol for the accurate quantification of the Py scale is developed and described, and from that the local composition was determined and correlated with the degree and nature of the aggregation of hydrotropes in aqueous solutions. Good correlations (R^2>0.96) were found between π^* and Py for 1,n-alkanediols series due to the higher contribution of dipolarity/polarizability to the solvent-solute solvatation in hydrotropy. A transition point, from hydrotropic to micellar aggregation, was identified for 1,2-hexanediol aqueous solutions, which presented local compositions higher than the unit and low correlation between π^* and Py scales, unlike observed for the remaining systems.

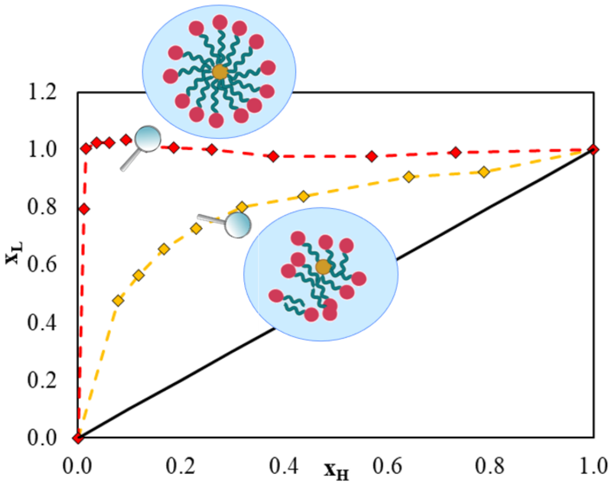

Fig. 1. Schematic representation of the local composition of hydrotrope around a hydrophobic solute in aqueous solutions (indirectly measured using pyrene) as a function of the bulk composition of hydrotrope. Note the different behaviors of hydrotropes (example in yellow) and surfactants (example in red), as well as the expected behavior of a thermodynamic ideal mixture (black line).

New experimental data and correlations for the oil-brine interfacial tension of Brazilian pre-salt fluids

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Low salinity water injection (LSWI) is an enhanced oil recovery (EOR) method that explores physicochemical interactions between phases. One of the most applied ways to achieve a higher oil recovery is related to reducing interfacial tension (IFT), allowing viscous forces to overcome capillary forces [1]. IFT is related to intermolecular forces in the interface and is affected by phase composition and system conditions [2,3]. The main objective of this work is to evaluate the effect of brine salinity on oil-brine IFT and predict its behaviour using simple correlations, which may help brine selection for LSWI. New oil-brine IFT's experimental data were determined at 61°C and 1 atm in a Drop Shape Analyzer using the reverse pendant drop method. Four different brines with total dissolved solids (TDS) of 3, 5, 30 and 225 kppm and dead oil of 26.9 °API were investigated. Correlations were developed to calculate oil-brine IFT using randomly 80% of a literature-reported IFT dataset. First, it considered the reservoir temperature (T), the °API of the oil phase, and TDS for brine salinity characterization as independent variables. The second approach considered the activity coefficient (γ) to account for non-ideal system behaviour alongside the °API. The correlations exhibited a good performance for oil-NaCl brine with an average absolute deviation of 4.9% for °API<30 and 10.5% for °API>30 when tested with the 20% IFT data remaining from the literature-reported dataset. They were also tested with the collected experimental data and Fig.1 shows that experimental and calculated IFT values are closely aligned, with a 6.3% average absolute deviation observed for the first approach. This confirms the efficacy of the simple correlations to describe the salinity effect on IFT and these results are better than those available in the literature. Additionally, this work reports new experimental data for typical pre-salt oil-brine IFT, indicating that the brine with 30 kppm presented a lower IFT for the evaluated scenario.

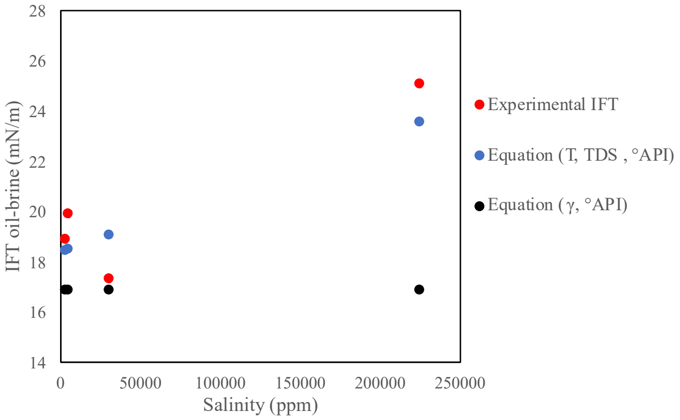

Fig 1. Comparison between experimental and calculated IFT by the developed correlations.

References

[1] M. Y. Chiang, K. S. Chan, D. O. Shah, *Journal of Canadian Petroleum Technology* **1978**, *17*, 61-68.
[2] M. Lashkarbolooki, S. Ayatollahi, M. Riazi, *Energy and Fuels* **2014**, *28*, 6820-6829.
[3] E. Hosseini, Z. Chen, M. Sarmadivaleh, D. Mohammadnazar, *Journal of Petroleum Exploration and Production Technology* **2020**, *11*, 451-475.

Poster Communication II-P39: Wednesday, September 11th, 16:40h - 18:00h

Predictive modelling stream towards an effective solvent swap operation

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Solvent swap is a common unit operation within the pharmaceutical industry enabling solvent's exchange in preparation for the isolation of an Active Pharmaceutical Ingredient (API) or intermediate. This operation has a significant impact on the sustainability of the process and for this reason it is detrimental to reduce its environmental footprint, minimize its waste generation, decrease operation cycle time, among others [1].

The use of predictive models allows to identify the most important parameters that impact operational outcomes before starting the development work in the laboratory. This screening increases the efficiency and robustness of the operation relying on low resources to reach fine-tuned results.

Bearing that in consideration, this work is focused on identifying and finding strategies that improve prediction accuracy of the distillation Dynochem® model to further direct towards an enhance solvent swap operation by reducing reliance on analytical resources, minimizing solvent waste, and shortening operation cycle time. As result, integrate the predictive model with a process control system can provide a reliable and accurate real-time prediction and, consequently, allowing a proactive decision-making and process optimization.

