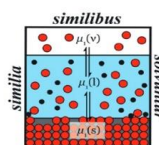




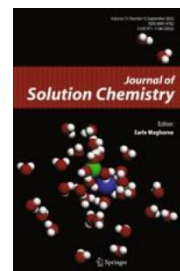
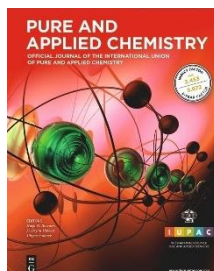
International **S**ymposium  
on **S**olubility **P**henomena  
and Related Equilibrium Processes



# BOOK OF ABSTRACTS

4<sup>th</sup> – 9<sup>th</sup> September 2022

Virtual Meeting - Polytechnic Institute of Bragança



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Dear Delegates,

Welcome to the 20th edition of the International Symposium on Solubility Phenomena and Related Equilibrium Processes held at the Polytechnic Institute of Bragança, in Portugal, from 4 to 9 of September, 2022, including the meeting of IUPAC Subcommittee on Solubility and Equilibrium Data (SSED). This biennial IUPAC symposium once again gathers international experts on solubility studies, or related subjects, to exchange scientific research and technological applications within the academic, scientific, and technical communities.

From ancient Greece, the concept of a symposium encompasses the discussion in a vivid, enlightening, and convivial way. The current impediments to set up an in-person meeting did not limit this spirit or its objectives. The symposium aims to celebrate creativity, diversity, and friendship among participants, promoting the exchange of ideas and fruitful interactions. For that purpose, we have about 110 delegates from 25 countries, and your active participation is highly acknowledged.


The general importance of solubility phenomena and associated physical properties is addressed in a variety of settings ranging from green chemistry to nuclear waste disposal, always envisaging applications for a sustainable development. This edition includes the contribution of 7 invited lectures and 48 oral presentations distributed in eleven sessions, and 34 posters that will be presented in two dedicated sessions. The abstracts cover a broad range of topics in search for innovative solutions in a sustainable development framework (*e.g.*, greenhouse gases solubility, deep eutectic solvents and ionic liquids applications, remediation of mining and industrial impacts, mineral recovery from brines and seawater and energy storage, among others).

Two additional workshop sessions organized within the activities of the project “Workshop on Assessment of Reliability and Uncertainty of Solubility Data” will be open to the participants on Wednesday afternoon, aiming to give fundamental and practical knowledge on good practices for phase equilibria measurements, data analysis, and reporting high quality data to the scientific community.

The Franzosini award will be announced in a special session on Friday, in recognition of a promising young contributor to this area. On that same day, the best poster and oral presentation by young scientists will be also awarded.

Finally, we would like to express again our deepest appreciation to all the participants, but also to the members of the Organizing Committee and International Advisory Board for their contribution to the conference and acknowledge the institutional support of IUPAC, SSED, Instituto Politécnico de Bragança, Centro de Investigação de Montanha, Sociedade Portuguesa de Química, Springer, and the reference SCI publications Journal of Solution Chemistry and Pure and Applied Chemistry.

Our warmest regards,



Simão Pinho and Olga Ferreira

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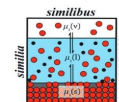
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## ***Invited Presentations***

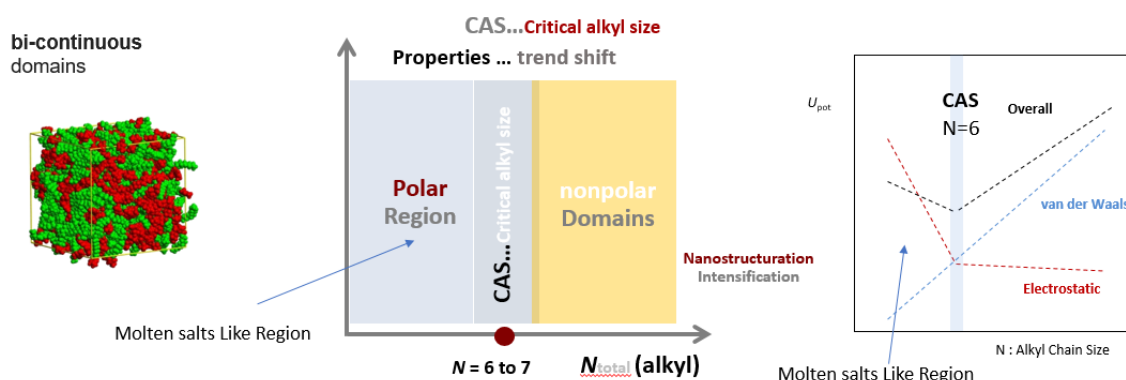
## PLENARY LECTURE 1

### NANOSTRUCTURATION EFFECT ON THE PROPERTIES OF IONIC FLUIDS

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The nanostructuration in the ionic fluids affects the trend of properties along the series and is dependent of the alkyl chain size, cation and anion nature. In some recent publications [1-5] a significant differentiation of the trend of the thermodynamic properties before and after CAS (critical alkyl size of  $n=6$ ) was observed due to the change of the cohesive electrostatic potential that rules the network packing both in solid and liquid phases. Further studies allowed us to unravel the role of IL nanostructuration and acidity on the preferential interactions established between the alcohol and the IL, the speciation and cohesive energy of protic ionic liquids [6] as well as their nucleation and growth of micro droplets of ILs deposited by physical vapor method onto different surfaces [7].



**Scheme 1.** Nanostructuration effect on the properties of ionic liquids.

We were able to give additional support to the nanostructuration effect on the thermodynamic and transport properties on several ionic liquids families. Ionic liquids form nanoaggregates constituted by anions and cations giving rise to a network of highly polar areas ruled by coulombic forces and nonpolar ones corresponding to regions of alkyl chains dominated by van der Waals interactions.

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## PLENARY LECTURE 2

### SOLUBILITY OF BIOMOLECULES

**Christoph Held**

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The knowledge on solubility of biomolecules is of utmost importance in the design of downstream processes such as crystallization. Solubility depends on the liquid-phase conditions such as temperature, pH, the solvent, and the presence of additives. Experimental solubility measurements are very expensive considering the diverse experimental conditions that need to be accessed as described above. Thus, modeling solubility based on physical properties such as melting properties of the pure biomolecules and their thermodynamic mixture behavior is highly desired. The talk will focus on the solubility measurement and modeling techniques for biomolecules such as amino acids, peptides, sugars and salts.

The first part of the talk will give an overview on solid properties of biomolecules that decompose before melting (such as amino acids), solubility measurements of these compounds and modeling [1]. The melting properties of amino acids, peptides and sugars were determined using Fast Scanning Calorimetry (FSC). Modeling solubility was then based on these FSC data by solving the condition of a solid-liquid equilibrium between the biomolecule in the saturated phase and in the solid phase. The temperature dependency of the melting enthalpy was taken into account by considering the difference in the heat capacities of the solid and liquid state. It was found that the melting properties dictates the solubility behavior to a large amount, and that the non-idealities in the mixture (i.e., activity coefficients at solubility conditions) must be considered to model solubility in water. Solubility was also considered in aqueous cosolvent mixtures (e.g., water + 2-propanol) [2] and in DESs [3].

The second part of the talk considers experimental solubility data of electrolytes and modeling with *ePC-SAFT advanced*. The study aimed at understanding the effect of the solvent on salt solubility [4] of chloride-based salts, bicarbonate-based salts, and carbonate-based salts in various organic solvents (e.g., methanol, ethanol). In interesting finding was that carbonate-based salts (especially  $\text{Cs}_2\text{CO}_3$ ) were highly soluble in the organic solvent NMP, while their water solubility was comparably poor. This was found to be the opposite for solubility of chloride-based salts. *ePC-SAFT advanced* allowed accurately predicting the salt solubility in various organic solvents.

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### PLENARY LECTURE 3

## ASSOCIATION-BASED ACTIVITY COEFFICIENT MODELS FOR NONELECTROLYTE AND ELECTROLYTE SOLUTIONS

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The classical nonrandom two-liquid (NRTL) activity coefficient model for nonelectrolyte solutions [1] and the electrolyte NRTL model for electrolyte solutions [2] have been considered among the most versatile and widely practiced molecular thermodynamic models to correlate and predict phase equilibrium behavior of multicomponent systems in support of industrial process simulation, design, and optimization. Derived from the two-liquid theory, these NRTL models rely on the “binary interaction parameters” to account for the combined short-range physical van der Waals interactions and chemical associations that dictate the liquid structure and energetics of the system at a microscopic level. However, without explicitly accounting for specific chemical associations such as hydrogen bonding and ion hydration, these NRTL models fail to accurately correlate and predict phase behavior of highly associating nonelectrolyte systems such as methanol – alkanes binaries and aqueous electrolyte solutions with highly charged ionic species such as lithium and magnesium salts.

Extensively applied to equations of state such as Statistical Associating Fluid Theory and Cubic Plus Association, Wertheim’s perturbation theory has recently been integrated with the NRTL models to explicitly account for the associations [3-5]. Specifically, the association contribution is formulated with species-specific association site numbers and association strengths, and a water self-association reference term while the physical interaction contribution remains captured with the NRTL binary interaction parameters. The resulting association NRTL models reduce to the classical NRTL models when the association strengths are negligible. With refined theoretical basis and superior accuracy over the classical NRTL models, the association models enable accurate correlation and prediction of fluid phase equilibria including solubilities of multicomponent association systems with minimum numbers of adjustable parameters. This presentation shows the association NRTL models yield drastically improved correlative and predictive results for many highly challenging and impactful multicomponent association systems, electrolytes and nonelectrolytes.

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## PLENARY LECTURE 4

### DES, ES AND ILS: TAILORING SOLVENTS FOR SUSTAINABLE APPLICATIONS

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The need to develop new solvents and materials with tailored properties to afford more sustainable and circular processes as prompt a large number of research in recent years. In particular, the establishment of Deep Eutectic Solvents (DES) as a new class of solvents was essentially grounded on naïve comparisons with Ionic Liquids (ILs), since the first DES were composed of solid at room temperature ionic liquids, such as choline chloride. The easiness of DESs preparation afforded the quick preparation and utilization of a massive number of solvents and their use in wide variety of applications with a minimal fundamental knowledge of their thermophysical properties and phase equilibria studies. As time went by, the understanding of DES nature lead to the thermodynamic definition of DES and, consequently, to its differentiation from other classes of solvents.

This talk aims at dispelling some myths about DES and establish fair comparisons with other classes of solvents, such as ILs, eutectic solvents and volatile organic compounds (VOCs), so that clear and sound conclusions can be withdrawn. Several important parameters typically used to characterize solvents and that have been much used to justify DESs wide range of applications, such as vapor pressure, thermal stability, polarity, toxicity and water miscibility, were accessed for these different solvents and comparisons were established.

Several examples will be used to illustrate the application of each one of these classes of solvents and to demonstrate that the specific properties of each solvent determine their role in advancing the sustainability of chemical processes.

#### **Acknowledgements**

This work was funded by national funds through FCT - Fundação para a Ciência e a Tecnologia - under the projects CQE (UIDB/00100/2020 and UIDP/00100/2020) and PTDC/EAM-AMB/2023/2021.

## INVITED LECTURE 1

### PHARMACEUTICALS AND IONIC LIQUIDS

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Features of commercially available solid pharmaceuticals such as low solubility, poor bioavailability or the polymorphism, can be avoided by preparing new pharmaceutical active ingredients in the ionic form. Recent studies about novel ionic liquids with the potential pharmaceutical application reported that transformation to ionic liquid form improves lipophilicity of drugs, and thus better permeability through a cell membrane compared with solid salts. In addition, these liquids shown better stability, drug release and tunable therapeutic effect in comparison with the compounds they are made from. By combining well-known solid drugs into one ionic compound any dual-functional effect can be established, due to a virtually unlimited number of possibilities for the large variety of cation-anion combinations.

In this work, several new bioinspired salts of agmatine with bioanions such as salicylate and nicotinate were synthesized and characterized. The successful incorporation of agmatine into the structure of ionic liquids together with biorelevant anions provides a new field of biologically acceptable double-acting compounds, which may be applied in agriculture and pharmacy. Also, four ionic liquids based on local anesthetics lidocaine (xylocaine) and procaine, namely lidocainium ibuprofenate, lidocainium salicylate, procainium ibuprofenate and procainium salicylate, were synthesized and fully characterized. Synthesized synergetic ionic liquids based on local anesthetics and anti-inflammatory compounds tend to spontaneously associate in aqueous solutions. This property of drug-based ionic liquids can improve their permeability through the skin. The formation of ion pairs enables their transdermal application because it increases the lipophilicity of the drug enough to pass through the skin and exert its pharmacological effect, but reduces their ability to be further absorbed into the bloodstream.

Physico chemical and volumetric features, interactions with water molecules, aggregation and self-aggregation as well as structure maker/breaker properties were calculated and discussed for all investigated ionic liquids and compared with the conventional active pharmaceutical ingredients.



## INVITED LECTURE 2

# ILLUSTRATIONS OF THE SYNERGY BETWEEN THERMODYNAMICS AND CHEMICAL REACTION INTO THE TRIPTYCH "BIOPRODUCTS-BIOENERGY-WATER"

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Growing food and energy needs, along with imminent water stress due to global warming accentuated by an increase in anthropogenic greenhouse gas emissions, make essential wise solutions for sustainable development. An alternative is the polygeneration concept which is based on process intensification turning possible to simultaneously obtain several products, chemical or energetic, from a single source, preferably renewable. Integration of parabolic trough collectors (PTCs) as a concentrated solar power technology with an organic Rankine cycle (ORC) to produce electricity and drinking water through a hybrid desalination process, where reverse osmosis (RO) and low-temperature multi-effect distillation (LTMED) are combined while valorizing the produced brine, is an illustration. This scenario can be further strengthened by harnessing biomass in line with the concepts of biorefinery and green circular economy to generate energy carriers and high value-added products from conversion technologies meeting eco-design, eco-energy, and eco-materials criteria. Production of ethyl biodiesel and biolubricants from non-edible oilseed plants by reactive liquid-liquid extraction and reactive distillation using transesterification as a conversion route is an illustration, too.

This presentation aims to highlight, by the two illustrations mentioned above, the synergy between thermodynamics and chemical reaction in the triptych "bioproducts-bioenergy-water" which is an essential issue either environmentally, economically, or even socially, to the resulting employment opportunities and the required education upstream. In particular, the simulation of various ORC designs will be addressed to point out the optimal configuration coupling the PTCs with the RO-LTMED desalination system based on thermodynamic criteria (energy efficiency and exergy destruction) and economic analysis. Furthermore, since the choice of working fluid is an additional key lever, the simulation results will address the use of an alkane commonly admitted as a good candidate or an ester proposed as a green alternative. Regarding biolubricant production from ethyl biodiesel reliable information about the vapor-liquid equilibria (VLE) of mixtures containing fat alcohols and fatty acid esters (as well as the liquid-liquid and vapor-liquid-liquid equilibria with the presence of glycerol and eventually water) will be addressed. In particular, complete experimental VLE data for mixtures of relevance for the biolubricant and related biofuel industries will be provided, and the predictive performance of Dortmund modified UNIFAC model checked. The chemical equilibrium shifting for the transesterification reaction favoring ethyl biodiesel production by liquid-liquid extraction with glycerol, or favoring biolubricant production by distillation of ethanol (coproduct) will also be highlighted.

## WORKSHOP SESSION 1

### ASSESSMENT OF RELIABILITY AND UNCERTAINTY OF SOLUBILITY DATA

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Experimental data on thermodynamic properties of pure compounds and mixtures, including solubilities, are a crucial part of any industrial design (*e.g.*, for development or optimization of chemical, separation, and transport processes). Before using such data in any application, it is essential to assess their reliability. Uncertainty is an important attribute of any numerical data. Uncertainty estimates are reported in most scientific publications nowadays, but how reliable are they? Our analysis of multiple scientific publications shows that they cannot be blindly trusted and should be verified.

General ways of thermodynamic data validation, which give an idea about the magnitude of possible errors in the reported data, are discussed in Ref. [1] and will be summarized at the workshop with a focus on solubility data. To facilitate verification of experimental methods and equipment for phase equilibrium studies covering LLE, SLE, and VLE measurements, an IUPAC project [2] suggests reference systems and solubility data for them, also including an online support page (<https://trc.nist.gov/reference-systems>) developed to provide additional calculation support for the suggested mixtures. This aspect will also be covered at the workshop. Some statistics of the observations from the literature will be given and representative cases will be shown. The participants will be encouraged to also share their experience and ideas on the following topics: use of solubility data and effects of erroneous data on their applications; types and reasons of errors; testing of experimental methods and equipment; practice of verification of published solubility data; building uncertainty budgets for own measurements and evaluations; existing problems and possibilities to improve the situation; collaboration opportunities.

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## WORKSHOP SESSION 2

### GAS SOLUBILITY IN MATERIALS – A TECHNICAL EVALUATION OF LITERATURE DATA

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The accurate determination of gas solubility in materials (solid, liquid or in porous liquid) is directly related to the experimental method used, its calibration and assumptions made during the data analysis. Literature data are quite often reported without providing all requested information to allow any scientist to reproduce nor to, even, (re)estimate related uncertainty.