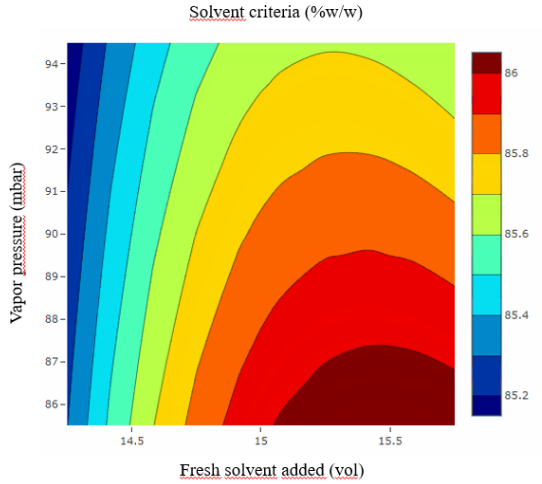

Fig. 1. Contour Plot: effect of varying vapor pressure and fresh solvent added on the solvent criteria.

References

[1] Johann G. Stichlmair, Harald Klein, Sebastian Rehfeldt, *Distillation: Principles and Practice*, John Wiley & Sons, Inc., Hoboken, New Jersey (2021).

Screening of F-gas recovery from commercial blends by phosphonium-based ionic liquids using soft-SAFT EoS and COSMO-RS models

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The current aim of lowering global concentrations of fluorinated gases (F-gases) has triggered the study of different methodologies for their capture and recycling. Among these, solubilization into novel liquid solvents, particularly ionic liquids (ILs), shows promise as an encouraging route to the circular economy of these compounds. To that end, the study and screening of suitable ILs has imposed the use of theories with increasing predictive capabilities in recent years.

The solubilization capabilities of F-gases in phosphonium-based ILs were analyzed using a combined methodology involving the soft-SAFT equation of state (EoS) and the COSMO-RS model. While COSMO-RS functions as a purely predictive model, the EoS was parameterized to experimental data with special attention to the molecular features of the ILs to grant a physically consistent framework. Results for solubility isotherms show that, on the one hand, the considered SAFT models perform qualitatively according to available experimental data. COSMO-RS, on the other hand, performs with variable accuracy, with an expected difficulty to grant reliable results at the whole molar fraction range.

To analyze the separation of selected commercial F-gas blends through ILs, ternary phase diagrams were computed, as shown in Fig. 1. Results show that the EoS fully characterizes the thermodynamic equilibrium of such systems and provides insights into the solubilization preferences for each solvent. Selectivity was used as a key indicator to quantify these preferences, and promising results were obtained for the selective separation of hydrofluorocarbon-hydrofluoroolefin blends by [P_{66614}][Cl] IL at low to moderate pressures.

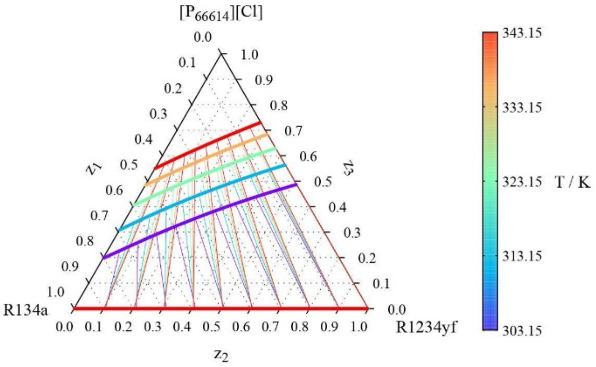

Fig. 1. Ternary equilibrium diagram of the R134a (1) + R1234yf (2) + [P_{66614}][Cl] (3) system at different temperatures.

Estimation of Water in Oil Emulsions Relative Viscosity Using an Artificial Neural Network Ensemble

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An ensemble of Artificial Neural Networks was applied to estimate de relative viscosity of water in crude oil emulsions at atmospheric pressure and 50 s^{-1} shear rate. A database of 1277 measurements of the relative viscosity of Brazilian crude oil emulsions was used to train the models [1]. System temperature, crude oil *API* gravity, emulsion water content and the oil wax appearance temperature (WAT) were used as input variables. The hyperparameters of the networks, including the number of layers, number of neurons and optimizer learning rate were adjusted using a random search algorithm to find the best network architecture. The Exponential Linear Unit (ELU) activation function was used in the hidden layer neurons. A 5-fold cross validation was applied to the best architecture found and the weighted average of the networks predictions was used to estimate the relative viscosity. The ensemble was compared with empirical correlations available in the literature, using the average absolute error (AAE), the average absolute relative error (AARE) and the coefficient of determination (R^2) as performance criteria [2,3,4]. The ensemble exhibited a better performance than the tested correlations and can be applied with accuracy for a wider range of relative viscosities. It was found that high values of relative viscosities cannot be correct predicted using the selected input variables.

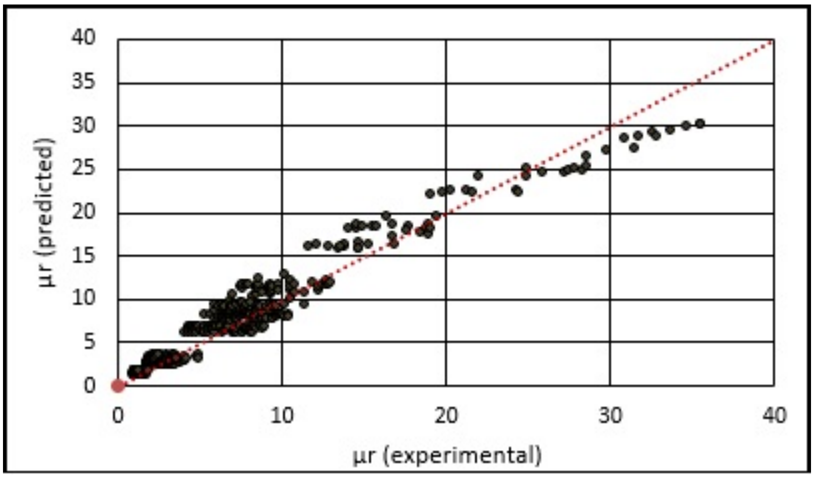

Fig. 1. Predicted vs experimental relative viscosity.

References

[1] M. C. K. De Oliveira, L. R. Miranda, A. B. De Carvalho, D. F. S. Miranda, *Energ. Fuel Viscosity of water-in-oil emulsions from different API gravity Brazilian crude oils* **2018**, *v. 32*, n. 3, p. 2749-2759.
[2] A. Kalra, A. Venkatraman, K. Raney, B. Dindoruk, *SPE Symp. Improv. Oil Recovery* Prediction and Experimental Measurements of Water-in-Oil Emulsion Viscosities During Alkaline/Surfactant Injections **2012**.
[3] H. P. Ronningsen, *SPE Int. Oilfield Chem. Symp* Correlations for predicting viscosity of W/O-emulsions based on North Sea crude oils **1995**.
[4] C. F. Nascimento, V. V. D. Lubisse. *UFRJ Uma Correlação Para A Viscosidade Relativa De Emulsões De Água Em Óleo Utilizando Técnicas De Machine Learning* **2020.**

Determination and correlation of physical properties of systems {$N_{4444}Cl$ + Na_2SO_4 or $(NH_4)_2SO_4$ + H_2O} at 298.15 K

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Aqueous Biphasic Systems (ABS) are a liquid-liquid fractionation technique [1], where two aqueous solutions are mixed under specific thermodynamic conditions [2], it is considered a possible replacement to the conventional solvent extraction process [3]. ABSs are usually applied in chemical or biotechnological partitioning processes [4], metal separation, environmental remediation [5], purification and preconcentration [6], etc. ABSs made up mostly of a polymer and a salt, ionic liquid (IL) + polymer + water or IL + polymer + salt + water [7], but there is very little information regarding the study of IL + salt + water systems for the extraction of metals and much less studies on the physical and chemical properties of solutions of these systems. Studies of physical and chemical properties of aqueous solutions are of great importance in chemical engineering because they help to understand the fundamentals of separation, fluid transport and wastewater treatment, properties such as density and viscosity help the design of a process, among them mass balance and equipment design stand out [8]. The results obtained in this study of the physical properties of systems {tetrabutylammonium chloride ($N_{4444}Cl$) + sodium sulfate (Na_2SO_4) or ammonium sulfate $(NH_4)_2SO_4$ + water}, are a step to be able to carry out the extraction of metals with these systems, which They are a promising alternative to replace the conventional solvent extraction currently applied in the industry. The physical properties (refractive index, density, speed of sound and dynamic viscosity) of 2 ternary systems were measured: {$N_{4444}Cl$ + Na_2SO_4 + H_2O} and {$N_{4444}Cl$ + $(NH_4)_2SO_4$ + H_2O} and their constituent binary systems, at different mixtures of diluted solutions at 298.15 K, were determined experimentally and correlated using Othmer's rule, obtaining good agreement between the experimental data and the correlated ones with average absolute deviations (AAD) between 0.00008 to 0.51184, in addition the values of the parameters were calculated of the Othmer equation. Figure 1 shows the comparison of the refractive index and speed of sound between the ternary {$N_{4444}Cl$ + Na_2SO_4 + H_2O}, the binary systems that constitute the ternary and the values calculated by the Othmer equation.

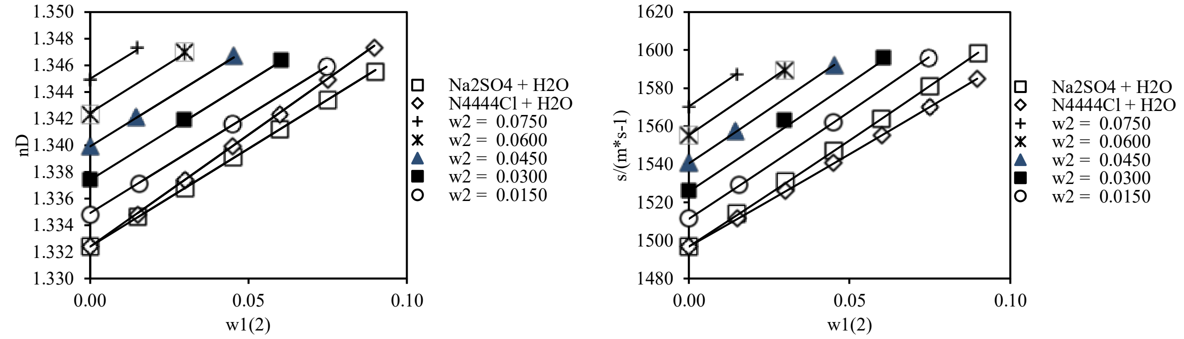

Figure 1. Refractive index (nD) and Speed of sound (s) at 298.15 K for the ternary system: $N_{4444}Cl$ + Na_2SO_4 + H_2O, for different mass fractions of Ionic Liquid ($N_{4444}Cl$), and its constituent binary systems, in different mass fractions of salt (w1) and Ionic Liquid (w2); (—) values calculated by the Othmer equation.

References

[1] M. Iqbal, Y. Tao, S. Xie, Y. Zhu, D. Chen, X. Wang, L. Huang, D. Peng, A. Sattar, M. A. B. Shabbir, H. I. Hussain, S. Ahmed and Z. Yuan, *Aqueous two-phase system (ATPS): an overview and advances in its applications. BMC Part of Springer Nature, Biological Procedures Online*, **2016**, *18*. https://doi.org/10.1186/s12575-016-0048-8.