Such an issue can be, also, related to the emergence of turnkey commercial pieces of equipment allowing scientists to measure fluid phase equilibrium data thanks to a “black box”. As a consequence, several data have been reported in the open literature using such equipment without providing details on its calibration nor on its evaluation using at least a recommended system.

During this workshop, a series of raw data will be proposed to participants to calculate : i) the gas solubility in advanced materials, ii) derived thermodynamic properties and to propose a methodology to be followed to determine measurement uncertainties. More precisely, three classes of materials will be used, namely MOF, Ionic Liquids and Porous Liquids to emphasize potential issues on reported data and missing information.

Finally, a discussion on the recommendation of model systems to be used to truly evaluate pieces of equipment will be proposed, along with a list of requested data and properties to be reported in any scientific paper dealing with gas solubility measurements.

## FRANZOSINI AWARD

### SOLUBILITY PHENOMENA AND CHEMICAL EQUILIBRIUM OF RADIONUCLIDES IN THE SYSTEMS RELEVANT FOR NUCLEAR WASTE DISPOSAL: URANIUM/PLUTONIUM(VI) AND NIOBIUM(V)

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Radioactive nuclides (RNs) are produced by various anthropogenic activities such as nuclear power generation, nuclear weapon programs, nuclear medicine, rare-earth mining, and research. The mobilization from legacy waste in the past, global fallout from nuclear weapon testing, and severe accidents have contributed to the RNs release into the environment. Even if the radioactive waste is disposed of in an engineered repository system with multiple barriers, RNs can migrate to the biosphere once the safety functions of barriers are debilitated. Natural waters may play an important role in carrying RNs into the natural fluids by interacting with wastes, thus leading to leaching/dissolving radioactive materials. The solubility defines the source-terms (i.e., upper concentration limits) of RNs transport in the environment. Thus, a profound understanding of solubility phenomena and relevant chemical equilibria of RNs is required to remediate contaminated sites and assess repository safety.

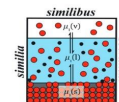
In this communication, three topics are presented: 1) Chemical equilibrium of uranium(VI) in weakly alkaline systems containing  $Mg^{2+}/Ca^{2+}$  and  $CO_3^{2-}$  at varying temperatures, 2) Formation of  $Mg^{2+}/Ca^{2+}$ -Pu(VI)- $CO_3$  complexes, and 3) Solubility of niobium in cementitious systems and characterization of the solubility-controlling phases. Uranium (U) is the major element in spent nuclear fuel. In a deep geological repository, the temperature can increase due to the decay heat from high-level wastes during early operational phases. The formation of  $M_xUO_2(CO_3)_3^{2x-4}$  ( $M$  = alkaline earth metal ions with  $x = 1$  and  $2$ ) has been extensively investigated due to the strong and stable complexation, facilitating U mobility in the environment. However, the information available on thermodynamic data to examine the temperature impact on the ternary M-U(VI)- $CO_3$  system is scarce. The chemical models predicting the formation constants are examined and uranium speciation at a high temperature is discussed [1].

Here we provide the first experimental evidence using Vis-NIR absorption spectroscopy on the formation of ternary complexes of plutonium(VI) with  $CO_3^{2-}$  and  $Ca^{2+}/Mg^{2+}$ . The formation of strongly stabilized complexes of Pu(VI) may affect plutonium chemistry in certain systems, and thus deserves dedicated experimental efforts beyond purely scientific interest [2].

Stable  $^{93}Nb$  is present in structural components of nuclear reactors and active  $^{94}Nb$  ( $\beta^-$ - $\gamma$  emitter, half-life of  $2.04 \cdot 10^4$  a) is generated by the neutron activation of  $^{93}Nb$ . Specific wastes containing  $^{94}Nb$  are disposed of in repositories for low- and intermediate-level radioactive waste (LILW). Cementitious materials are extensively used in LILW repositories. However, the solubility behaviour of Nb(V), the relevant stable oxidation state in cementitious systems at high pH, remains ill-defined. In this context, the solubility of Nb was investigated in cementitious porewater conditions and special focus was given to the detailed characterization of the solubility-controlling solid phases [3].

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## ***Oral Presentations***

## THERMAL PROPERTIES AND STRUCTURE OF BIS(1-HEXADECYL-3-METHYLIMIDAZOLIUM) TETRACHLORONICKELATE IONIC LIQUID

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Ionic liquids are usually considered to be organic salts liquid at room temperature. However, they are defined more broadly as showing melting temperatures lower than 100 °C and liquid at their temperature of application. Higher-melting dicationic ionic liquids are particularly interesting as to their fundamental properties and may find their use in a broad range of applications [1].

As a continuation of our previous work [2,3], bis(1-hexadecyl-3-methylimidazolium) tetrachloronickelate was studied by means of DSC in terms of its thermal properties (phase transitions and heat capacity) to assess its application potential as a thermal energy storage material, particularly as a phase-change material. At the same time, the relationships between its properties and mesoscale structures were studied by means of SAXS/WAXS. While the enthalpy of melting of the stable crystal is below the recommended threshold of 100 J/g, its high heat capacity in liquid phase suggests that the studied ionic liquid may be considered as an interesting additive to conventional thermal fluids. Moreover, from the fundamental point of view, interesting phase and structural behaviours were observed.

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## ***i*SenseDSC: REFURBISHMENT AND OPTIMIZATION OF A HIGH PRECISION MICROCALORIMETER**

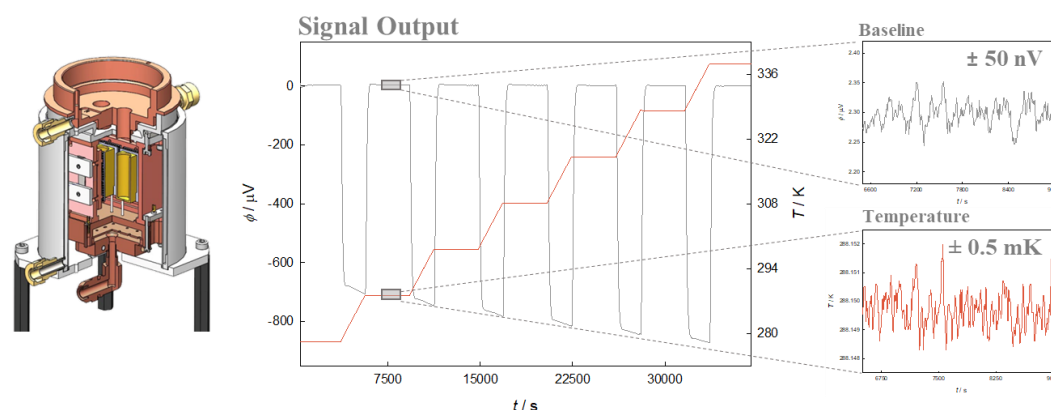
**Rodrigo M. A. Silva\***, Ana I. M. C. Lobo Ferreira, Luís M. N. B. F. Santos

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In this work, the refurbishment, upgrading and test of a differential scanning microcalorimeter, SETARAM microDSC III, is presented. Several changes and upgrades were made to the old apparatus in order to improve the resolution and signal output stability. The original heat pump was replaced by a last generation liquid-liquid thermoelectric cooler assembly (Laird Thermal Systems).

Furthermore, the overall insulation of the calorimeter was reinforced, the temperature control system was rebuilt, with the aim of improving the temperature control of the calorimeter block. Finally, to improve calorimetric signal output, a new signal pre-amplifier (originally developed in the former Thermochemistry Laboratory of the University of Lund) was installed.



**Figure 1.** Signal output and stability/resolution analysis.

Afterwards, the performance of the calorimetric system was evaluated. Temperature calibration and stability, calorimetric noise level, time constant, calorimetric signal linearity and temperature dependence of the calorimetric sensitivity were some of the evaluated parameters. The changes allowed us to achieve a temperature stability better than  $\pm 0.5$  mK, a calorimetric signal noise level under  $\pm 50$  nV and a calorimetric sensitivity ranging from 100 (at  $T = 283$  K) to 110 mV/W (at  $T = 333$  K).

For the high precision heat capacity measurement, the incremental temperature step method was implemented. Sapphire (NBS SRM 720) was used as calibrant and the overall performance of the system was tested/evaluated with recommended substances, namely: benzoic acid, anthracene and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) ( $[C_6C_{11}im][NTf_2]$ ). The obtained results revealed low dispersion (0.5 %) and an uncertainty better than 1 % (for heat capacity measurements with mass ranging from 100 to 1500 mg and temperature range from 283 to 333 K). The new *i*SenseDSC microcalorimeter system (refurbished and upgraded version of SETARAM microDSC III) can measure the heat capacities of solids and liquids with high precision, enhanced resolution, and stability. The *i*SenseDSC is able to measure excess heat capacities of liquids mixtures and solutions providing an additional tool for the study of intermolecular interactions.

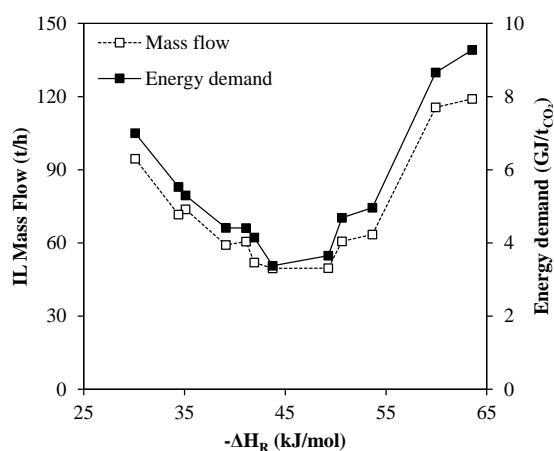
## IMPROVEMENT OF CO<sub>2</sub> CAPTURE PROCESSES BY TAILORING THE REACTION ENTHALPY OF APROTIC N-HETEROCYCLIC ANION-BASED IONIC LIQUIDS

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Combined DFT and COSMO-RS quantum chemical calculations were successfully applied to design Aprotic N-Heterocyclic Anion-based Ionic Liquids (AHA-ILs) covering a wide range of reaction enthalpy values. Functionalizing pyrrole, pyrazole, imidazole, 3/4-triazole, indole, indazole and benzimidazole anions with five different substituents (CN, CF<sub>3</sub>, Br, S-CH<sub>3</sub> and CH<sub>3</sub>) located at multiple positions on each heterocyclic ring was analyzed. More basic and smaller anions were confirmed to achieve more exothermic reaction. CH<sub>3</sub> was found to be the substituent that least affects the enthalpy of reaction, but it could rise the exothermicity when it was further away from the N-CO<sub>2</sub> bond. On the contrary, the CN group increases the enthalpy 32 - 45 kJ/mol on average. 12 representative AHA-ILs with an enthalpy from -30 to -64 kJ/mol were evaluated on post-combustion, biogas and pre-combustion CO<sub>2</sub> chemical capture processes consisting of an adiabatic absorption column plus an IL regeneration at vacuum pressure through Aspen Plus Rate-Based simulations following our COSMO-based/Aspen Plus methodology. An optimal range of enthalpy values from -43 to -54 kJ/mol minimized both solvent and energy requirements (see Figure 1) and, thus equipment and operating costs regardless of operating conditions. Tuning the enthalpy of reaction allows the cyclic capacity optimization and hence keeping costs at minimum. 0.7, 1.1 and 1.8 mol/kg were the cyclic capacity values of best performing AHA-ILs at post-combustion, biogas and pre-combustion operating conditions, respectively. A non-synthesized [P<sub>66614</sub>][4-BrPyra] (-49.3 kJ/mol) achieved competitive technical-economic results compared to the most promising AHA-ILs in identical CO<sub>2</sub> capture processes. In fact, [P<sub>66614</sub>][4-BrPyra] reduced 0.1 - 4.4 GJ/t<sub>CO<sub>2</sub></sub> the global energy demand depending on the CO<sub>2</sub> capture system and indeed operating costs up to 0.13 M\$/year compared to [P<sub>66614</sub>][2-CNPyra]. Therefore, studies linking molecular and processes scales definitively contribute to address the experimental research of new CO<sub>2</sub> capture technology based on ILs.



**Figure 1.** Mass flow and energy required according to the heat of reaction for pre-combustion processes.



## **THERMODYNAMIC PROPERTIES OF LITHIUM BIS((TRIFLUORMETHYL)SULFONYL)AMIDE AND ITS SOLID-LIQUID EQUILIBRIUM WITH WATER**

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Lithium bis((trifluoromethyl)sulfonyl)amide (LiNTf<sub>2</sub>) is an inorganic salt often used to synthesize ionic liquids (ILs). Introduction of the NTf<sub>2</sub><sup>-</sup> anion improves thermal stability of the resulting ILs, so they can be vaporized without decomposition. Also, this salt has a large aqueous solubility of  $w \approx 0.86$  near room temperature. Therefore, the properties of (LiNTf<sub>2</sub> + H<sub>2</sub>O) can potentially be used to verify the models for concentrated electrolytes.

The heat capacities of various phases and enthalpies of phase transitions of LiNTf<sub>2</sub> were measured by adiabatic calorimetry at  $T = (5 \text{ to } 370) \text{ K}$  and differential scanning calorimetry at  $T = (233 \text{ to } 551) \text{ K}$ . The equilibrium solid-to-solid temperature  $T = 423 \text{ K}$  could only be found in the DSC measurements for the samples containing the water impurity. The high-temperature phase was supercooled, and new phase transitions were found in the resulting sequence of metastable polymorphs.

The compound is highly hygroscopic and even small amounts of water in the salt samples could be detected in the measurements by both methods. We analyzed the solid-liquid equilibrium (SLE) data available in the literature [1,2] using the calorimetric results obtained in this work. The  $\ln x_2$  vs.  $T^{-1}$  slope change near the solid-to-solid phase transition temperature  $T = 423 \text{ K}$  was found to be unexpectedly low. Possible interpretations of this behavior included (i) large uncertainty of the high-temperature data and (ii) metastable SLE at  $T < 423 \text{ K}$ . Additional thermodynamic data were found to be required for adequate description of the observed behavior of the LiNTf<sub>2</sub> concentrated solutions.

### **Acknowledgements**

A. B. and E.S. are grateful to the State Program of Scientific Investigations "Materials science, new materials and technologies" (project No. 1.1.2). D.Z. gratefully acknowledges the financial support by the German Science Foundation (DFG) with Grant ZA 872/3-1, 407078203.

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## ENCAPSULATED IONIC LIQUIDS (ENIL) FOR CO<sub>2</sub>/CH<sub>4</sub> SEPARATION USING FIXED BED COLUMNS

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Ionic liquids (ILs) are being highly investigated as solvents in CO<sub>2</sub> capture. An important factor in the capture of CO<sub>2</sub> by ILs is the kinetic one. ILs generally present a high viscosity compared to traditional organic solvents. The available data indicate that CO<sub>2</sub> absorption processes are controlled mainly by mass transfer kinetics, an effect that is increased in chemical absorption, where the reaction products raise the viscosity of the medium. In this context, encapsulated ionic liquids (ENILs) [1] are presented, which consist of carbon microcapsules (particle diameter 500 nm) with a porous shell and a hollow core filled by IL, in amounts even above 80% in mass. ENIL materials have shown that they can overcome kinetic limitations in CO<sub>2</sub> capture processes, taking advantage of the high absorption capacity of ILs.

In the present work, 6 ENIL systems were prepared with various ILs, which were tested in CO<sub>2</sub> capture for the treatment of biogas streams (CO<sub>2</sub>/CH<sub>4</sub>: 40/60) through experiments in a fixed-bed column. The results showed that the IL maintains the absorption capacity of CO<sub>2</sub> as well as selectivity to CO<sub>2</sub>, promoting a rapid kinetics of the process and a high utilization of the bed.

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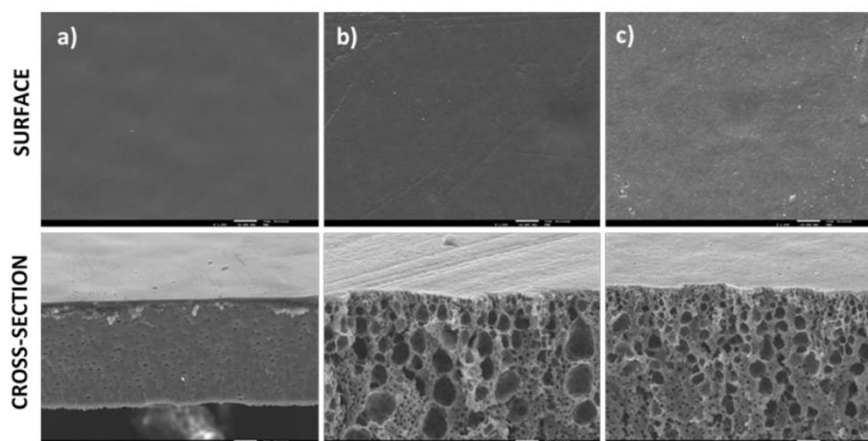
## ASYMMETRIC POLY(IONIC LIQUID)–IONIC LIQUID MEMBRANES FOR GAS SEPARATION

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Non-solvent induced phase separation (NIPS) is one of the most used techniques to produce polymeric membranes from a wide variety of polymers. Nevertheless, this method has never been employed before in the preparation of poly(ionic liquid) (PIL)-based membranes [1,2]. The use of PILs and their derived materials incorporating ionic liquids (PIL–IL) has emerged as a highly promising strategy to design dense membranes with improved CO<sub>2</sub> separation [3,4]. In this context, considering that membrane thickness is a critical parameter for their industrial scale application, this study is a step forward in the preparation of integral asymmetric PIL–IL membranes, with a top dense thin layer and a bottom porous layer. Solutions of poly([Pyr11][NTf<sub>2</sub>]) PIL and 20 wt% of [C<sub>4</sub>mpyr][NTf<sub>2</sub>] IL in acetone/dimethylformamide and acetone/formamide mixtures were prepared. The effect of several parameters of phase inversion process, namely, casting solution concentration and evaporation time, on the morphology (Figure 1) and gas separation performance of the resulting asymmetric PIL–20 IL NTf<sub>2</sub> membranes, was evaluated and compared to those of dense PIL–20 IL NTf<sub>2</sub> membrane. The results indicate that the choice of the appropriate solvent mixture strongly impacts membrane morphology and gas separation properties.



**Figure 1.** SEM images of PIL–20 IL NTf<sub>2</sub>/acetone: dimethylformamide membranes at solvent ratios of 80:20 and casting evaporation times of (a) 1, (b) 5 and (c) 10 min.

From SEM analysis, it was shown that the type of co-solvent used, dimethylformamide or formamide, as well as, different evaporation times strongly influenced the PIL–20 IL NTf<sub>2</sub> membrane morphology. Regarding the CO<sub>2</sub> permeances of the resulting asymmetric PIL–20 IL NTf<sub>2</sub> membranes a significant increase was observed. In particular, for PIL–20 IL NTf<sub>2</sub>/acetone: formamide (85:15) membrane a 10- fold increase in CO<sub>2</sub> permeance was obtained compared with dense membranes, whereas only a small decrease in selectivity was observed.

### Acknowledgements

Bruna F. Soares gratefully acknowledges the financial support of FCT/MCTES (Portugal) for PhD fellowship 2021.05450.BD.

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## DESIGN OF BIOGAS UPGRADING PROCESSES BASED ON IONIC LIQUIDS

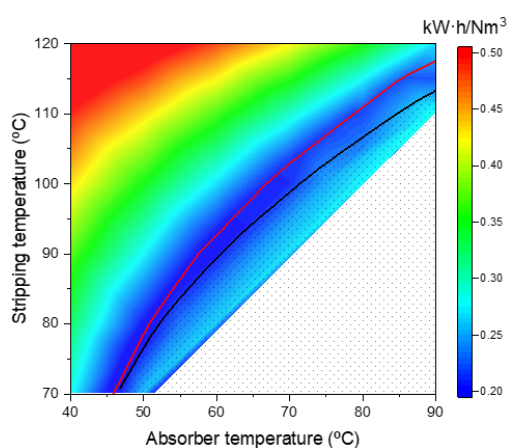
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Biogas stands out as an alternative to traditional sources of energy since it presents a high methane content, and it is mainly produced by anaerobic digestions of organic wastes. Typical biogas streams do not only consist of biomethane but also carbon dioxide, water, ammonia, hydrogen sulfide or siloxanes, depending on the source of the organic waste. Therefore, it is important to remove all these contaminants to obtain a high-quality stream in a process known as biogas upgrading. Currently, there is not a predominant technology, all of them presenting advantages and drawbacks to be solved. In this work, we test a biogas upgrading process based on CO<sub>2</sub> chemical absorption by ionic liquids (ILs).

The complete CO<sub>2</sub> capture process for biogas upgrading based on chemical absorption with [P2228][CNPyr] ionic liquid was modeled and improved to minimize solvent and energy consumptions by means of COSMO-based/Aspen methodology [1]. Temperatures of absorption (40-90 °C) and stripping (70-120 °C) columns were screened to reach a biomethane product with 97 % purity from upgrading an industrial flow (300 Nm<sup>3</sup>/h) of raw biogas with 40 % (mol) of CH<sub>4</sub> and 60% of CO<sub>2</sub> in two scenarios to deliver biomethane at 6 bar: pressurizing biogas before feeding to absorber and comprising biomethane once left the absorber. It was found that using an absorber operating pressure of 6 bar allows to efficiently use the exothermic nature of the reaction to cover the thermal energy requirements of the process, reaching a nearly autothermic CO<sub>2</sub> capture process (Figure 1), with specific energy consumption (0.211 kWh/Nm<sup>3</sup>) lower than all reported data of conventional technologies, and, correspondingly, competitive process cost (but without considering IL price).



**Figure 1.** Specific energy consumption at 6 bars for methane purity of 97%. Dotted zone corresponds to operating limits ( $T_{Abs}^{Out} > T_{Str}$ ). Red line are the cases where no cooling after regeneration is provided.

Finally, the proposed improved process was successfully applied in the upgrading of an industrial biogas stream, demonstrating efficient multicomponent capture with high recovery of CO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>O and siloxanes. The biogas upgrading process based on AHA-ILs was found able to produce biomethane with standard of quality and with specific energy consumption and investment cost competitive with conventional technologies.

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## MIXED MATRIX MEMBRANES COMPOSED OF ENCAPSULATED AMINO ACID-BASED IONIC LIQUIDS FOR GAS SEPARATION APPLICATIONS

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Energy-efficient separation of gases has attracted intensive attention both in research and in industry. Among several approaches proposed for improving carbon dioxide (CO<sub>2</sub>) absorption for suitable industrial implementation, chemical absorption using amino-acid-based ionic liquids (AA-ILs) has attracted special interest because of the great affinity of the amino acid anion or cations in ionic liquids with CO<sub>2</sub> finally contributing to high adsorption selectivity [1]. Unfortunately, the use of AA-ILs alone presents several disadvantages that need to be addressed before their scale-up and ultimately industrial applications, as their high viscosity and regeneration energy demand, lead to high operational costs and make the process unfeasible

Membrane-based gas separation technology through gas-liquid membrane contactors has been reported as one of the alternative methods to efficiently and economically separate carbon dioxide from the flue gas of fossil fuels combustion.

The separation of gases by membranes is more effective and energy-saving with lower production and equipment costs than some traditional gas separation methods, such as adsorption or distillation. However, most polymeric membranes suffer from the trade-off between mass transport rates and separation efficiency. Polymeric membranes show high gas permeation flux but low selectivity, and vice versa. Moreover, the membrane gas-liquid contactors based on MMMs themselves do not provide any selectivity properties but only act as a barrier for separating the liquid phase from the gas phase and provide a large gas-liquid contact area for mass transfer. To overcome such weakness, mixed matrix membranes (MMMs) can provide promising potentials in high-performance gas separation, by combining the high separation properties of the inorganic filler with the low cost and flexibility of the polymers [2]. For filler selection, carbon sub-micro carbon capsules are promising adsorbents for gas storage and separation due to their high surface area and porosity, adjustable pore sizes, and controllable surface functionality. The use of adsorbents on a membrane contactor improves the separation selectivity and the mass transfer driving force, allowing high membrane fluxes and low gas outlet CO<sub>2</sub> concentration, highlighting the potential of the technology to take advantage of the green solvents discussed presented here [3,4].

This work focuses on the development and characterization of novel encapsulated AA-ILs-based MMMs for gas separation with high permeability and selectivity, as well as good thermal and chemical stability. The studies include fabrication and optimization of dense membranes and spinning coat of hollow fiber membranes with encapsulated amino acid-based ionic liquids, designing MMMs with good filler/include interaction and good interfacial morphology, as well as evaluating the permeation and selectivity performance of all the prepared membranes for gas capture and separation.

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## EXTRACTION OF DYES FROM POLYESTER FIBRES USING IONIC LIQUIDS

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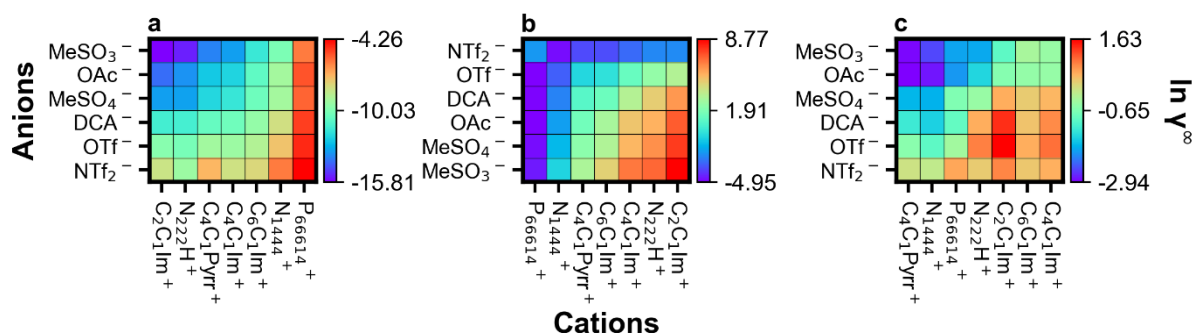
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At present, only about 1% of the textile waste is recycled and re-introduced into new garment production. One of the possible paths to improve textile recycling is to design environmentally friendly solvents able to dissolve fibres and additives without degrading them, allowing for their reutilisation. Ionic liquids have shown promising properties to promote sustainable recycling of textile waste [1].

In this work, we have used ionic solvents for the extraction of dyes from textile fibres. We started by an *in silico* screening of a large number of possible ionic liquids using COSMO-SAC [2]. By the calculation of infinite dilution activity coefficients, an estimation of the solvation ability of 600+ ionic liquids was done for 10+ dyes.

Methyl Orange (MO), Crystal Violet (CV) and Disperse Red 13 (DR13) were selected along with 17 ionic liquids for their experimental solubility determination. By the saturation method and UV-VIS measurements, the most promising ionic liquids, namely C<sub>2</sub>/C<sub>4</sub>-methylimidazolium acetate and ammonium-based ILs, could be highlighted for all three dyes.



**Figure 1.** COSMO-SAC calculated infinite dilution activity coefficients ( $\ln \gamma^\infty$ ) of MO (a), CV (b) and DR13 (c) in ionic liquids.

The four most promising ionic liquids for the solubilisation of DR13 – [C<sub>4</sub>C<sub>1</sub>Im][OAc], [C<sub>2</sub>C<sub>1</sub>Im][DCA], [N<sub>1444</sub>][DCA] and [N<sub>222</sub>H][MeSO<sub>3</sub>] – were selected for the discolouration of polyester fibres. White fabrics were first dyed following a currently used industrial process and then were treated with the chosen ionic liquids. The filtrated liquid extracts were analysed for dye traces using UV-VIS measurements to quantify the amount of dye extracted.

We show that ionic liquids can be designed to act as selective extraction solvents for specific additives in textile industry by combining computational and experimental screenings.

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## **REACTION-EXTRACTION PLATFORMS TOWARDS CO<sub>2</sub>-DERIVED CYCLIC CARBONATES CATALYZED BY IONIC LIQUIDS BY COSMO MODELS**

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Carbon capture and utilization (CCU) is a valid strategy to reduce emissions and promote the valorization of CO<sub>2</sub> to produce chemicals, fuels, and materials of interest [1]. The utilization of CO<sub>2</sub> can take different routes to produce compounds such as formic acid, formaldehyde, methanol, urea and dimethyl ether [2]. Nevertheless, cyclic carbonates stand out among them for their potential application as an extracting solvent [3].

The synthesis of cyclic carbonates by the reaction of CO<sub>2</sub> with epoxides is a relevant route for the fixation of CO<sub>2</sub> into valuable products. Due to the thermal stability of CO<sub>2</sub>, the presence of catalysts is necessary, where in recent years, ionic liquids are taking a great relevance [4].

Recently, liquid-liquid extraction was proposed to efficiently regenerate catalysts. ILs can be classified in hydrophobic and hydrophilic species, modulating their behavior with water [5]. Hydrophobic ionic liquids can be separated by fatty alcohols [6], while hydrophilic ionic liquids work similarly with water in both separation and reaction steps [7].

This work covers a systematic study based on COSMO models to understand the role of liquid-liquid extraction as regeneration scheme for a wide number of ionic liquid catalysts and cyclic carbonates products, moving from molecular level to process scale. The findings provide a comprehensive development of the processes to narrow down the feasible possibilities and provide a guide for selecting the best process-catalyst pair for each CO<sub>2</sub>-derived cyclic carbonate.

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## LOW ENERGY-DEMANDING SEPARATION OF PROPYLENE CARBONATE AND IONIC LIQUID CATALYST AFTER CO<sub>2</sub> CONVERSION

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Global warming solutions mainly consist of reducing the current alarming CO<sub>2</sub> levels in the atmosphere. Two main strategies are implemented to achieve said purpose: Carbon Capture and Storage (CCS), which aims to concentrate CO<sub>2</sub> and store it, and Carbon Capture and Utilization (CCU), which uses CO<sub>2</sub> as feedstock of new processes to produce value-added compounds.

In particular, CO<sub>2</sub> valorization with epoxides to obtain cyclic carbonates using ionic liquids (ILs) as catalysts is being studied as reaction path due to the high yields obtained [1]. The challenge to design a CO<sub>2</sub> conversion process based on ILs is to solve the product/catalyst separation efficiently and sustainably, especially dealing with a homogeneous catalytic step. The common strategy proposed in the literature consists of a distillation step in which the IL is obtained as pure compound in the residue and the carbonate is recovered as distillate [2]. Nevertheless, propylene carbonate (PC) presents a high boiling point, which requires high reboiler temperatures, incompatible with ionic liquids thermal stability. This distillation can be achieved by displaying extreme vacuum conditions, but it implies high electricity expenses. Recently, IL/PC separation by liquid-liquid extraction (LLE) was successfully employed in a system using amino acid-based ionic liquids [3]. However, the question arises as to whether this methodology can be used with other ILs of different nature.

In this work, CO<sub>2</sub> conversion reactions using ILs in the presence and absence of water as well as liquid-liquid equilibria involving different {water + PC + IL} mixtures have been experimentally studied. Different types of ILs -based on amino acid and halide anions- have been used. Then, Aspen Plus commercial simulator is used to design the process and calculate energy consumption of the distillation- and LLE-based separation strategies.

The results show that water can be used to enhance the reaction conversion, especially with amino acid based ILs. Also, in most cases, water can be successfully used as extracting agent with high IL partition coefficients and high IL/PC selectivities. In addition, it was demonstrated that, at process scale, this novel strategy can reduce energy demands in comparison with the conventional carbonate distillation.

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## **EXTRACTIVE DISTILLATION FOR REFRIGERANT BLENDS SEPARATION: SOLVENT SELECTION AND PROCESS SIMULATION**

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Hydrofluorocarbons (HFCs) are fluorinated gases (F-gases) used extensively in the refrigeration and air conditioning (RAC) sector. Given their high global warming potential (GWP), environmental agreements have been taken at the international level to reduce their production and consumption. Specifically, the Kigali Amendment and Regulation EU517/2014 call for a reduction of 85% in HFCs emissions by mid-century. In order to reduce the effects of their release into the atmosphere, they are currently blended with low-GWP hydrofluoroolefins (HFOs), thus reducing the overall GWP of the refrigeration fluids [1].

In addition, a shift towards a more circular economy model is desired. To this end, the reclamation of F-gases at the end-of-life of RAC equipment is desired, with the aim of reuse them in new RAC equipment, and hence, avoiding their emission to the atmosphere. As refrigerant blends often present azeotropes or close boiling points mixtures of F-gases, conventional separation processes become ineffective. In this context, the goal of this research is the development of an innovative extractive distillation process using ionic liquids (ILs). High chemical and thermal stability, extremely low volatility, and excellent solvent properties, among others, make ILs suitable entrainers [2].

To do so, we have assessed the solubility of the main F-gases currently used in several low-viscosity cyanide-based ILs, over wide temperature and pressure ranges. Experimental data of three HFCs, difluoromethane (R32), pentafluoroethane (R125), and 1,1,1,2-tetrafluoroethane (R134a), and two HFOs, 2,3,3,3-tetrafluoropropene (R1234yf) and 1,3,3,3-tetrafluoropropene (R1234ze(E)), have been achieved using the isochoric saturation method, and the Non-Random Two-Liquid (NRTL) activity coefficient model has been applied to model the absorption isotherms. In this way, a thermodynamic analysis has been conducted in order to analyse the influence of the IL solvent properties on the resulting F-gas absorption capacity and expected selectivity. Afterwards, these thermodynamic data have been used to design an extractive distillation process to separate the commercial blend R410A (50/50 wt. % R32/R125), working with the process simulation software Aspen Plus. The main process variables, such as operating pressure and temperature, column inlet stages, reflux ratio and S/F ratio among others, have been optimized to achieve a high purity refrigerant product (99.95 wt. %) that fulfils the quality standards for commercialization. Eventually, the best solvent and process characteristics have been selected based on the process economic evaluation. Thus, the use of ILs as solvents to accomplish the separation of refrigerant gases appears as a promising approach to achieve the objectives of F-gas emissions established in international agreements aimed at climate change mitigation.