[2] D. da Silveira Leite, P. L. G. Carvalho, L. R. de Lemos, A. B. Mageste and G. D. Rodrigues, *Hydrometallurgical recovery of Zn(II) and Mn(II) from alkaline batteries waste employing aqueous two-phase system. Separation and Purification Technology*, **2019**, *210*, 327–334. https://doi.org/10.1016/j.seppur.2018.07.038.
[3] F. J. Deive and A. Rodríguez, *(Liquid+liquid) equilibrium of aqueous biphasic systems composed of 1-benzyl or 1-hexyl-3-methylimidazolium chloride ionic liquids and inorganic salts. The Journal of Chemical Thermodynamics*, **2012**, *54*, 272–277. https://doi.org/10.1016/j.jct.2012.05.004.
[4] J. V. D. Molino, D. de A. Viana Marques, A. P. Júnior, P. G. Mazzola and M. S. V. Gatti, *Different types of aqueous two-phase systems for biomolecule and bioparticle extraction and purification. Biotechnology Progress*, **2013**, *29*, 1343–1353. https://doi.org/10.1002/btpr.1792.
[5] A. Hamta and M. R. Dehghani, *Application of polyethylene glycol based aqueous two-phase systems for extraction of heavy metals. Journal of Molecular Liquids*, **2017**, *231*, 20–24. https://doi.org/10.1016/j.molliq.2017.01.084.
[6] Z. Tan, Y. Yi, H. Wang, W. Zhou and C. Wang, *Extraction, preconcentration and isolation of flavonoids from Apocynum venetum L. leaves using ionic liquid-based ultrasonic-assisted extraction coupled with an aqueous biphasic system. Journals Molecules*, **2016**, *21*, 262. https://doi.org/10.3390/molecules21030262.
[7] M. Claros, M. E. Taboada, H. R. Galleguillos, and Y. P. Jimenez, *Liquid–liquid equilibrium of the CuSO4 + PEG 4000 + H2O system at different temperatures. Fluid Phase Equilibria*, **2014**, *363*, 199–206. https://doi.org/10.1016/J.FLUID.2013.11.038.
[8] F. J. Justel and Y. P. Jimenez, *Physical properties of {Fe2(SO4)3 + PEG 4000 + H2O} solutions at high temperatures. The Journal of Chemical Thermodynamics*, **2021**, *161*, 106540. https://doi.org/10.1016/J.JCT.2021.106540.

(Liquid + liquid) equilibrium of ($N_{4444}Cl$ + Na_2SO_4 or $(NH_4)_2SO_4$ + H_2O) ternary system at different temperatures

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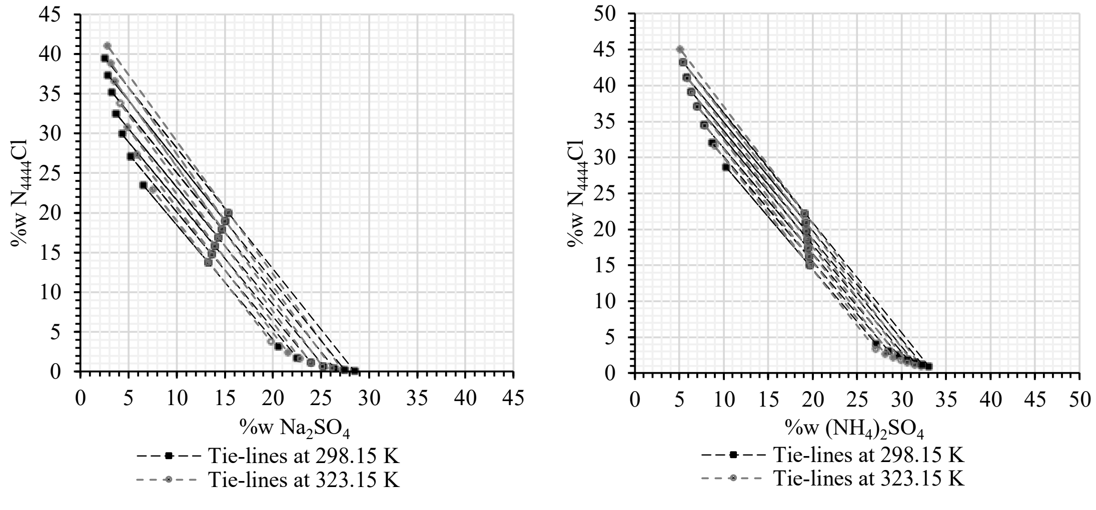
Aqueous Biphasic Systems (ABS) are a liquid-liquid fractionation technique [1], they are clean alternatives to traditional extraction systems with organic solvents [2], because the main component of the two phases is water [3]. ABSs are formed when two polymers, a polymer and a cosmotropic salt, two salts (one chaotropic salt and the other cosmotropic salt), ionic liquid (IL) + polymer + water, or IL + salt + water, etc. They are mixed in appropriate concentrations or at a particular temperature. In recent years, studies on the use of ILs in mineral processes as a green alternative have increased exponentially [4]. ILs have unique properties as new green solvents and according to their chemical synthesis they can be divided into protic ionic liquids (PILs) and aprotic ionic liquids (AILs) [5]; Just a few years ago, a growing interest in PILs began, which presents favorable results in the extraction of metals [6] that have a simpler chemical synthesis mode, and also present lower production costs and environmental impacts [7]. In the present work, the equilibrium data (liquid + liquid) of the systems (tetrabutylammonium chloride ($N_{4444}Cl$) + sodium sulfate (Na_2SO_4) or ammonium sulfate $(NH_4)_2SO_4$ + water) were determined experimentally at different temperatures (298.15 K and 323.15 K) by the calibration curves method, where $N_{4444}Cl$ is a PIL. The reliability of the compositions of the tie lines was determined using the correlation equations given by Othmer-Tobias and Bancroft, where the tie lines were satisfactorily described with correlation coefficient (R) values between 0.9973 to 0.9998, the values of the corresponding parameters of each equation were also calculated. The influence of the temperature on the phase equilibrium was analyzed by applying the slope of the tie line (STL) concept, likewise the tie line length (TLL) was calculated. The results showed that for the systems under study, the increase in temperature from (298.15 to 323.15 K) led to an increase in the STL and according to the calculated TLL, it was observed that the effect of temperature was insignificant within the investigated range. Figure 1 shows the effect of temperature on the lines of the systems studied.



(a) (b)

Figure 1. Effect of temperature on the tie lines for the systems (a) $N_{4444}Cl$ + Na_2SO_4 + H_2O and (b) $N_{4444}Cl$ + $(NH_4)_2SO_4$ + H_2O at 298.15 K and 323.15 K.

References

[1] M. Iqbal, Y. Tao, S. Xie, Y. Zhu, D. Chen, X. Wang, L. Huang, D. Peng, A. Sattar, M. A. B. Shabbir, H. I. Hussain, S. Ahmed, Z. Yuan, *Aqueous two-phase system (ATPS): an overview and advances in its applications. Biological Procedures Online*, **2016**, *18*. https://doi.org/10.1186/s12575-016-0048-8.

[2] F. J. Deive, A. Rodríguez, *(Liquid + liquid) equilibrium of aqueous biphasic systems composed of 1-benzyl or 1-hexyl-3-methylimidazolium chloride ionic liquids and inorganic salts. The Journal of Chemical Thermodynamics*, **2012**, *54*, 272–277. https://doi.org/10.1016/J.JCT.2012.05.004.