### **Acknowledgements**

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## IN SILICO SOLVENT SCREENING IN PHARMACEUTICAL DRUG DEVELOPMENT

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The choice of a proper solvent is crucial in many operations in the pharmaceutical industries. This includes separation processes, formulation processes, chemical reactions, and many more. In Silico prediction methods, like the Conductor-Like Screening Model for Real Solvents, COSMO-RS [1,2], which is used in this talk, are valuable tools that allow for fast screening of large sets of solvents and solvent mixtures. The results of the screening can be used to narrow down the number of solvents to a reduced list of suitable candidates that can then be used to perform more accurate measurements.

The authors present the theoretical background, the general approach and some illustrative examples. A special focus is placed on the prediction of solvent effects on crystal growth. The morphology is particularly important as many physical properties that are relevant to pharmaceutical development, such as powder flow, compressibility, and dissolution rate, depend on the morphology of the crystal. Controlling the shape of crystals is an important goal in crystal engineering. The authors present a workflow that is able to predict the effects of the solvent on crystal growth. The activity coefficient of the crystal growth faces as constructed by Materials Studio [3], are used for a hierarchical clustering. The solvents are classified according to trends in their interaction strength [4]. As a result, we can define solvent groups that trigger the growth of the same crystal morphology.

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## **SOLUBILITY OF ORANGE PEEL OIL COMPONENTS IN SUPERCRITICAL CO<sub>2</sub>+ETHANE AZEOTROPIC MIXTURE**

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Supercritical technologies have become attractive and economically viable alternatives for the processing of natural products during the last few years. CO<sub>2</sub> is the most used supercritical fluid because it is inexpensive, non-flammable, non-hazardous at low exposure levels, and it is readily available at high purity [1]. According to several authors [1,2], the fractionation of orange peel oil by supercritical CO<sub>2</sub> (SCCO<sub>2</sub>) is technically feasible at pressures between 88 bar and 110 bar and temperature between 303 K and 333 K. On the other hand, ethane has also been proposed as an alternative solvent for the deterpenation of citrus fruit essential oils [3-5]. According to previous studies, the use of ethane rather than CO<sub>2</sub> enables obtaining five-fold and ten-fold oils at lower pressure (ca. 60 bar) and with substantially lower solvent consumption. The main drawback of using ethane as solvent is its flammability, however, mixtures of CO<sub>2</sub>+ethane can be design as non-flammable solvent for the deterpenation of citrus oils. Particularly, this is the case of the azeotropic CO<sub>2</sub>+ethane mixture, with the additional advantage that it can be recycled minimizing changes in the solvent composition, which is key for achieving a stable operation.

In this work, we research the solubility of orange peel oil in CO<sub>2</sub>, in ethane and in the azeotropic mixture CO<sub>2</sub>+ethane (66 mol% CO<sub>2</sub>) in a dynamic cell of 50 ml at 333 K in a range of pressure between 60 bar and 110 bar according to the solvent. Also, we compare the selectivity of the three solvents to extract limonene and raffinate the oxygenated compounds in the peel oil. The solubility values of orange peel oil in pure CO<sub>2</sub> and ethane agree with previous experimental data reported in the literature. Regarding the solubility in the azeotropic ethane/CO<sub>2</sub> mixture, it is worth highlighting that it varies significantly with the operating pressure between 4 mg extract/g solvent at 60 bar to 27 mg extract/g solvent at 110 bar. Finally, the selectivity of the fractionation process, defined as mg limonene per mg of linalool extracted, switches between 228 and 244.

Previous studies carried out with the GCA-EOS (Group Contribution with Association Equation of State) show that the model can predict the phase equilibria of orange peel oil with CO<sub>2</sub> mixtures as well as with ethane. Thus, in this work we also challenge GCA-EOS predictive capacity to model the experimental cumulative extraction curves obtained under equilibrium conditions. The results show that the GCA-EOS is a robust tool to design and optimize the supercritical deterpenation process using the azeotropic mixture.

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## MODELING CO<sub>2</sub> SOLUBILITY AND pH IN AQUEOUS AND ORGANIC SOLUTIONS USING ePC-SAFT

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The development of innovative chemical processes for converting carbon dioxide (CO<sub>2</sub>) into useful platform chemicals is of interest in the industry and society. CO<sub>2</sub> is abundantly available in the atmosphere; it is the main flue gas in the energy industry and chemical industry.[1] Several techniques for carbon-capture processes already exist, and two approaches are commonly used. The first approach is carbon capture and storage (CCS). Therein, CO<sub>2</sub> is stored under high pressure in deep saline aquifers, which contain high salt concentrations. The second approach is carbon capture and utilization (CCU). In CCU processes, a suitable salt is required as a base to catalyze the overall reaction. In this context, a suitable salt shall be very soluble in the water-poor reaction system, and it shall increase the CO<sub>2</sub> solubility in the reaction mixture [1]. In conclusion, high CO<sub>2</sub> solubility and high salt solubility are prerequisites for CCS and CCU processes. The experimental effort to study both, the CO<sub>2</sub> solubility and the salt solubility in complex systems is tremendous, as solubility depends on numerous conditions (e.g., temperature, pressure, and solvent composition). Further, the CO<sub>2</sub> solubility also depends on the present pH in the liquid phase and determines whether only physisorption occurs or both, physisorption and chemisorption occur [2]. Thus, also the influence of electrolytes (e.g., NaCl vs. NaHCO<sub>3</sub>) on the pH is a crucial step towards understanding the salt influence on CO<sub>2</sub> solubility.

Accounting for all these aspects, the equation of state (EOS) *ePC-SAFT advanced* [3] was used in this work to predict the CO<sub>2</sub> solubility in aqueous systems [2] and in organic electrolyte solutions (e.g., NaCl, KCl) for a broad range of conditions (temperature, pressure, electrolyte concentration, solvent composition). As a result, salting-out effects were present in most of the investigated systems, and the CO<sub>2</sub> solubility decreased with increasing salt concentration. In addition, the pH in the aqueous phase was predicted for selected systems, and the influence on the CO<sub>2</sub> solubility was studied. As a result, the influence of NaCl on the pH and subsequently on the CO<sub>2</sub> solubility is not very pronounced. The pH remained in the range of the salt-free system (3<pH<4), and mainly physisorption was present. On the other hand, bicarbonates drastically increased the pH (7<pH<8) and strongly changed CO<sub>2</sub> solubility. Here, physisorption and chemisorption must be taken into account. Moreover, *ePC-SAFT advanced* was used to model the salt solubility [4] of chloride-based salt, bicarbonate-based salts, and carbonate-based salts in various organic solvents (e.g., methanol, ethanol). Here, ion-specific and solvent-specific effects were evaluated and analyzed. As a result, carbonate-based salts (e.g., Cs<sub>2</sub>CO<sub>3</sub>) are promising candidates for CCU processes, while chloride-based salts have poor solubility in organic solvents.

In conclusion, *ePC-SAFT advanced* allowed accurately predicting the CO<sub>2</sub> solubility in complex multi-component mixtures and modeling the salt solubility in various organic solvents. Consequently, *ePC-SAFT advanced* is a powerful EOS, which helps significantly reducing the process development of both, CCU and CCS processes.

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## **EXTENDED SPECIFIC ION THEORY (ESIT) WITH ION PAIRING: 1-1 AND 2-2 ELECTROLYTES IN REGULAR AND MODIFIED MOLALITY SCALE**

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The Extended Specific Ion Theory is a second-order extension of the specific ion theory (SIT) which accounts for both unlike-ion and like-ion interactions. The purpose of the model is to predict the activity coefficient of electrolyte solutions. The Extended Specific Ion Theory is based on the idea that ion interactions are in fact competitive effects of ion-water interactions. Prior research on 1-1 electrolytes indicated that ion pairing needs to be accounted for in order to achieve accuracies on the order of 1 % deviation up to molalities of 6 mol kg<sup>-1</sup>.

In the present study, the theory was tested in a modified molality scale (mol per kg solution, a scale also used by the Plummer and Busenberg studies of alkaline earth carbonate solubility) and extended to 2-2 electrolytes, which display the strongest ion pairing and are therefore a good test for the theory.

It was found that for 1-1 electrolytes, the use of the modified molality scale largely removes the need for introducing ion pairs. In most cases, the modified molality scale improves the agreement between the model and experimental data. In the case of 2-2 electrolytes, ion pairs with a stability constant on the order of 200 were needed to provide a satisfactory fit. Assuming the ion pair to be ideal only works for molalities up to about 1 mol per kg. To extend the validity range, a second-order interaction coefficient between the ion pair and the ionic strength is needed.

## A THERMODYNAMIC MODEL FOR NEODYMIUM OXALATE IN AQUEOUS SOLUTIONS OF HNO<sub>3</sub>, HCl, HClO<sub>4</sub>, AND Nd(NO<sub>3</sub>)<sub>3</sub> AT 298 K AND 0.1 MPa

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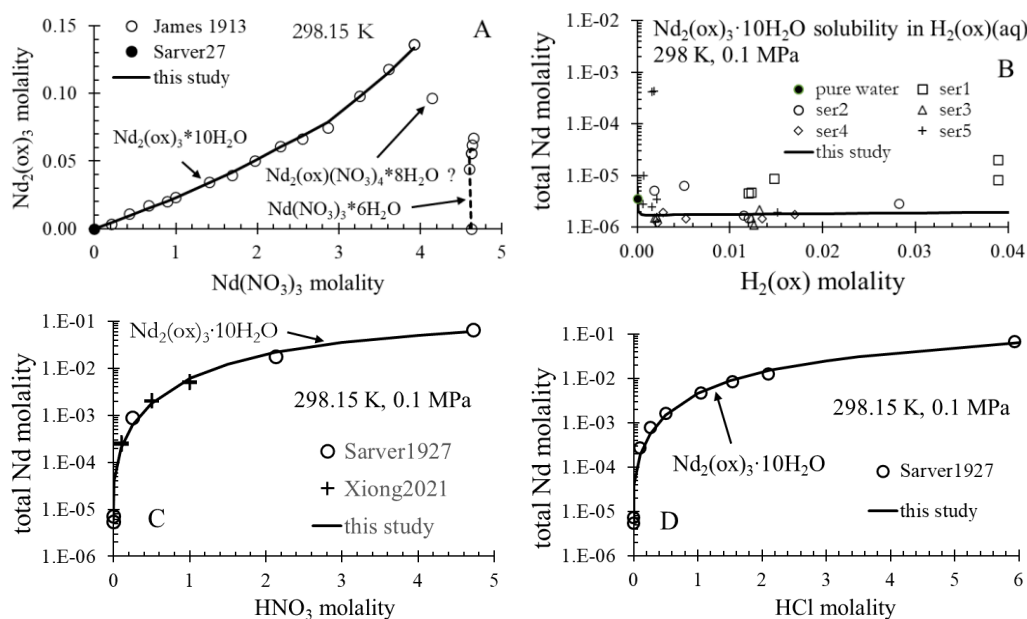
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Published thermodynamic models and data for neodymium oxalate in aqueous solutions of HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and Nd(NO<sub>3</sub>)<sub>3</sub> were reviewed and a new Pitzer model constructed. The model reproduces the Nd(NO<sub>3</sub>)(aq) isopiestic data to ionic strength > 36 mol·kg<sup>-1</sup>. The NdNO<sub>3</sub><sup>2+</sup> and Nd(NO<sub>3</sub>)<sub>2</sub><sup>+</sup> species comprise > 50% of the Nd solute fraction at  $m_{Nd,tot} > 0.4$  mol·kg<sup>-1</sup>. These ion-pairs have a significant effect on the model structure and were neglected in prior Pitzer models for Nd-oxalate + nitrate mixtures. Existing Pitzer models for the Nd(ClO<sub>4</sub>)<sub>3</sub>, HCl, HClO<sub>4</sub>, and HNO<sub>3</sub> systems are adequate. Prior Nd-oxalate Pitzer models contain physically unrealistic interactions and high-order mixture parameters involving Nd-oxalate species. Starting from the oxalic acid model of Oakes et al. [1], this model contains only  $B_{MX}$  parameters and a single  $\theta_{ccr}$ . Model and experimental solubilities are shown in Figure 1.



**Figure 1.** Solubilities in the common-ion Nd(NO<sub>3</sub>)<sub>3</sub> (A) and H<sub>2</sub>(ox) (B) systems and non-common-ion HNO<sub>3</sub> (C) and HCl (D) systems calculated from this study (solid lines) compared to measurements from the sources cited in the figures [2-5]. The model solubility of Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O is also shown in (A). All of the data in (B) are from [2].

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## MODELING PHASE EQUILIBRIA AND ELECTRICAL CONDUCTIVITY FOR LITHIUM-ION BATTERY APPLICATIONS

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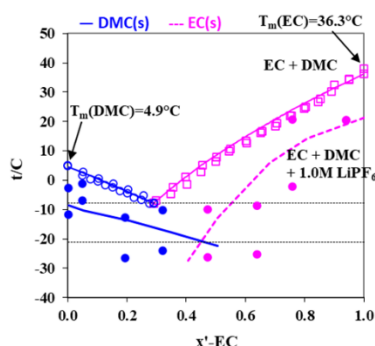
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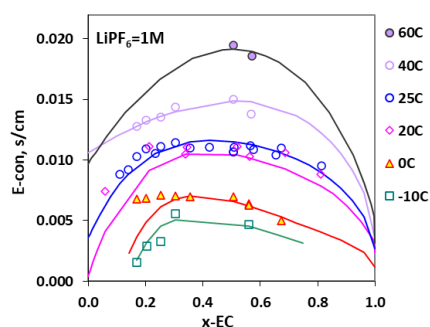
As a result of ever-increasing energy demand, development of efficient energy storage technology has become strategically important. Li-ion batteries (LIBs) have attracted enormous attention in recent years because of their distinct advantages in this regard. As a key component, the LIB electrolyte plays a crucial role in providing ion-conductive medium for transporting  $\text{Li}^+$  ions between electrodes, thus affecting the performance of the battery. The non-aqueous electrolytes containing lithium salts in aprotic organic solvents is an important class of battery electrolyte. In this class, organic carbonates possess the required features for battery applications and are found to be suitable solvents for lithium salts such as  $\text{LiPF}_6$ . Properties of the battery electrolytes can be tuned by mixing two or more of the carbonate solvents and adjusting their compositions and salt concentrations. Composition of these carbonates have important implications for the battery operation; the best ionic conductivity can be achieved through adjusting the salt concentration together with solvent composition and temperature.

In this work, a thermodynamic model, the Mixed Solvent Electrolyte (MSE) model [1], has been applied to the non-aqueous electrolyte systems pertinent to the LIB applications. A combined analysis has been performed for solid-liquid equilibria determined from the MSE model, together with electrical conductivities calculated from a predictive electrical conductivity model [2]. The MSE model predicts phase equilibria to define appropriate operating (liquid) range, whereas the conductivity model determines the variations of conductivity with temperature, solvent composition, and salt concentration, so that conditions with good electrical conductivities can be defined for optimal battery operation.

In this presentation, phase equilibrium results for systems relevant to lithium-ion battery applications will be presented, the effects of solvent composition and salt concentration on the solid-liquid equilibria and electrical conductivities will be discussed. These results, as demonstrated in Figures 1 and 2, can provide insights into the lithium-ion battery design for improved performance.



**Figure 1.** Phase diagram for ethylene carbonate (EC) + dimethyl carbonate (DMC) with (lower lines) and without (upper lines)  $\text{LiPF}_6$ .



**Figure 2.** Electrical conductivities in  $\text{LiPF}_6$  + DMC + EC at various temperatures as a function of solvent composition (as mole-fraction of EC) at 1.0 M  $\text{LiPF}_6$ .

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## FORMATION AND SOLUBILITY OF ABELLAITE, $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})(\text{s})$

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At the WIPP (Waste Isolation Pilot Plant, Carlsbad, New Mexico, U.S.A.), lead-lined containers are used to emplace remotely handled transuranic nuclear wastes. After closure of the WIPP, the lead-lined containers are expected to interact with Na-bearing brine infiltrating the repository in the presence of carbonate minerals. For example, anoxic corrosion of lead followed by carbonation could be a mechanism controlling the dissolved concentration of lead. Experimental solubility studies of Pb-carbonate solids in Na-bearing solutions were conducted to evaluate these interactions. It is expected that lead in brine would suppress dissolved actinides.

Excess  $\text{PbCO}_3(\text{s})$  (cerussite) was added to solutions at 6 incremental concentrations of mixed  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  in duplicate (i.e., 12 reactors in total).  $\Sigma\text{Na}$  loadings in the reactors ranged from 0.13 to 2.9 M.  $\Sigma\text{CO}_3$  loadings ranged from 0.08 to 1.6 M. Experiments and measurements were conducted under ambient laboratory temperature ( $24.5 \pm 4.3^\circ\text{C}$ ,  $\sim 1$  bar) and closed to the atmosphere. Eight measurements were conducted over a time period of 238 to 720 days. No systematic change in  $\text{pH}$ ,  $\Sigma\text{Pb}$ ,  $\Sigma\text{CO}_3$ ,  $\Sigma\text{Na}$  was observed with time. The observed scatter was confined to acceptable experimental precision, indicating the equilibrium attainment during the course of the experiment.

Solid samples collected at the bottom of the reactors were analyzed using X-ray diffraction (XRD). Formation of  $\text{NaPb}_2(\text{CO}_3)_2(\text{OH})(\text{s})$  (abellaite) at the expense of cerussite was observed at the six concentrations of the mixed salts. Mass balance evaluation was consistent with the following reaction:  $2\text{PbCO}_3(\text{s}) + \text{Na}^+ + \text{H}_2\text{O} = \text{NaPb}_2(\text{CO}_3)_2(\text{OH})(\text{s}) + \text{H}^+$  with one exception.

Based on the Pitzer activity model for the background electrolyte ions ( $\text{Na}^+$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) in Harvie et al. [1], the dissolution constant for cerussite and the dissociation constants for three  $\text{Pb}^{+2} - \text{CO}_3^{2-}$  complexes at zero ionic strength were adopted from Powell et al. [2] and tested for their accuracy with respect to the experimental data of this study. Use of the constants of Powell et al. [2] without modifications or amendments required the introduction of a higher-order complex,  $\text{Pb}(\text{CO}_3)_3^{4-}$ . This species was chosen, rather than setting the ionic interactions among other existing species, to delineate the experimental data within the uncertainty. The solubility constant for the secondary mineral abellaite was determined along with the adoption of  $\text{Pb}(\text{CO}_3)_3^{4-}$ . No new Pitzer interaction parameters other than for the background electrolyte ions ( $\text{Na}^+$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) were necessary. The computed  $\log K$  of abellaite indicates that this phase is less soluble than cerussite of Powell et al. [2]. Quality of measurements, details of model parameterization, and implication of abellaite for the WIPP geochemistry will be presented in the conference.

### Acknowledgements

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## **THERMODYNAMIC CHARACTERISTICS OF SALT DISSOLUTION PROCESSES IN A THREE-COMPONENT WATER-SALT SYSTEM CsCl–CaCl<sub>2</sub>–H<sub>2</sub>O**

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The work is a continuation of research devoted to obtaining thermodynamic characteristics of dissolution processes of solid double salts using the calorimetry method. Dissolution and formation enthalpies make it possible to solve such important issues as the conditions for establishing chemical equilibrium, the possibility of chemical reactions, determining the influence of parameters on the state of equilibrium, reciprocal influence of ions and many others. The study of three-component water-salt systems is hindered by the lack of thermodynamic reference data and phase diagrams. Thus, obtaining experimental data for ternary water-salt systems is an urgent task at the present time.

In this work, dissolution processes of solid phases in the CsCl – CaCl<sub>2</sub> – H<sub>2</sub>O system were investigated by calorimetry method. According to the literature data, joint compounds are formed in this system with a different ratio of components: 2CsCl·CaCl<sub>2</sub>·2H<sub>2</sub>O, CsCl·CaCl<sub>2</sub>, CaCl<sub>2</sub>·5CsCl. Three double salts were obtained from concentrated solutions and their structure and composition were characterized [1]. Dissolution heats of these salts and mixtures of their constituent components were measured. Standard formation enthalpies and enthalpies of double salts formation from constituent components were calculated. Using thermodynamic results on previously studied ternary chloride systems, the influence of the nature of cations on the measured thermal effects and found heats of formation was analyzed.

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## THE PHASE EQUILIBRIA OF AQUEOUS ELECTROLYTES IN CONFINEMENT UNDER MARTIAN CONDITION

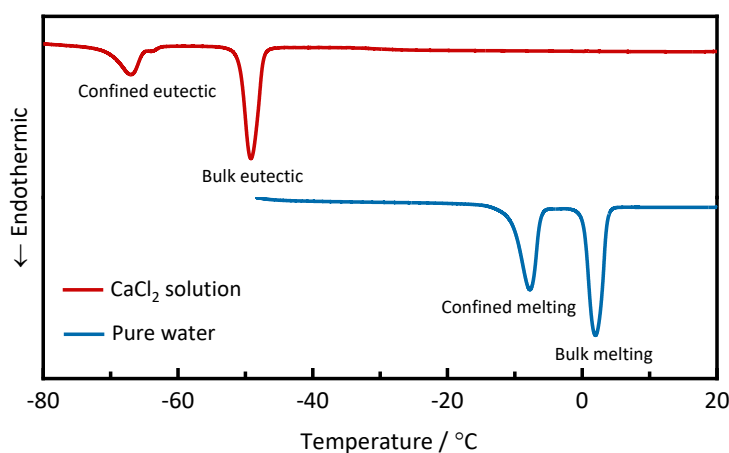
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The discovery of chlorides and perchlorates has profoundly influenced our view of liquid water on Mars [1,2]. These salts attract much attention, because their hygroscopic nature and low eutectic temperature allow for the possibility of liquid water on the surface of Mars today. Recent studies showed the confined space exert significant effect on the phase boundary on salt solution, particular in the freezing and deliquescent process [3,4].

In this work, we perform experiments to investigate the eutectic temperature and deliquescence humidity of Mars-relevant salts ( $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{Ca}(\text{ClO}_4)_2$ , and  $\text{Mg}(\text{ClO}_4)_2$ ) in bulk and various size pores (3–10 nm). The results indicate that, compared with water, the confinement effect on melting temperature of salt solutions is more significant (Fig. 1). It was found that freezing of concentrated solutions in narrow pores can even be suppressed completely. In order to understand the salt and confinement effects on the stability field of a liquid water phase, we develop an ion interaction model (based on Pitzer theory) to calculate the phase diagram of cryogenic aqueous solutions.



**Figure 1.** Calorimetric melting curve of pure water and electrolyte solution in confinement.

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## SOLUBILITY IN "THE PROPERTIES OF GASES AND LIQUIDS" 6<sup>TH</sup> ED.

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The Properties of Gases and Liquids" (PGL) [1] traditionally dedicates part of its space to modeling and prediction of solubility phenomena. The 6th edition extended the list of models discussed in that context and also provided an intensive assessment of the capabilities of those models.

Two chapters are dedicated to phase equilibria, to which solubility belongs, in PGL 6th Ed. [2], one to Vapor-Liquid Equilibria (VLE), and one to Solid-Liquid and Liquid-Liquid equilibria (SLE and LLE, respectively). In addition to the empirical and predictive activity-coefficient (AC) models and cubic equations of state (EOS) described in the previous PGL editions, more sophisticated models are discussed in the 6th Ed such as COSMO-RS [3], PC-SAFT [4] and molecular simulations. Examples of practical use of the various methods for solubility calculations are given. Assessment of the models was based on collections of experimental VLE, LLE, and SLE data, either published (e.g., [5,6]) or extracted from the Source database [7]. Proprietary methods have been tested in collaboration with their developers. Empirical AC models were tested with a simple (one-term) temperature dependence, in contrast to multi-term series used in process simulations.

Model testing needed development of criteria and methods for identification of doubtful data, as well as protocols and formats. Certain subsets of experimental data, as well as the source code of certain models, will be made available on the web sites in support of PGL hosted by Brigham Young University (Provo, UT) [8] and Thermodynamics Research Center (NIST, USA) [9].

Collaboration opportunities exist in making model data and methods available for the community and continuing cross-validation of data and models.

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## HIGH PRESSURE MULTIPHASE PHASE EQUILIBRIA OF CO<sub>2</sub>-WATER-LIGNIN DERIVATIVES

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In the context of lignocellulosic biomass valorization, the fractionation of biooils to recover added-value products is a great challenge. There are several pathways to break down these natural polymers, among which are thermal treatments, such as pyrolysis and hydrolysis, as well as base-catalyzed depolymerization or oxidative cleavage [1]. Regardless of the conversion technology, lignin degradation gives rise to a wide variety of polyfunctional aromatic rings, with different oxygenated substituents, such as hydroxyls, ethers, ketones and aldehydes, to name a few. It is worth highlighting that the great deal of compounds that are produced is strongly dependent on both, the raw material, and the type of treatment. Therefore, bio-oil refining calls for more research on separation technologies. In particular, pioneering works in the field of high pressure technology apply CO<sub>2</sub> extraction as a solvent-free non-destructive analytical method for the characterization of bio-oils; and, more recently, several reviews consider CO<sub>2</sub> extraction as a feasible technology for large-scale recovery of valuable compounds.

The design and optimization of separation processes requires a robust thermodynamic model able to predict the phase behavior of bio-oils. Lignocellulose derived bio-oils are complex multicomponent mixtures that comprise a large number of asymmetric compounds, show non-ideal behavior due to the presence of water and organo-oxygenates and contain polyfunctional molecules whose properties are generally unknown. Since the large number of compounds comprising the bio-oil belong to the few organic families mentioned above, the use of a group contribution approach is a convenient choice to facilitate the thermodynamic modeling of these mixtures.

The Group Contribution with Association Equation of State (GCA-EOS) [2] is particularly suitable for this purpose. It has already shown excellent performance to model the phase behavior of complex mixtures containing natural products and biofuels. As part of this work, we extend the GCA-EOS to describe the phase behavior of aromatic compounds from low- to high-pressure phase equilibrium data and their binary mixtures with CO<sub>2</sub>. Next, we challenge the GCA-EOS to predict high-pressure multiphase behavior of lignin-derived polyfunctional aromatic compounds with CO<sub>2</sub> and water, in order to assess the technical feasibility of using high-pressure CO<sub>2</sub> to fractionate a typical hydrolysate mixture reported in the literature.

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## **DESIGNER SOLVENTS BY CICLOADDITION REACTIONS OF CO<sub>2</sub>: CARBONATES AND BIOCARBONATES**

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Current paradigm in the development of technologies to minimize CO<sub>2</sub> emissions and, thus, its concentration in the atmosphere, is moving from carbon capture and storage (CCS) to carbon capture and utilization (CCU) technologies [1]. Among a wide range of CCU processes and products, the cycloaddition reactions of CO<sub>2</sub> to epoxides to form carbonates is a strong research line nowadays [2]. More than promoting effective routes of fixing CO<sub>2</sub>, carbonates stand as products of interest to design new separation processes due to their well-known characteristics, as high boiling points and low viscosities, drafting their use as extracting agents [3]. Considering the epoxide structure and nature, two main opportunities are envisioned: i) carbonates as designer solvents, by tuning the epoxide structure to enable adequate physical and extractive properties and ii) biocarbonates, by limiting the use of epoxides derived from renewable sources, being available in the literature carbonates derived from terpenes [4], which immediately named them as biocarbonates.

In this work, two different databases are optimized by Turbomole software v. 7.4 and used in CosmoTherm v. 19 to evaluate the designer solvent role of carbonates to be used in different applications, considering or not the sustainability of the reactant. Carbonates, which are derived from petroleum-based reactants, are evaluated as extracting agents in the dearomatization of challenging low aromatic content naphthas, whereas biocarbonates, which are derived from terpenes, are evaluated as extracting agents in several extractions, ranging from phenols to volatile fatty acids, from waterwater. Results suggest that carbonates and biocarbonates are effective designer solvents to solve separation problems of quite different nature with competitiveness with leading solvents in each case.

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## HIGH TEMPERATURE VAPOR-LIQUID EQUILIBRIUM OF ALCOHOLS+WATER MIXTURES

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Mixtures of alcohols and water have been researched over the years, but more recently has been an increase of interest in these types of mixtures due to its importance to biodiesel and refinery industries. These oxygenated compounds when added to gasoline can increase the octane number, reduce exhaust gas emissions, and enhance combustion. n-Butanol in fact can be produced by a biomass fermentation process instead of a fossil fuel process and replace gasoline [1].

The general interest to produce biofuels like bio-butanol has increased due to environmental concerns, the continuous increase in crude oil prices and limited resources of fossil energies. Many countries have the commitment to achieve the carbon neutrality by 2050, bio-butanol can be one solution to reach this envisaged goal.

The most popular process to produce bio-butanol is ABE (acetone, butanol, and ethanol) process and n-butanol needs to be separate from acetone, ethanol, and water [2]. In the past years, the interest in the ABE process has increased dramatically due to the crude oil price. For this process to be more efficient, a good recovery of n-butanol is necessary. To achieve this, accurate vapor-liquid equilibrium data is needed for the design of new distillation columns or for revamping the units that already exist [3].

In this project accurate VLE data at high temperatures will be presented for the mixtures water + methanol and ethanol + butanol. Software ASPEN PLUS V11 will be used for modelling the systems retrieving new NRTL parameters.

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## **DEEP EUTECTIC SOLVENTS. A NEW APPROACH TO THE SEPARATION AND PURIFICATION OF SUBSTANCES FOR THE FOOD AND COSMETIC INDUSTRY**

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Ethanol production in 2010 amounted to 85 billion liters [1] and in 2020 105 billion liters [2]. The amount of ethanol produced over the past ten years has increased by 21 billion liters, which indicates an increase in demand for this product. The use of ethanol is very widespread. For example, in addition to the obvious use of ethanol to provide transport, ethanol is used in industries to generate electricity, ethanol can be combusted in stationary engines for heat and electricity generation for domestic heating and cooking, bioplastics are produced on the basis of ethanol, ethanol is widely used in the cosmetic and food industries as a solvent and active ingredient. The growing interest in production of ethanol stimulates an increase of research devoted to the search for new ways to obtain and extract key products, such as ethanol.

This article will focus on the study of a model system containing ethanol and formic acid ester (ethyl formate) namely, the efficiency of ethanol extraction using DESs. DES is a new generation of solvents that serve as an alternative to ionic liquids. Interest in the development and research of DESs arises from their potential as environmentally friendly solvents, their unusual solvation properties, and inexpensive cost [3].

In this work the properties (viscosity and density) of DES based on choline chloride and various hydrogen bond donors (glycerol, glutaric acid, ethylene glycol, urea) and the use of these DESs to extract ethanol are presented. Such a study will help to track such patterns that affect the separation, as the length of the extractant chain, the temperature of the study, the donor of the hydrogen bond in the initial DES, and others on the example of a model system consisting of ether and alcohol.

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## TERPENE BASED DEEP EUTECTIC SOLVENTS FOR THE REMOVAL OF TEXTILE DYES

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The textile industry is a significant generator of wastewater effluents, coming from several wet processing operations such as pretreatment, dyeing, washing finishing, coating and printing. The dyeing process is the most significant in volume and toxicity of the generated effluent streams, which will contain unspent dye and other auxiliaries [1]. Several families of methods are currently employed for decolorization of textile wastewater effluents, mainly biological (enzymatic or bacterial degradation), oxidative (chemical or advanced oxidation) and physical (coagulation, absorption and adsorption) [2]. Of all these methods, only physical methods allow for a complete recovery of all agents involved in the treatment step: water, separating agent and unspent dye. Of these, liquid liquid extraction offers a high degree of flexibility when coupled with designer solvents such as Deep Eutectic Solvents (DESs) [3]. Low environmental impact and low cost DESs, highly tuned for concrete pollutants can be designed based on natural components such as terpenes or carboxylic acids [4].

In this work, several natural components like Thymol, Camphor and Menthol have been coupled with carboxylic acids such as Decanoic Acid to form novel solvents tuned to increase interaction with textile dye molecules in aqueous solutions. The solvents have been chemically and thermally characterized under Nuclear Magnetic Resonance (NMR) spectroscopy and Differential Scanning Calorimetry (DSC) and applied to extract several dye classes under varying conditions. The dyes have been selected to be representative of a wide variety of textile dyeing processes, including direct (Direct Yellow 27), reactive (Remazol Brilliant Blue) and acid dyes (Acid Violet 43). High extraction efficiencies of up to 80% have achieved for several dye/DES systems.

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## **EFFICIENCY OF DEEP EUTECTIC SOLVENTS BASED ON CHOLINE CHLORIDE FOR THE SEPARATION OF ALCOHOL-ESTER SYSTEMS FOR THE POTENTIAL USE IN THE BIOFUELS PRODUCTION**

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Nowadays, the development of green chemistry is extremely relevant. It is aimed to reduce the negative impact of chemical production on the environment as well as the unavoidable consumption of raw materials. Further development of science and technology is aimed to find alternative environmentally friendly solvents.

Deep eutectic solvents (DESs) are considered one of the most promising eco-friendly and economically viable alternatives to traditional volatile organic solvents and ionic liquids [1-2]. DES is a liquid at ambient temperature system consisting of a hydrogen bond donor (HBD) and acceptor (HBA), which have a higher melting point than the DES they form. The efficient use of environmentally friendly solvents has an important impact in optimizing synthesis and purification processes in various types of chemical technology, particularly, in the production of esters which are actively used in the biofuels production.

The liquid-liquid equilibria (LLE) in heterogeneous systems ethanol-ethyl formate – DES and 1-propanol-1-propyl formate – DES were studied at 313.15 K and atmospheric pressure. The investigation was carried out with DESs based on choline chloride (ChCl) and some HBAs: urea (Ur) and glutaric acid (Glu).