[3] N. Tang, Y. Wang, M. Liu, L. Liu, C. Yin, X. Yang, S. Wang, *Ionic liquid as adjuvant in an aqueous biphasic system composed of polyethylene glycol for green separation of Pd (II) from hydrochloric solution. Separation and Purification Technology*, **2020**, *246*, 116898. https://doi.org/10.1016/J.SEPPUR.2020.116898.

[4] N. Nasirpour, M. Mohammadpourfard, S. Zeinali Heris, *Ionic liquids: Promising compounds for sustainable chemical processes and applications. Chemical Engineering Research & Design: Transactions of the Institution of Chemical Engineers*, **2020**, *160*, 264–300. https://doi.org/10.1016/j.cherd.2020.06.006.

[5] P. Vallet, S. Bouzón-Capelo, T. Méndez-Morales, V. Gómez-González, Y. Arosa, R. de la Fuente, E. López-Lago, J. R. Rodríguez, L. J. Gallego, J. J. Parajó, J. Salgado, M. Turmine, L. Segade, O. Cabeza, L. M. Varela, *On the physical properties of mixtures of nitrate salts and protic ionic liquids. Journal of Molecular Liquids*, **2022**, *350*, 118483. https://doi.org/10.1016/J.MOLLIQ.2022.118483.

[6] A. R. Abouelela, A. A. Mussa, M. Talhami, P. Das, A. H. Hawari, *Industrial sludge valorization and decontamination via lipid extraction and heavy metals removal using low-cost protic ionic liquid. The Science of the Total Environment,* **2022**, *835*, 155451. https://doi.org/10.1016/j.scitotenv.2022.155451.

[7] G. Inman, I. C. Nlebedim, D. Prodius, *Application of ionic liquids for the recycling and recovery of technologically critical and valuable metals. Energies,* **2022**, *15*, 628. https://doi.org/10.3390/en15020628.

Aggregates formation and thermophysical properties of aqueous solutions of ionic liquids based on hydrogen sulphate anion and substituted hydroxylammonium cations

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Ionic liquids (ILs) present several attractive properties in different fields of science and industry. Notably, ILs containing substituted sulfate anions are attractive solvents for dissolving metal oxides when combined with various cations. One of the outstanding thermophysical properties with industrial application is the ability of these ILs to self-organize, forming clusters such as micelles or hydrotopes, which can play the role of surfactants. This study aims to investigate the ability to form aggregates in three ionic liquids formed from the combination of 2-hydroxyethylammonium $[2HEA]^+$, N-methyl-2-hydroxyethylammonium $[m\text{-}2HEA]^+$, $[e\text{-}2HEA]^+$ combined with the hydrogen sulfate anion $[HSO_4]$, in addition to analyzing its thermophysical properties, such as refractive index, density and viscosity, pure and in aqueous solutions. The ILs were synthesized through a stoichiometric Bronsted reaction, and these compounds were characterized using proton nuclear magnetic resonance (NMR) (1H), confirming their structures and purity. The thermophysical properties of these ILs were measured over a temperature range of 288 to 323 K, in 5 K increments, under ambient pressure. The same range was used for mixtures, and solutions were prepared gravimetrically across the entire concentration range. Density and viscosity were measured using an SVM3000 viscodensimeter and refractive index with the RXA170, both manufactured by Anton Paar. The concentration points of aggregates in diluted aqueous binary solutions of ILs were quantitatively calculated based on experimental conductivity data. The conductivities of the diluted aqueous ionic liquids solutions were indirectly measured by electrochemical impedance spectroscopy (EIS) in a modular gravimetric potentiostat from Metrohm PGSTAT302N. Dynamic light scattering (DLS) was used to measure the size of the agglomerates formed in a Zetasizer nano ZS, and the results were correlated with the concentration of the aqueous solutions, allowing the identification of their formation structures. In order to understand the effect on the properties of the alkyl substitution on cation, sigma profiles and semi-empirical quantum calculations performed with the Molecular Orbital Package (MOPAC)[1] were used. The induced charge surfaces for each ion (sigma profiles) were obtained using the JCOSMO package [2]. The addition of methyl or ethyl groups enhances the packing and thus the density, and the order $[2HEA]^+ > [m2HEA]^+ > [e2HEA]^+$ is observed. The same order is observed for viscosity as the lateral chain lowers the tangling in the ILs, increasing the fluidity. The refractive index and the concentration at the aggregation point follow the order $[e\text{-}2HEA]^+ < [m\text{-}2HEA]^+ < [2HEA]^+$, and this result is correlated with the order of ionization potential and dipole moment calculated through MOPAC. Adding a methyl or an ethyl group to the cation only slightly changes the conformational energy and this property could not be directly used to explain the aggregation.

References

[1] MOPAC2016, James J. P. Stewart, *Stewart Computational Chemistry, Colorado Springs, CO, USA, available in HTTP://OpenMOPAC.net* (2016).

[2] F. Ferrarini, G. B. Flôres, A. R. Muniz, R. P. de Soares. *An open and extensible sigma-profile database for COSMO-based models* 64: 9, 3229-3553. (2018) https://doi.org/10.1002/aic.16194

Selective recovery of platinum from spent automotive catalytic converters via hydrometallurgy and adsorption

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In the European Union's Critical Raw Materials (CRM) list, Platinum Group Metals (PGM) - encompassing platinum, palladium, rhodium, osmium, iridium, and ruthenium - are identified as materials facing a significant risk of supply scarcity.[1] A key utilization of this metals is in the manufacture of automotive catalytic converters (CCs), essential for mitigating pollutants produced during combustion processes and correspondig of more then 60% of the market share for Pt, Pd and Rh.[2] In recent decades, propelled by the surge in global vehicle manufacturing and the implementation of stricter environmental standards, there has been a significant and swift rise in the accumulation of used automotive catalytic converters (SACCs) without a corresponding rise in the rate of recycling.[3] As a result, SACCs present a significant challenge for waste management while also holding promise as a secondary reservoir of vital and strategic materials. The extraction of platinum (Pt) from SACCs can be achieved through a hydrometallurgical process consisting of three main stages: leaching (dissolving), purification (isolation), and refining (recovery of purified metal). In this study, instead of using conventional highly acidic solutions, we introduced an alternative approach for the leaching process. This involved utilizing a "water-in-salt" solution composed of aluminum chloride and aluminum nitrate, that efficiently dissolved 91% of Pt. Salts concentration, solid:liquid ratio, temperature and time of reaction were optimized. The analysis revealed that temperature emerged as the primary influential factor, and the empirical kinetic data were effectively elucidated using the chemical reaction control model. For the purification, an adsorption with the ionic exchange resin Ambersep 900® was carried out, reaching a selectivity of 90% for Pt. The Freundlich isotherm model were the best fit for the process, indicating that Pt sorption occurs in a multilayer way. Furthermore, the kinetics data were accurately described by Ho's model, suggesting that chemisorption serves as the predominant sorption mechanism. To the refining, thiourea was used as a stripping agent, resulting in a platinum purity of 98%.