For the investigation deep eutectic solvents (ChCl/Ur (1:2) and ChCl/Glu (1:1)) were prepared in given molar ratios. In these ratios, the lowest melting points of the DESs are achieved. Systems with different ratios of components were mixed for the study of LLE. Samples from each equilibrium phase were analyzed by <sup>1</sup>H NMR spectroscopy. Phase diagrams based on obtained LLE data were constructed. Distribution coefficients and selectivity values were calculated for the evaluation of the separation efficiency of the studied alcohol-ester systems. Correlation of experimental LLE data by NRTL equation was carried out. Calculated data showed a good agreement with experimental data.

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## DESIGN OF DEEP EUTECTIC SYSTEMS: PLASTIC CRYSTALLINE MATERIALS AS EUTECTIC MIXTURE CONSTITUENTS

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Deep eutectic solvents (DES) are a class of solvents that can be prepared by mixing two or more compounds to form a solution with a eutectic temperature significantly lower than the melting temperature of pure constituents. DESs are considered designer solvents as their properties can be tuned by selecting the constituents and their molar ratio. Having a liquid solution at the desired operating temperature is of utmost importance to employing DESs as solvents in various applications. The solid–liquid equilibria (SLE) phase diagram provides information about the melting temperature of the mixture at any molar ratio [1]. However, as DESs can be prepared from a large pool of substances, obtaining the SLE phase diagram experimentally becomes a demanding task that often accompanies many difficulties [2]. Therefore, understanding DES formation is a vital goal to preselect the constituents and define the suitable molar ratio range to tune the solvent properties accordingly.

Based on various studies [1,3-5], DESs were found to form due to significant negative deviation from ideal behavior and very low melting enthalpy and entropy of constituents. The very low melting entropy is a unique character of substances with highly disordered and symmetrical crystal structures, i.e., plastic crystalline materials [6].

Various commonly used DES constituents, particularly choline chloride [3], are plastic crystalline materials. However, the influence of plastic crystallinity on the depression at the eutectic point has not been discussed explicitly. Plastic crystalline materials undergo various phase transitions [7], complicating measuring and modeling SLE in plastic crystalline-based eutectic systems. In this work, the SLE phase diagram of various eutectic mixtures containing plastic crystalline materials was measured. The eutectic temperatures of plastic crystalline-based eutectic systems were compared with those of eutectic mixtures containing common crystallized solids. It was found that plastic crystalline materials can form eutectic mixtures showing a large difference between the eutectic temperature and the melting temperature of pure constituents. Therefore, the selection of DES constituents can be narrowed down from arbitrary salts and organic substances to plastic crystalline materials. The current work findings will aid in selecting DES constituents to improve the design approaches and the utilization of DES in various applications.

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## **POLY(ETHYLENETEREPHTALATE) AND POLYETHYLENE TARGETED SOLUBILIZATION AND RECOVERY WITH GREEN SOLVENTS**

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The recyclability of polymers is of crucial importance in the present days considering the amount of plastic waste that is generated every day. According to the Eurostat Statistics, between 2005 and 2014, EU produced around 15 million tons per year of plastic packaging waste. Usually, this type of waste consists of a mix of different of various polymers and even aluminum foils therefore the recycling of this type of waste is challenging as it has low yield, high energy consumption and CO<sub>2</sub> emissions as lower quality and uneven end product. Thus, a more efficient and greener approach to this problem is needed. The specific solubilization of each polymer in a given solvent that can dissolve a given polymer without solubilizing the remaining ones is a good approach as the yield of this strategy is much higher and both the polymer and solvent can then be recovered by precipitation using an antisolvent. This approach results in the recovery of each polymer with high yield, purity and almost no changes from the original material [1-2]. Nevertheless, this strategy still makes use of organic volatile solvents that make the process not environmentally safe, health hazardous and also economically unfavorable due to loss of the solvent.

The process designed for the recycling of water bottles, uses NADES (natural deep eutectic solvents) composed of terpenes (menthol and thymol) as well as terpenes that are liquid at room temperature (limonene) to the target solubilization of PET and PE from water bottles and water bottle cap, respectively. The Hansen solubility parameters were used to screen the best solvents (NADES or biobased solvents) for each one of the polymers. The dissolution of PET is accomplished in about 7 minutes and can then be precipitated using a mixture of water and ethanol which results in a remarkable 99 % recovery of polymer and 99% recovery of the solvent. The recovered PET was analyzed by FTIR, X-ray diffraction and RMN and exhibited almost no changes from the original PET others than a slight increase in crystallinity [3]. The selective dissolution of the PE with high efficiency was already accomplished and the method has already proven to be capable of dissolving only the targeted polymer when a mixture of both polymers. PET and PE are present. The recovered PE will also be analyzed with FTIR, X-ray diffraction and RMN.

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## ZOOMING IN WITH QSPR ON SOLUTION ENTHALPIES OF API'S IN EUTECTIC MIXTURES

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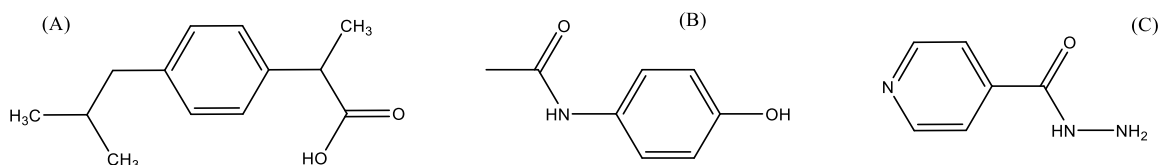
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Deep eutectic solvents (DES) are a class of solvents that in recent years has gained a lot of attention. This is evidenced by the numerous publications regarding their characterization and potential applications [1]. However, solute-solvent-solvent interactions in these media remain somewhat misunderstood. Within this context, and following previous work, we present herein the solution enthalpies of three API's, ibuprofen, paracetamol and isoniazid, (Figure 1) in different eutectic mixtures, water-eutectic mixtures, and pure organic solvents.



**Figure 1.** API's used (A) – Ibuprofen, (B) – Paracetamol, (C) – Isoniazid.

Experimental results were obtained using a Thermometric 2225 semi-adiabatic isoperibol solution calorimeter at 298.15 K. Solute selection reflects the required chemical diversity for subsequent analysis and the eutectic mixtures were chosen based on their solubility for each solute but also for their low viscosity, which was ensured by using water as a co-solvent in certain mixtures. The solvents used were characterized by the Kamlet-Taft parameters,  $\alpha$ ,  $\beta$  (solvent's acidity and basicity by hydrogen bonding, respectively) and  $\pi^*$  (solvent's dipolarity/polarizability), using the characteristic absorption band maximum wavelengths of five solvatochromic probes, namely 4-nitroanisole, 4-nitrophenol, 4-nitroaniline, *N,N*-dimethyl-4-nitroaniline and 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate.

A quantitative structure-property relationship (QSPR) methodology [2], was applied to the individual solutes' results, according to the expression:  $\Delta_{\text{sol}}H_{\text{m}}^0 = a_0 + a_1\pi^* + a_2\alpha + a_3\beta$ . The use of this approach allowed the identification of the most relevant parameters to describe the solution process of each solute.

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## **SOLUBILITY STUDIES OF AMINO ACIDS IN THE EUTECTIC SOLVENT CONSTITUTED BY UREA AND SODIUM ACETATE TRIHYDRATE**

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It is estimated that more than 50% of the feedstock of seafood processing industry in the world ends up as waste, exceeding 20 million tons annually [1]. This waste consists mainly of fish tissues, including fins, heads, skins and viscera, with valuable protein content, thus representing a potential alternative source of bioactive compounds such as collagen. Collagen is one of the most abundant proteins and plays a significant role in the formation of connective tissues and the metabolism of their regeneration. It is a natural biodegradable polymer, thus it can be used as biomaterial in tissue engineering: skin reconstruction, drug delivery, or peripheral nerve regeneration, among others. Traditional methods for collagen recovery consist of multi-step extractions with strong acids or alkali solutions, followed by several neutralization steps. These complex and harsh processes, with a high demand in terms of chemicals and energy requirements, usually lead to low quality products. Moreover, in most cases the effluent cannot be recovered or reused, which is in clear lack of alignment with the most elemental principles of circular economy and green chemistry.

In this context, extraction with (deep) eutectic solvents is emerging as an alternative to overcome these problems. Low volatility, liquid character and tunability of eutectics can be elements particularly attractive for their use in the recovery of valuable bioactive compounds. In addition, they can be prepared using natural and biodegradable components, so they can be non-toxic and environmentally friendly by design. This work aims to explore a eutectic solvent constituted by GRAS components for the extraction of collagen from fish waste. In a first stage of the project, the solubility of four amino acids present in collagen has been studied in the above-mentioned eutectic solvent. This system shows a eutectic behaviour with melting temperature of 304 K when combined in a 60 mol% concentration of urea, which enables its utilization at the most common extraction temperatures. L-Proline,  $\beta$ -alanine, L-arginine and glycine solubilities have been tested in this mixture at different temperatures.

An increase in solubility has been observed with increasing temperature, reaching values even higher than 0.30 in mass fraction of amino acid in the case of L-proline or  $\beta$ -alanine, at a moderate temperature of 338 K. These results encourage us to believe that the tested eutectic solvent could become the basis of an alternative method to extract collagen from fish processing by-products, contributing to their valorisation.

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## **STUDIES ON THE CONTROLLED RELEASE OF METAL IONS FROM NANOMATERIALS USING NEOTERIC SOLVENTS FOR AGRICULTURAL APPLICATIONS**

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In the face of global population growth, the concept of sustainable agriculture and food security is becoming more and more important. Among the inefficient practices, the use of fertilizers in agriculture is a major concern, as only about 30% of the applied fertilizers are used by the crops, leading to energy, water and arable land unnecessary wastes [1]. Therefore, sustainable alternatives are being pursued and among them, customized nanomaterials (NMs) stand out due to their potential in controlling nutrients release and stimulate plant defences and against diseases [2].

Currently investigated nanoscale micronutrients comprise metals and metal oxides. Besides increasing nutrient absorption, metal oxides such as copper oxide (CuO) and iron oxide (Fe<sub>2</sub>O<sub>3</sub>), are known for their effectiveness in attenuating disease damages [1]. This ‘healing power’ is related with micronutrients plant nutrition what emphasizes the process sustainability. For example, Ma et al. [1] found that the foliar application of Cu-based NMs significantly suppressed soybean infection by *Fusarium virguliforme*, and that this activity correlated directly with material structure and dissolution.

The overall goal of this work is to investigate the release of metal ions from NMs in aqueous solutions containing ionic liquids (ILs) and deep eutectic solvents (DES). These neoteric classes of solvents, well known due to their many properties and applications, are attractive options for the controlled release of metal ions from NMs for agricultural applications. Metal oxide nanoparticles such as CuO, cerium oxide (CeO<sub>2</sub>), Fe<sub>2</sub>O<sub>3</sub>, iron(II,III) oxide (Fe<sub>3</sub>O<sub>4</sub>), and iron(III) oxide-hydroxide (FeOOH) were investigated along with the ILs and DES that are made up of plant growth regulators based biomolecules. ILs and DES were characterized through NMR while nanoparticles were characterized by powder XRD, DLS, and TEM. The dissolution experiments were performed using dialysis membranes and centrifugal filter units and metals quantified using TXRF spectrometer ultra-trace element analysis. This work will foster the development and understanding of different mechanisms in the field of plant nanotechnology.

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## IONIC LIQUIDS AND THEIR ANALOGUES ZWITTERIONIC COMPOUNDS AS A PATHWAY TO ALTERNATIVE HYDROTROPES

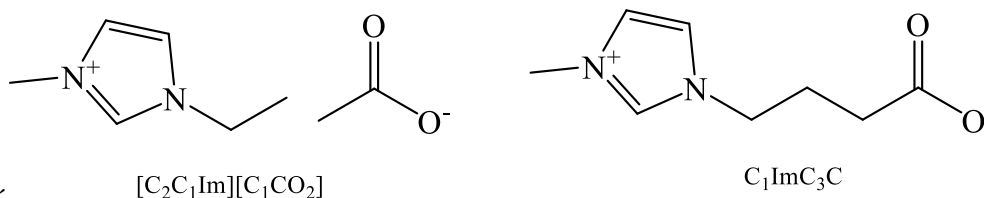
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The pharmaceutical industry faces great challenges when formulating new pharmaceutical products, namely the poor solubility of drug molecules in water. The development of new strategies to enhance the solubility of drugs in water has been increasing. Hydrotropy, a molecular phenomenon that consists in the use of hydrotropes to enhance the solubility of hydrophobic compounds in aqueous solutions [1], has been broadly applied. However, despite the numerous studies on hydrotropy, its mechanism of action has not yet been fully understood, emphasizing the need for more studies. Moreover, the continuous search for new classes of hydrotropes is crucial since an universal hydrotrope does not exist.

In this work, aqueous solutions of ionic liquids (ILs) and their analogous zwitterionic compounds (ZIs) were prepared to investigate the solubility enhancement of poorly water-soluble compounds. ILs – organic salts with melting temperatures below 100 °C – and ZIs – compounds where the ion pair is covalently tethered – with similar chemical structure to ionic liquids (ZILs) present very distinct properties and applications. The solubility of two molecules – syringic acid and pyrene – and one pharmaceutical drug – ibuprofen – in aqueous solutions of ILs and ZILs (Figure 1) was determined. The solubility curves of the solutes were determined according to the isothermal shake-flask method [2]. To better explain hydrotropy mechanism, the polarizability/dipolarity ( $\pi^*$ ) of ILs and their analogues ZILs was determined, allowing a comparative study between ILs and ZILs hydrotropic effect and solvatochromic parameters.



**Figure 2.** Chemical structure of both IL (left) and ZIL (right).

The obtained results demonstrated that the studied ILs and analogous ZILs are potential hydrotropes for bioactive solutes and pharmaceutical molecules. These compounds were able to induce considerable increments in the aqueous solubility of the studied solutes, when compared to pure water. In a general way, the obtained results revealed that both ILs and ZILs present similar hydrotropic behaviour when studying the same solute; however, ILs seem to be superior in terms of the hydrotropic effect, reaching higher solubility enhancements than their analogous ZILs.

### Acknowledgements

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## LIQUID-LIQUID PHASE BEHAVIOR OF BINARY MIXTURES OF ACETONITRILE AND N-ALKANES

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Mixtures of acetonitrile and molecular solvents are of interest for fundamental research. Acetonitrile exhibits a high dipole moment and shows partial miscibility with a couple of common molecular liquids, typically connected with the appearance of upper critical points. In contrast to other solvents which are able to form hydrogen bonds, acetonitrile allows for the study of molecular interactions influenced by a dipole moment without the appearance of hydrogen bonds. Recently, binary mixtures of acetonitrile and normal alkanes have also been considered as potential candidates as reference materials for the sake of validation of procedures for the determination of liquid-liquid equilibria [1]. Such mixtures indicate characteristic shifts of the phase behavior due to a gradual variation of chain lengths of the alkane. A similar behavior has also been observed in binary mixtures of *n*-alkanes and ethanol as a hydrogen bond forming component [2].

The present study focuses on the characterization of the liquid-liquid phase behavior of acetonitrile and *n*-octane using the synthetic method connected with a cloud point detection. Due to the hydrophilic nature of acetonitrile, special care has been taken on the influence of residues of water on the phase behavior, here the water contents of the components are fully monitored. In order to validate the experimental results and to allow for a better comparison with data from literature, complementary investigations on mixtures of acetonitrile and *n*-hexane, *n*-heptane, and *n*-decane have been performed.

The critical solution temperature, the critical composition and the parameters characterizing the shape of the phase body are finally determined by a numerical analysis of the phase diagrams presuming Ising criticality and a nonlinear diameter. Results are compared with data from literature, analogies with results obtained from *n*-alkane/ethanol mixtures [2] are described.

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## CHROMIUM BEHAVIOUR IN THE ENVIRONMENT

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In the natural environment, under normal conditions, the more common chromium species is chromium(III), which generally occurs in minerals with very low water solubility, with chromite ( $\text{FeCr}_2\text{O}_4$ ) being the most exploited for industrial application. Under this oxidation state, the total concentration of chromium in natural waters is very low and has a low environmental impact. Chromium is also on the list of trace elements believed to be essential for microorganisms, plants and animals, especially vertebrates, although it can also be potentially toxic.

Under very special conditions, it is possible to find chromium(VI) as tetraoxidochromate(2-) ion in the natural environment, as in crocoite ( $\text{PbCrO}_4$ ). In addition to this solid phase, some other very rare minerals containing lead chromate have been found. The very rare minerals lópezite ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and tarapacáite ( $\text{K}_2\text{CrO}_4$ ) have been found in highly arid regions as northern Chile or South Africa.

The most famous crocoite minerals occur in Tasmania resulting from the alkaline alteration of chromite associated with many other processes that promote solid phase dissolution, oxidation of chromium(III) to chromium(VI) and reactions with lead(II) ions [1].

Is it possible to promote the oxidation of chromium(III) to chromium(VI) in different environmental media such as soils or the reduction of chromium(VI) to chromium(III)? What conditions will be needed? These were questions that deserved investigation since chromium(VI) is toxic to living beings. Experimental results with different soils under different conditions were conducted and the results will be presented.

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## REMEDIATION OF SOILS CONTAMINATED WITH TOTAL PETROLEUM HYDROCARBONS THROUGH WASHING WITH SURFACTANT'S SOLUTIONS

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The soil fulfils vital functions for life on Earth and it is urgent to protect it from all sources of contamination. However, with the increase in industrial activity, environmental liabilities arising from petroleum by-products have been found. According to JRC Technical reports 'Status of local soil contamination in Europe' estimates the occurrence of about 2.8 million potentially contaminated sites in Europe, with more than 650 thousand contaminated sites already registered in national inventories [1]. Biological, chemical, and thermal remediation techniques have been developed to remove/reduce or immobilize pollutants. Ex-situ soil washing is one of the promising ways to concentrate contaminants, allowing soil cleaning and the reuse of extracted oils. In this work, an ex-situ soil washing process using two surfactants, sodium dodecyl sulfate (SDS) and polyoxyethylene sorbitan monooleate (Tween 80), was tested in the decontamination of an artificially contaminated sandy soil with burnt oil. The choice of surfactants was based on their physicochemical characteristics, with preference for surfactants that have a low critical micelle concentration (CMC), low toxicity, high hydrophilic-lipophilic balance (HLB) value and low cost [2,3]. An optimization of the washing conditions was carried out, including a kinetic study of experimental parameters, such as stirring speed, liquid-solid ratio, number of washing stages, concentration of surfactant, effecting soil washing was carried out. An TPH removal efficiency of  $80.7\% \pm 3.2\%$  was obtained with Tween 80 after 5 hours of washing and  $90.7\% \pm 2.8\%$  with SDS after 2 hours at 200rpm on an orbital shaker and L/S of 15. The performance of using microfoams of both surfactants was also evaluated, observing an improvement of about 10% for the SDS, using the same contaminated soil. After washing, the oil was removed by liquid-liquid decantation and particles by centrifugation, reusing the solution again, with positive results for the reused SDS solution. Finally, the discharge of the washing solution was considered and activated carbon was used to ensure its safe disposal, resulting in a reduction in the COD value of 2800 and from 3400 mg/L O<sub>2</sub> to 22mg/L O<sub>2</sub>.

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## SOLUBILITY PHENOMENA IN ENHANCED OIL RECOVERY

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Worldwide petroleum consumption is expected to increase at an annual rate of 0.6% between 2021 and 2050. Until renewable energies and materials can replace crude oil in all of its applications, oil resources at our disposal should be exploited efficiently. After primary and secondary conventional extraction, approximately two-thirds of the original crude oil remains in the reservoir trapped by capillary forces that retain the oil in the pores of the rocks [1]. Among chemical enhanced oil recovery techniques, surfactant flooding is a well-established method that increases oil recovery through water/oil interfacial tension reduction and wettability alteration. The surfactant must meet many requirements: it must be miscible in water, stable in the presence of salts, and show a significant and equilibrated solubilization of oil and water [2]. The search for this surfactant has been carried out many times in an arbitrary manner, frequently performing a large number of interfacial tension measurements until the goal is reached. However, the study of the solubility phenomena involved (brine, oil and surfactant) is the shortest way to reach the objective.

When oil and brine are mixed in the presence of surfactants, a microemulsion system is formed. Winsor type III microemulsions are related to ultra-low water/oil interfacial tensions, thus high oil recovery can be achieved using these systems [3]. Ionic liquids have become a powerful tool in the improvement of EOR applications due to, among other interesting properties, their tunability. In this work, two ammonium-based surface active ionic liquids were blended with linear alkyl benzene sulfonates, to improve the properties of these traditional anionic surfactants. The encased-glass-pipette method was implemented to study the phase behaviour and temperature influence was also assessed. Brine stability and interfacial tension of optimal blend ratios were tested. The adequate phase behaviour led to an optimal extraction, as demonstrated by means of core-flooding experiments using real carbonate reservoir rocks.

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## **SORPTION OF HYDROGEN SULPHIDE IN CELLULOSE + CEMENT HYDRATE BLENDS**

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Concrete reinforced with fibres such as cellulose are widely used in engineered structures for their favourable mechanical and durability properties [1-3]. The inclusion of cellulose fibres in concrete has been shown experimentally to improve the durability of the material [4]. Previous work [5] demonstrated that H<sub>2</sub>S that possesses the largest affinity for sorption into cement hydrate of all components commonly associated with fermenting or decaying organic matter (i.e. CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, etc.). Hence mitigating its sorption into the material is of key importance where preventing corrosion of buildings and infrastructure is concerned. The present contribution considers the sorption of hydrogen sulphide in humid environments into blends of cement hydrate + cellulose. The effects of both temperature and cellulose content are studied for solid material exposed to a synthetic gas mixture having a similar composition to gas produced by anaerobic digestion of plant matter [6]

Cavities of different volumes were formed inside cement hydrate based on the molecular model of Pellenq and co-workers [7] which were then packed with amorphous cellulose molecular chains, following which molecular simulations were undertaken to study the sorption behaviour. Monte Carlo (MC) [8] simulations in the grand canonical ensemble were used to simulate adsorption into the solid material at ambient pressure. Three independent simulations employing configurational bias [9] were used to generate each data point. The atomistic condensed-phase-optimized molecular potentials for atomistic simulation studies (COMPASS) [10] was used to describe all intra- and intermolecular interactions. The chemical potential of all species in the vapour reservoir in equilibrium with the adsorbed fluid was computed over the temperature range 273 K to 323 K using the Soave-Redlich-Kwong cubic equation of state [11].

The results of this study may suggest ways forward in terms of the effect of cellulose content on mitigating sorption of hydrogen sulphide into concrete. The role of the ambient temperature is also demonstrated, thereby illustrating the interplay between the composition of the material and the environment in which it is located.

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## VOLUMES OF FUN WITH ELECTROLYTE SOLUTIONS

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The volumetric properties of electrolyte solutions continue to attract interest for many reasons. Scientifically, the volumes of electrolytes (and their component ions) are appealing because, in addition to their importance for quantifying the effects of pressure on chemical equilibria and kinetics, they are far more tangible than most thermodynamic properties. Technologically, density is one of the most important physico-chemical properties of industrial process solutions required, for example, for pump and pipeline sizing. Such properties are often required over very wide ranges of concentration and temperature where the database is often limited or even non-existent. This talk will describe some of our recent investigations on certain aspects of the volumetric behavior of various electrolyte solutions. Topics to be covered will include the following.

- How well do we know the standard molar volumes of simple electrolytes?
- How does chemical speciation affect the volumetric properties of sulfuric acid?
- How do aqueous solutions of nitric acid behave at high temperatures?
- How do the volumetric properties of electrolyte mixtures depend on composition?
- How are the volumetric properties of ions affected by the solvent?

## **ANALYSIS BY CYCLIC VOLTAMMETRY OF A CONCENTRATED TERNARY SYSTEM OF LITHIUM ACETATE-CESIUM ACETATE-WATER**

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Currently, a large number of research are aimed at replacing lithium-ion batteries with electrolytes of the "water-in-salt" type – highly concentrated solutions of electrolytes that differ in a significant window of electrochemical stability, and most importantly are non-toxic.

As a basis for such systems, LiTFSI ( $\text{LiC}_2\text{F}_6\text{NO}_4\text{S}_2$ ) can most often be found. Its extremely high solubility in water makes it possible to create "water-in-salt" systems that have shown stability up to 1000 cycles with almost 100 % Coulomb efficiency [1]. For this reason, further studies using this electrolyte are continuing [2]. But LiTFSI cannot be called non-toxic due to the presence of fluoride groups, in addition, its cost is quite high. Therefore, an alternative system was proposed - potassium and lithium acetates, which showed an electrochemical stability window (ECS) of more than 3 volts [3].

We decided to replace potassium acetate with cesium acetate in order to test the ECS of the new system with a different ratio of components, based on the very high solubility of cesium acetate in water, as well as the significant mobility of the cesium ion. During the work, the densities of solutions were measured, and their exact molar concentrations were determined. Cyclic voltammograms were obtained for each sample using glass-carbon and silver-chloride electrodes, on the basis of which a conclusion was made about the ECS window of this system, as well as the possibility of its expansion. According to the results, a significant increase in the window was noted in comparison with dilute solutions, and the area of the optimal ratio of components was also determined, where the ternary system shows the largest ECS window. The obtained data were correlated with a similar system of lithium and potassium acetates.

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## NEUTRALIZATION OF TRICALCIUM ALUMINATE HYDRATES WITH HYDROCHLORIC ACID

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Tricalcium aluminate (TCA,  $3\text{Ca}(\text{OH})_2 \cdot 2(\text{Al}(\text{OH})_3)$ ) is the most reactive component of Portland cement; therefore, a significant body of research has focused on the physico-chemical aspects of the hydration processes of this solid [1,2]. However, the reactions associated with the neutralization of TCA in aqueous solutions are still not fully understood, despite these processes being critical for the resistance of concrete against an aggressive chemical environment (e.g. sulphate attack) [3]. Thus, the goal of our work is to gain insights into the dissolution and neutralization behaviour of hydrated TCA.

To this end, we synthesized TCA via a novel method, reacting CaO with a supersaturated sodium aluminate solution ( $[\text{NaOH}]_{\text{T}} = 7.50 \text{ M}$  and  $[\text{Al}(\text{III})]_{\text{T}} = 5.90 \text{ M}$ ), at  $95 \text{ }^\circ\text{C}$ . We compared the thus obtained solid with TCA prepared according to the well-established calcination method [4]. Using a wide range of experimental techniques (XRD, SEM, SEM-EDX, FT-IR, TG/DTG,  $\text{N}_2$  adsorption, ICP-MS, Al MAS NMR,  $\text{CO}_2$ -TPD), we find that there are only slight differences between the two types of TCA samples.

The dissolution and the neutralization of these solids were studied via titrating suspensions of TCA with hydrochloric acid (HCl). From the titration curves, we conclude that six equivalents of the acid are sufficient for the neutralization of TCA, i.e. to reach  $\text{pH} \approx 7$ . Strikingly, the addition of HCl first yielded hydrocalumite ( $\text{Ca}_2[\text{Al}(\text{OH})_6]\text{Cl}$ , a layered double hydroxide) as reactive intermediate. This solid then transforms into amorphous  $\text{Al}(\text{OH})_3$  upon further acidification of the suspension. Eventually, all of the solid dissolve at a pH of  $\sim 2.3$ , resulting in  $\text{CaCl}_2$  and  $\text{AlCl}_3$ .

Overall, our findings shed light on the complex mechanism of TCA neutralization, which helps understanding the nature of the transformation of Portland cement upon contact with acidic agents.

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## PROTON TRANSFER FROM CARBONIC ACID IN AQUEOUS SOLUTION

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Carbonic acid ( $\text{H}_2\text{CO}_3$ ) is a chemical compound of fundamental significance, which although being unstable chemically, plays an important role in host of aqueous systems, which maintain life processes and affect human environment. Due to its short lifetime and presence of the undissociated  $\text{CO}_2$  in aqueous solution the chemical reactivity of this unstable elusive molecule is still largely ignored. little is known about the impact of the intact  $\text{H}_2\text{CO}_3$  in nature. Howbeit, it has been established that carbonic acid acts as an intermediate in the acidification of seawater [1], in the chemistry taking place in earth's upper atmosphere [2], in deep space chemistry [3], and especially in the human body [4]. The aqueous bicarbonate buffer is crucial pH buffer in the human organism, and the traditionally underestimated intact carbonic acid plays a key role in stabilising the pH in the blood plasma and in the protonation reaction, which occur there. It was shown that  $\text{H}_2\text{CO}_3$  is capable of efficiently protonating bases with biologically-relevant  $\text{pK}_a$ s [5]. Herein, we deepen our understanding of the proton transfer from carbonic acid to important organic bases such as Imidazole and Histidine.

In order to establish that  $\text{H}_2\text{CO}_3$  acts as a protonation agent, similar to stable carboxylic acid, such as lactic acid, we performed protonation experiments using a stopped-flow spectrometer configured into a double-mixing mode: in the first mixing step carbonic acid is formed by mixing aqueous solutions of bicarbonate and a strong mineral acid, whereas at the second step the designated unprotonated organic base of biological relevance is added to the carbonic acid solution. During the proton transfer from carbonic acid to the base, the pH of the solution changes concomitely with the appearance of the protonated base. The pH change is recorded, and the equilibrium concentrations of participants are calculated. The experiment is performed in a wide range of temperatures, allowing to determine the lifetime of carbonic acid, the activation energy of the protonation reaction, the reactions rate constants, and thermodynamic functions, such as reaction enthalpy, entropy, and Gibbs energy.

The comparison of the thermodynamic functions with literature data has shown a good correspondence, confirming the goodness of obtained results. Whilst our detailed kinetic investigations have shown the preferable reaction route to be by direct protonation of the base by intact carbonic acid, meaning carbonic acid and the base have to directly encounter each other prior to protonation.

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## CURATION OF SCIENTIFIC DATA AT RISK OF LOSS: DATA RESCUE AND DISSEMINATION

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According to Downs and Chen [1], the term data rescue refers to “efforts that enable the sustained use of data that otherwise might go unused”. The need of data rescue is directly related to the problem of data loss. This is not exclusive of the ‘equilibrium-solubility world’ [2], but it is particularly acute in this scientific domain. In general, scientific data may need to be rescued at any stage along the data life cycle. This is the case here: i) original ‘titration data’ need to be preserved; ii) the accessibility of scientific papers is in jeopardy due to demise of paper journals and books in libraries and to legal constraints; iii) non-critical and critical compilations cannot be accessed any more [3]. Last year (ISSP19), I discussed some aspects of these issues and a lively debate ensued, which continued after the conference. This communication is an attempt to maintain the momentum going, as well as to interrogate the bodies that have so far been involved in data collection and critical evaluation (e.g. CODATA, NIST, IUPAC, etc.), as well as scientists in the field.

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## **SOLUBILITY, TRLFS AND IWA MEASUREMENTS OF Eu(III) IN DILUTE TO CONCENTRATED NITRATE AND SULFATE SYSTEMS: THERMODYNAMIC AND (SIT, PITZER) ACTIVITY MODELS**

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High inventories of nitrate are expected in specific waste streams in the context of nuclear waste disposal of low and intermediate level waste. Sulfate naturally occurs in the pore water of clay systems, in brines possibly forming in rock salt formations, and as a component in some cement phases (ettringite, monosulfate). Based on the similar ionic radii and equal charge, Eu(III) is often considered as inactive, redox-stable analogue of trivalent actinides expected in the waste, e.g. Pu(III) and Am(III). Thermodynamic and activity models describing the solubility and ion interaction processes of Eu(III) in dilute to concentrated nitrate and sulfate solutions can provide relevant inputs for the description of trivalent actinides under repository-relevant conditions [1,2]. In this study, solubility data determined for the Eu-Na-Mg-SO<sub>4</sub>-NO<sub>3</sub> system are combined with spectroscopic methods (TRLFS) and iso-water activity (IWA) measurements with the aim of deriving thermodynamic and (SIT, Pitzer) activity model parameters of these systems.

Diluted to concentrated aqueous solutions containing Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, MgSO<sub>4</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> were prepared and contacted with the binary, well characterized solid phases Eu<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O(cr) and Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O(cr). Solubility samples were continuously stirred, and the concentration of Eu(III) in the liquid phase was monitored by ICP-OES until attaining equilibrium conditions. Solid phases were characterized by XRD analysis for identification after terminating the solubility experiments. Indeed, literature available for other lanthanides previously reported the formation of some double salts [3,4].

The new experimental data obtained in this study for the system Eu-Na-Mg-SO<sub>4</sub>-NO<sub>3</sub>, in combination with previously reported solubility and isopiestic data are considered to derive the thermodynamic and (SIT, Pitzer) activity model parameters for these systems. The optimization routine is implemented in PEST [5], an optimization software, and chemical equilibria are calculated using the PhreeSCALE software [6] and the dedicated database. The ThermoChimie database is considered as basis for the development of the SIT models [7].

### **Acknowledgements**

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## THERMODYNAMIC DATABASE FOR THE SOLUBILITY ASSESSMENT IN CONCENTRATED BRINES

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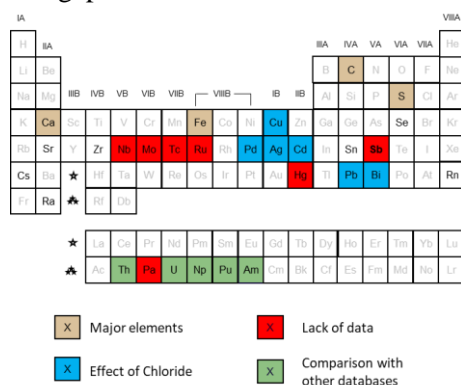
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An estimation of the concentration limits and aqueous speciation of an extensive list of radionuclides and chemical elements is required to support the preparation of the safety case for a deep geological repository in Canada. Crystalline and sedimentary rocks are being considered.