Acknowledgements

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References

[1] EC-European Commission, *Study on the Critical Raw Materials for the EU 2023 – Final Report*, **2023**.
[2] IPA - International Platinum Group Metals Association, *On the Occasion of the IPA' s 25th Anniversary We Present: 25 Prominent and Promising Applications Using Platinum Group Metals*, **2012**.
[3] N. Bahaloo-Horeh and S. M. Mousavi, *J Hazard Mater*, **2020**, 400, 123186.

Valuable and critical metals recovery from tantalum capacitor waste through liquid-liquid extraction

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Tantalum capacitors, with their high capacitance density and reliability, have become indispensable components in several electronic devices, from smartphones to aerospace technology. However, the rapid pace of technological advancement and shortened life cycle of electronic goods result in the significant generation of waste tantalum capacitors (WTCs), contributing to the growth of the electronic waste (e-waste) crisis. Tantalum (Ta), a key component of WTCs, is a rare and valuable metal, categorized by the European Union as a critical material [1]. However, despite tantalum capacitors demand accounting for around 34% of the total Ta production [2], the recycling rate of this metal from current end-of-life products is still less than 1% [3]. Therefore, it is urgent to develop an efficient and cost viable technology to recovery Ta, among another valuable metals, from this e-waste. The recycling of WTC presents unique challenges due to the complex composition of the material and the difficulty to extract and refine Ta. In this work, we present an innovative approach using a hydrometallurgical process in which Ta is not extracted to the liquid phase, but instead it remains in the solid fraction. With this approach, not only Ta can be recovered from WTC, but also manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn) and silver (Ag). After dismantling and milling, the WTC powder was submitted to a leaching step with sulfuric acid solution. In this media, Mn, Ni, Cu and Zn are dissolved, while Ta and Ag remain in the solid phase. The liquid phase undergoes the precipitation of Mn, followed by successive liquid-liquid extractions using an organic phase consisting of a mixture of dodecane and Cyanex® 272 at different pH values. Subsequently, the metals are individually recovered in aqueous solutions with purities of 93, 98, 98 % for Zn, Cu and Ni, respectively, all of them with more them 97% of total recovery. Finally, Ag was separated from Ta using diluted nitric acid solutions. Ag presented purity equal 96%, and Ta 98%.

Acknowledgements

This work was developed partly within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). This work was further supported by national funds through FCT/MCTES (PIDDAC): LSRE-LCM, UIDB/50020/2020 (DOI: 10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI: 10.54499/UIDP/50020/2020); and ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020*).* AMF and F. Braga acknowledges FCT for the research contract CEECIND/00361/2022 (DOI: 10.54499/2022.00361.CEECIND/CP1720/CT0020) and the Ph.D. grant 2023.01749.BD, respectively. MCH thanks Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq 305649/2021-3).

References

[1] EC-European Commission, *Study on the Critical Raw Materials for the EU 2023 – Final Report*, **2023.**
[2] Agrawal, M., Jha, R., Singh, R., & Singh, K. K., *Sustainable Production and Consumption*, **2022**, *34*, 385–394.
[3] Agrawal, M., Singh, R., Ranitović, M., Kamberovic, Z., Ekberg, C., & Singh, K. K., *Sustainable Materials and Technologies*, **2021,** 29, e00323.

Gibbs films of ionic liquids: organization and stability of 1-alkyl-3-methylimidazolium chloride films by MD simulation

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Understanding the structure and stability of films of ionic liquids is essential in the development of new and innovative technologies in different areas such as materials science and electrochemistry, among others [1]. The use of ionic liquids presents many advantages such as very low volatility, the fact that they remain liquid over a wide range of temperatures and the countless possible combinations of cations and anions, that led these compounds to be called ‘designer solvents’ [2]. Ionic liquids of the 1-alkyl-3-methylimidazolium family are among the most studied. Their properties depend strongly on the length of the alkyl chain and the nature of the counter-ion.

In recent work, [3,4] the ability of the [$C_{18}mim^+$] and [$C_{20}mim^+$] cations, when combined with the [NTf_2^-] anion, to form Langmuir films was demonstrated. Under compression the films develop a trilayer. Contrarily, the same cations, when combined with a hydrophilic anion such as Cl^-, form Gibbs films which dissolve in the water subphase. These salts are known to form micelles in aqueous solution.

In this work, atomistic Molecular Dynamics simulations are used to study the organization and stability of the Gibbs films of [$C_n$mim]Cl ionic liquids at the surface of water. The influence of the alkyl chain length has been studied (n = 10,12,14,16,18,20) at different surface coverages. The simulation results clearly indicate the formation of “hemimicelle-type” aggregates, partially immersed in water. On compression, these are seen to plunge into the water subphase forming micelles.

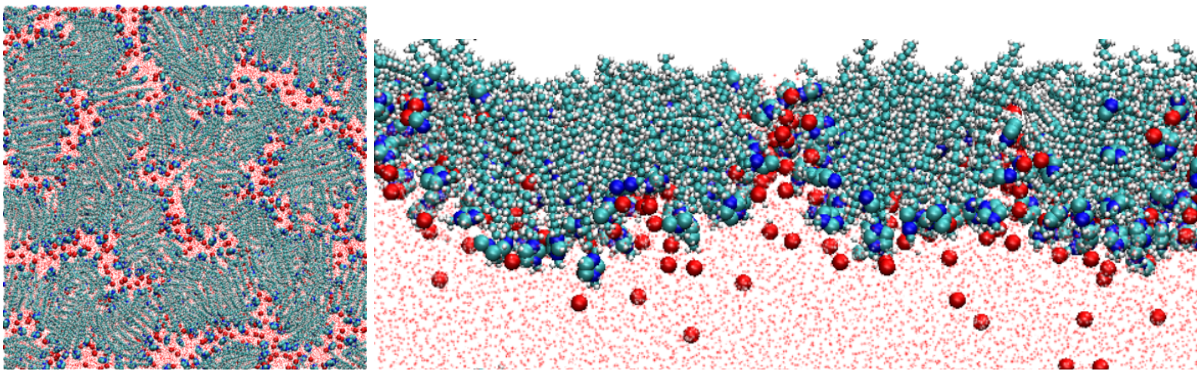

Fig. 1. Simulation snapshots of [$C_{18}mim^+$]Cl^- at the vacuum-water interface at 0.46 nm²/molec. (left) top view; (right) side view.

References

[1] Singh, S.K., Savoy, A.W., *Journal of Molecular Liquids* **2020**, *297.* [2] Plechkova, N.V., Seddon, K.R., *ChemPhysRev*, 2008, 37, 123-150. [3] E. J. M. Filipe, P. Morgado, M. Teixeira, K. Shimizu, N. Bonatout, M. Goldmann, J. N. Canongia Lopes, Crystalline-like structures and multilayering in Langmuir films of ionic liquids at the air-water interface, *Chemical Communications*, 2016, ***52***, 5585 – 5588. [4] S. Taßler, N. Bonatout, R. M. Valente, E. J. M. Filipe, T. Rego, H. Ibrahim, G. Brezesinski, M. Goldmann, P. Fontaine, Surface behaviour of 1-alkyl-3-methylimidazolium ionic liquids at the air-water-interface, Journal of Molecular Liquids, **2023**, 370, 121028.

Aneotropy: Unusual interfacial behaviour of mixtures of hydrogenated and fluorinated substances

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The well-known mutual phobicity between hydrogenated and fluorinated chains gives rise to unexpected and intriguing behaviour in the properties of their mixtures. Indeed, mixtures of hydrogenated and perfluorinated substances display large anomalies in phase equilibria, volumetric, dynamic and conformational properties [1,2]. Despite all efforts to understand this phenomenon at the fundamental level, its origin is still not known.

This peculiar behaviour extends to the interfacial properties of the mixtures, in particular the occurrence of a rare and not fully understood phenomenon named aneotropy, characterized by the existence of minima (or maxima) on the surface tension versus composition curve of liquid mixtures. In recent research, it was shown for the first time that mixtures of hydrogenated and fluorinated alcohols also display aneotropy [3]. In the present work the subject is further explored and extended to mixtures of fluorinated alcohols and hydrogenated amines, particularly primary and tertiary amines. New experimental data has been obtained for the liquid density, liquid-vapor surface tension. Other pertinent thermodynamic properties have also been measured and calculated, such as the excess molar volumes of the mixtures. Furthermore, atomistic molecular simulations of the bulk and interface have be conducted to better understand the organization of the liquid mixture and the detailed orientation and distribution of molecules at the interface.

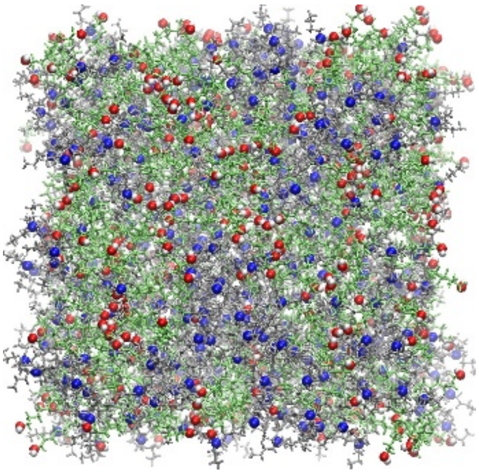

Fig. 1. Snapshot of a MD simulation depicting the bulk of an equimolar binary mixture of (tributylamine + 1H,1H-perfluoroheptanol). Nitrogen atoms are highlighted in blue, oxygen atoms in red, the fluorinated chain is depicted in light green, and the alkyl chain in grey.

References

[1] P. Morgado, L.F.G. Martins, E.J.M. Filipe, from nano-emulsions to phase separation: evidence of nano-segregation in (alkane + perfluoroalkanes) mixtures using ^{129}Xe NMR Spectroscopy, Phys. Chem. Chem. Phys. 21 (2019) 3742–3751.

[2] P. Morgado, H. Rodrigues, F. J. Blas, C. McCabe, E. J. M. Filipe, Perfluoroalkanes and perfluoroalkyl alkane surfactants in solution: Partial molar volumes in *n*-octane and hetero-SAFT-VR modelling, Fluid Phase Equilibria. 306 (2011) 76–81.

[3] J. Justino, M. Teixeira, D. Machacaz, P. Morgado, L. F. Vega, E. J. M. Filipe, Unusual interfacial behaviour of mixtures of 2,2,2-Trifluoroethanol with hydrogenated alcohols, Journal of Molecular Liquids, 2024, 393, 123684.

Self-Assembly of Compartmentalized Micelles

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The mutual phobicity between hydrogenated and fluorinated chains is at the origin of several unusual anomalies in the properties of pure components and mixtures. We have recently shown that mixtures of hydrogenated and fluorinated ionic surfactants in aqueous solution exhibit intramicellar segregation [1], displaying hydrogen-rich and fluorine-rich domains and thus demonstrating the formation of compartmentalized micelles.

The compartmentalization of these nano systems is a fascinating topic. Their ability to solubilize solutes of different natures and to self-assemble with different structures has led to an increasing importance in areas ranging from detergents to drug delivery. It is thus obvious that an understanding of the self-assembly process is crucial for the design of those compartmentalized nano systems.

In this work, atomistic Molecular Dynamics simulations of 1-alkyl and fluoroakyl-3-methylimidazolium ionic liquids in aqueous solution were performed to study the self-assembly of different types of partially fluorinated surfactants and of mixtures of hydrogenated and fluorinated surfactants. The structure of both classes of compartmentalized micelles was determined analysing micelle size, composition, and radial distributions, showing that intramicellar segregation occurs in both cases. In the case of partially fluorinated surfactants, the fluorinated parts of the chains seem to aggregate in such a way to form the "core" of the micelle, while the hydrogenated parts and the ionic heads rest on the outer layer, indicating radial segregation, as shown in figure 1a). In the case of the mixed surfactant systems, a lateral segregation promoted by the phobicity between both types of chains is observed, visible in figure 1b). Clearly, different types of domains are formed within each aggregate, evidencing the formation of different morphologies of compartmentalized micelles. The influence of chain length, degree of fluorination and composition are addressed.

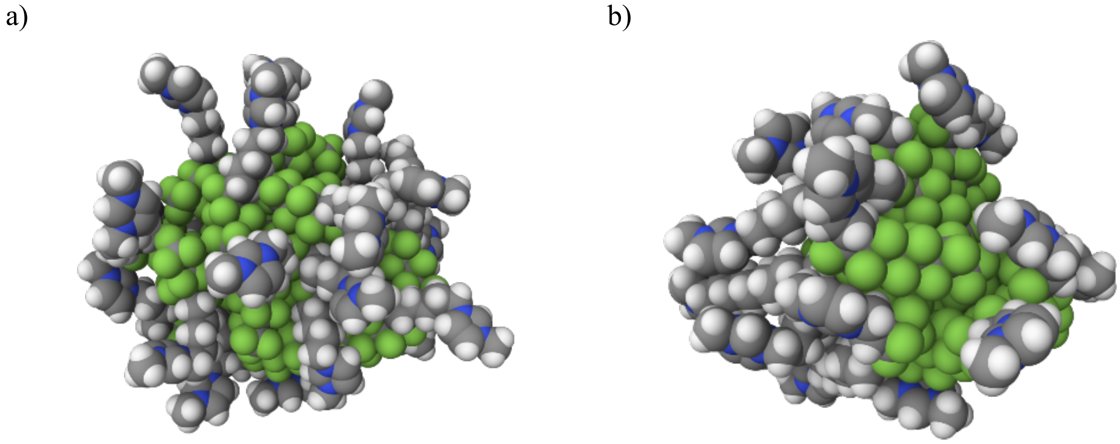

Fig. 1. Molecular Dynamics snapshots of compartmentalized micelles formed during the simulations. a) A partially fluorinated ionic liquid micelle. b) A mixed hydrogenated and fluorinated ionic liquid micelle. The atoms are coloured according to the following scheme: C in grey, N in blue, H in white, and F in green.

References

[1] G. M. C. Silva, P. Morgado, E. J. M. Filipe, *Journal of Colloid and Interface Science* **2024**, *654*, 906-914

Poster Communication II-P50: Wednesday, September 11th, 16:40h - 18:00h

New Fluorinated Surfactant-Free Microemulsions: experimental and molecular dynamics simulations

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Detergent-less or surfactant-free microemulsions (SFMEs) are ternary mixtures composed of two immiscible fluids and a third one, which promotes the solubilization of the three components. The third component, often known as hydrotrope, is typically a small molecule like ethanol or propanol. This unique type of emulsion presents diverse applications, such as drug delivery, due to its solubilization power. The presence of this type of microemulsions can also be found in daily life products, such as in Eau de Perfum or even repellents.

In this work, a new type of SFMEs involving a perfluorinated compound is presented, thus featuring the presence of coexisting aqueous, fluorinated and hydrogenated domains. The focus of the work is the study of this new type of microemulsion by experimental techniques, complemented with molecular dynamic simulations. The ternary liquid-liquid equilibrium phase diagram was determined, and the interfacial tensions of the coexisting phases were measured. The surface tension of solutions within the monophasic region were also measured at constant water/ethanol volume fraction and found to display a typical surfactant behaviour, enabling the determination of a critical aggregation concentration. The existence of aggregates was demonstrated by DLS and their size estimated. Finally, atomistic computer simulations provide a detailed description of the structure of the aggregates at the molecular level, and of the organization of the liquid-vapour interface.

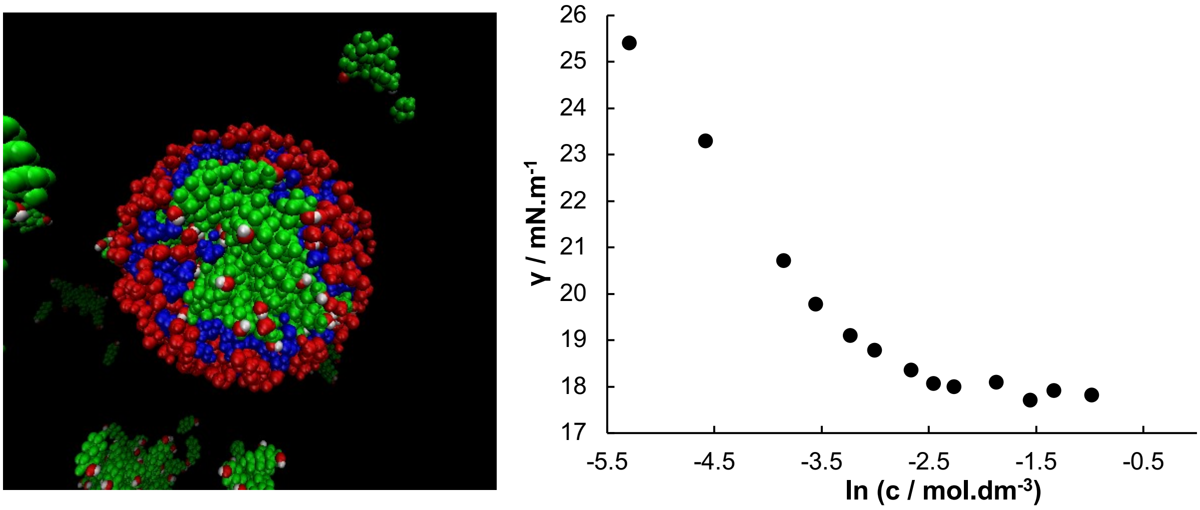

Fig. 1. Left: Snapshot of a fluorinated aggregate, with the fluorinated core in green and the ethanol, in blue, and water, in red, at the surface of the aggregate. Right: Experimental surface tension as a function of the logarithm of the concentration of 1H,1H-Perfluoroheptan-1-ol at a constant water/ethanol volume ratio of 1.15 and 297.15K.

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