High ionic strength groundwaters (~7 m) have been observed in some of the Canadian sedimentary rocks at the proposed repository depth. There are several approaches to deal with the ionic strength effect in thermodynamic data, such as the Debye-Hückel approach, the Specific ion Interaction Theory (SIT) or the Pitzer approach; the last one is frequently preferred in mixtures of electrolytes over 3-4 m ionic strengths [1]. The parameters needed to apply the Pitzer approach are available in several high-quality and traceable thermodynamic databases (TDBs) [2-4], although none of the TDBs is complete enough to fulfil the requirements of an extensive, multi-element solubility study. The present work developed a thermodynamic database to be applied specifically under the conditions of interest in the assessment for sedimentary rocks.

The main limitation for the development of such an extensive dataset is the lack of experimental data and the difficulty to guarantee the consistency of the whole thermodynamic data assemblage. Considering this complexity and with the aim to overcome the lack of data, the following approach has been followed: i) selection of the thermodynamic data for each element, with a special emphasis on stability constants and Pitzer coefficients, ii) speciation and solubility calculations at high ionic strength for the different systems of interest, iii) identification of families of elements, shown in Figure 1, with common behaviour, iv) comparison of the calculated results with those calculated by other thermodynamic databases and with experimental data (when available), and finally v) identification of uncertainties and of remaining data gaps.



**Figure 1.** Periodic table showing some of identified groups that help to build the database.

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## IMPACT OF GLUCONATE ON THE SOLUBILITY AND REDOX CHEMISTRY OF TECHNETIUM

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$^{99}\text{Tc}$  is one of the main fission products of  $^{235}\text{U}$  and  $^{239}\text{Pu}$  (~ 6%) in nuclear reactors. Due to its long half-life ( $t_{1/2} \sim 2.1 \cdot 10^5$  a), redox sensitive character and large inventory in spent nuclear fuel,  $^{99}\text{Tc}$  plays an important role in the context of safety assessment of repositories for radioactive waste. Under reducing conditions as those foreseen in underground repositories, Tc is expected to form the sparingly soluble  $\text{Tc}^{\text{IV}}\text{O}_2(\text{am, hyd})$  whereas the soluble and mobile pertechnetate anion will form under oxidizing and redox-neutral conditions. Gluconate (GLU) is a polyhydroxycarboxylic acid used as cement additive. GLU is known to form strong complexes with hard Lewis acids such as Ln(III) or An(IV) [1]. In the case of technetium, previous studies have shown a significant impact of GLU on the solubility of  $\text{TcO}_2(\text{am, hyd})$ , although so far no chemical and thermodynamic models are available for this system [2]. Previous applications of the system  $\text{Tc(VII)} + \text{Sn(II)} + \text{GLU}$  in the radiopharmaceutical field have proposed the formation of intermediate oxidation states of Tc under these conditions [3]. The present work aims at obtaining a better understanding of the fundamental processes at the molecular level and an improved quantitative thermodynamic model description of the system using the concepts of established solution thermodynamics, novel XAS techniques and quantum chemical calculations.

All experiments were performed at  $t = (22 \pm 2)$  °C in Ar gloveboxes with  $< 2$  ppm  $\text{O}_2$ . The impact of GLU on the solubility of Tc was investigated from under- and oversaturation conditions with  $\text{TcO}_2(\text{am, hyd})$  and (in-situ reduction of)  $\text{Tc(VII)}$ , respectively. Solubility samples were prepared in 0.1–5.0 M NaCl solutions with  $9 \leq \text{pH}_m \leq 14$  and  $10^{-4} \text{ M} \leq [\text{GLU}]_{\text{tot}} \leq 0.5 \text{ M}$ . Reducing conditions were chemically set for each independent sample with  $\text{Na}_2\text{S}_2\text{O}_4$ , Sn(II), hydrazine or Fe powder except for a limited number of samples that remained redox-unbuffered. [Tc],  $\text{pH}_m$  and  $E_h$  values were monitored at regular time intervals. After attaining equilibrium conditions (assumed after repeated measurements with constant [Tc] and  $\text{pH}_m$ ), the redox speciation of Tc in the aqueous phase of selected samples was investigated by  $L_{3-}$  and K-edge XANES measurements. Solid phases of selected solubility experiments were characterized by XRD, SEM-EDS and EXAFS analysis. XAS spectra were recorded at the INE- and ACT-Beamlines at the KIT Synchrotron, KIT Campus North, in Karlsruhe (Germany).

The presence of gluconate clearly enhances the solubility of  $\text{TcO}_2(\text{am, hyd})$  compared to GLU-free conditions, in line with previous solubility data reported by Hess and co-workers [2].  $L_{3-}$  and K-edge XAFS measurements in combination with ab initio calculations confirm that  $\text{Tc(IV)-GLU}$  complexes dominate the aqueous speciation of Tc under reducing conditions, whereas  $\text{Tc(V)-GLU}$  complexes prevail in redox-unbuffered systems. Based on solubility data and speciation information obtained from spectroscopic and theoretical methods, chemical and thermodynamic models are provided for the system  $\text{Na}^+\text{-Tc(IV)-GLU}^- \text{-Cl}^- \text{-OH}^- \text{-H}_2\text{O(l)}$ . These results provide key inputs for source term estimations including the effect of gluconate in a variety of geochemical conditions relevant in the context of nuclear waste disposal.

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## CITRATE-MEDIATED PLUTONIUM REDOX AND EFFECT OF ELEVATED TEMPERATURE ON AMERICIUM-EDTA COMPLEXATION

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The two most important actinides in terms of activity at the Waste Isolation Pilot Plant (WIPP), located in New Mexico, USA, are plutonium and americium [1]. Predicting the behavior and fate of plutonium depends largely on its oxidation state (which can include +3, +4, +5, and +6 under environmental conditions), whereas americium is invariably in the +3 oxidation state. It is well-known that citrate and EDTA (two WIPP-relevant organic ligands) form strong, stable complexes with Pu and Am, making them more mobile than they would be otherwise. The redox effect of citrate on Pu, however, is not fully explored, in contrast to all of the previous work done on EDTA-mediated redox of Pu [2-10]. The impact of elevated temperature on EDTA or citrate complexation with transuranic actinides also appears to be absent from the literature. Using 0.1 mM Pu-242 and citric acid salts in 0.1 M NaCl, we conducted short-term (hours) experiments to determine the rate constant for the fast citrate-mediated Pu(VI) to (V) reduction, as well as longer-term (months) Pu(V) to (IV) experiments that were stored and sampled in an inert atmosphere (N<sub>2</sub>-circulated MBraun glove box). At each time point, the pH and E<sub>h</sub> of the sample were measured and spectra were acquired using a Varian Cary 5000 UV-Vis-NIR spectrophotometer equipped with a temperature controller. Samples were then filtered through 10 kDa filters and measured by ICP-MS to determine concentration, so as to check for precipitation and normalize spectral measurements. We conducted Am-EDTA studies from 25–90°C over the course of 30 days using 0.01 mM Am-243 and H-Na-EDTA salts in 0.1 M NaClO<sub>4</sub> using the same sampling procedure described for the Pu-citrate system. The resulting stability constants and rate laws contribute to a growing actinide thermodynamic database and provide insights into the extent and likelihood of Pu or Am mobility in the environment.

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***Poster Presentations***

## **EFFECT OF SOLVENT COMPOSITION ONTO COMPOSITION AND STRUCTURE OF METAL-ORGANIC FRAMEWORKS ON THE BASIS OF COPPER AND ZINC TEREPHTHALATES**

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Synthesis and study of metal-organic frameworks (MOFs) is one of the most extensively developed fields of modern coordination chemistry. Effect of pH, synthesis duration, temperature etc. on the formation and properties of MOFs is under consideration. Meanwhile far less attention is paid to very important factor namely to the effect of solvent composition on the composition and structure of crystallizing compounds.

To reveal this effect the study of solid phase formation in the systems  $\text{Cu}(\text{NO}_3)_2 - 1,4\text{-BDC} - \text{amide} - \text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 - 1,4\text{-BDC} - \text{amide} - \text{H}_2\text{O}$  (amide – N,N-dimethyl-formamide, DMF or N,N-dimethylacetamide, DMA) was undertaken in temperature range 90 – 180 °C. As the result, the crystallization fields of distinct MOFs were determined. In copper-terephthalate systems with low water content  $\text{Cu}_2(\text{BDC})_2(\text{amide})_2$  MOFs are formed at temperature up to 130 °C, upon heating they gradually transform to  $\text{Cu}(\text{BDC})(\text{NHMe}_2)_2$ . In water-rich solutions formation of copper basic terephthalate  $(\text{CuOH})_2(\text{BDC})$  takes place.

In the zinc-terephthalate systems higher variety of compounds formed have been found that can be explained by high lability of complexes forming by ions with  $d^{10}$  configuration. Dimethylamide formed under acid-promoted hydrolysis of amide can both coordinate to zinc ion and serve as counter-ion in protonated  $\text{NH}_2\text{Me}_2^+$  form.

The special attention will be paid to *anomal basicity of water* in DMF –  $\text{H}_2\text{O}$  systems effect that influence on both composition of MOFs and the conditions of their crystallization.

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## **THERMODYNAMIC ELUCIDATION OF THE RELATIONSHIP CHEMICAL SPECIES IN WATER SOIL EXTRACTS - PHYTOACCUMULATION**

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The impact of chemical elements on the biosphere is a function of their concentration and chemical form. Elucidation of the latter in soil solutions is of particular significance for the assessment of their phytoaccumulation.

In this study the relationship *chemical species in water soil extracts – phytoaccumulation* was studied in two Bulgarian regions differing in the pollution sources. The first one was the agro-industrial zone of Maglzh region in Central Sub-Balkan with its fertile soils, developed agriculture, livestock breeding and machinery construction factories and the second one was the largest coal industrial complex in South-Eastern Europe - Maritza iztok coal complex, Radnevo region. Trace metals (Mn, Ni, Cu, Zn and Pb) dynamics in the system *water soil solution – uncultivated grass vegetation* was investigated by experimental studies of the soils, their laboratory-prepared water extracts and their uncultivated grass vegetation, as well as by thermodynamic modelling of the trace metals chemical species in the water soil extracts. Two thermodynamic models were applied – the classical ion-association model for calculating the inorganic metal species and the Stockholm Humic Model (SHM) accounting for the complexation reactions of trace metals with organic matter. Computer program Visual Minteq was used. Experimental data for the total concentrations of major and trace metals, dissolved organic carbon and pH were used as input data for the calculations.

The highest mobility was registered for Mn followed by Zn and Cu. Ni and Pb were not extracted in the water. The organometallic species with fulvic acids were found to be the dominant ones in the case of Cu and Zn, while inorganic species, mainly free  $Mn^{2+}$  ions, were the dominant ones for Mn. The highest phytoaccumulation coefficients in the studied uncultivated grass vegetation were calculated for Cu and Zn, being 1-2 orders of magnitude higher than those of Mn. On this basis one could conclude that the domination of organometallic species of Cu and Zn probably facilitates their phytoaccumulation in the examined vegetation. Despite the high Mn content in the water soil extracts, its phytoaccumulation was very low, since Mn does not occur in organic complexes.

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## SOLUBILITY STUDIES OF MONOTERPENOIDS IN ORGANIC SOLVENTS

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Monoterpenoids belong to a large and structurally diverse class of natural compounds widely found in essential oils [1]. These compounds commonly present pleasant aromas and various biological and pharmacological activities, finding many applications in the perfume, cosmetic, food, and pharmaceutical industries [1,2]. To extract and purify monoterpenoids from their natural matrices through solvent-based separation processes, the knowledge of solid-liquid and liquid-liquid equilibrium information is essential. Complementary, evaluating predictive thermodynamic models to describe the equilibrium data is valuable in reducing the experimental effort.

Following our previous studies on aqueous solubilities of monoterpenoids [3,4], the solubility of four monoterpenoids ((-)-borneol, (1R)-(+)-camphor, L-(-)-menthol, and thymol) in organic solvents is investigated in this work. First, solubility experiments were conducted at 298.2 K and 313.2 K (except for L-(-)-menthol) for the selected monoterpenoids in seven organic solvents (acetonitrile, 1-butanol, ethanol, ethyl acetate, hexane, R-(-)-limonene, and 1,2-propanediol) using the isothermal shake-flask method. Then, two semiempirical thermodynamic models, the Abraham solvation model [5] and the NRTL-SAC model [6], and the fully predictive COSMO-RS model [7], were applied to describe the solubility data determined in this work and available in the open literature.

The consistency of the solubility data was confirmed by the low coefficients of variation, always lower than 4%. For all the systems, the solubility increases as temperature increases. Positive deviations from ideality were obtained for most of the binary systems with L-(-)-menthol and (-)-borneol (except in alcohols), while the opposite behavior is obtained for (1R)-(+)-camphor and thymol, with a few exceptions (e.g., (1R)-(+)-camphor + 1,2-propanediol, thymol + hexane). In the modeling step, very good representations of the available solubility data were obtained with the three thermodynamic models, with global average relative deviations varying between 15% and 25%.

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## OXIDE FILM FORMATION ON CONSTRUCTION MATERIALS OF THE NUCLEAR REACTOR FIRST CIRCUIT WITH WATER COOLANT

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In the nuclear power industry, titanium alloys are widely used as construction materials for heat exchange equipment at stationary and transport nuclear power plants (NPPs). High mechanical strength and radiation resistance as well as low cross-section of neutron activation reactions of titanium allow us to count on the further use of these materials in the design of nuclear power plants - in particular, as materials for the shells of fuel elements and reactor housings. In the primary circuit, a solid protective oxide layer on the surface of construction materials is formed consisting of titanium dioxide on top of which discrete crystallites composed of complex oxides of titanium and other metals forming during corrosion process present. The study of their formation is a fundamental basis necessary to solve actual problems of corrosion prevention, ensuring stable heat exchange, and decontamination of surfaces. Up to now the majority of works in this field are devoted to study of film formation at temperatures above 500 °C in atmosphere of oxygen, water vapours or another oxidizing medium and therefore can not be transferred to the conditions of nuclear reactor first circuit. Therefore the study of oxide layer formation under mild conditions (up to 300 °C) and especially – the establishment of coolant composition effect on film morphology and composition and possible incorporation of corrosion products into the oxide layer is very actual.

In this work we are going to present the results of model autoclave experiments simulating the conditions of light-water nuclear reactor first circuit. The principal phases presented in solid film were determined by XRD and compositions of solution species was found by ESI-MS. The relationship between chemical species in solution and solid phase composition is under discussion.

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## LIQUEFYING FLAVONOIDS WITH TERPENOIDS THROUGH DEEP EUTECTIC SOLVENT FORMATION

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Flavonoids are a sizable group of phenolic compounds found in natural matrices, that present relevant bioactivity in different dimensions [1]. Their extraction usually relies on the use of traditional organic solvents, which are often toxic, flammable, and environmental ubiquitous due to their volatility. The alternative use of deep eutectic solvents (DES) aims to provide a greener approach for these processes [2]. DESs are obtained when the mixture of two or more compounds results in negative deviations from ideality (mainly through the formation of hydrogen bonds between unlike compounds), reaching lower melting temperatures than the ones determined by ideal thermodynamic behaviour [3]. Previous works suggest that non-ionic DES, classified as Type V DES [3], can be formulated by mixing hydrogen bond acceptors (HBA) such as alcohols, ketones and amines with hydrogen bond donors (HBD) like phenolic compounds.

The focus of this work is the design of DES for the extraction of flavonoids. Flavone, flavanone and (-)-hesperetin were selected as representatives of this group, potentially acting as HBAs. The HBDs selected were thymol and menthol, both of which are terpenoids commonly used to prepare Type V DES. The solid-liquid equilibria phase diagrams of these mixtures were experimentally measured using an automatic melting point glass capillary device or by Differential Scanning Calorimetry. The experimental data was compared with values predicted by the computational Conductor-like Screening Model for Real Solvents (COSMO-RS) [4], in order to evaluate its ability to describe these systems. This tool was also used to provide insights on the interactions present in these mixtures.

The thymol systems with flavone and flavanone showed negative deviations, forming non-ionic Type V DES. On the other hand, the menthol systems with the same compounds, resulted mostly in positive deviations. Although both flavone and flavanone do not have any HBD group and, therefore, would always establish HBs with either thymol or menthol, only the first terpenoid containing systems showed negative deviations. This exemplifies that the existence of cross HBs does not guarantee negative deviations. The hesperetin molecule, containing both HBD and HBA groups, showed positive deviations when mixed with either terpenoid. Probably, the interactions in pure hesperetin are stronger than with either thymol or menthol. COSMO-RS was able to predict satisfactorily the behaviour of the systems studied and estimate the impact of the different contributions to the intermolecular interactions.

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## KAMLET-TAFT AND PY POLARITY SCALES AS TOOLS TO UNDERSTAND THE HYDROTROPY EFFECT OF ALKANEDIOLS

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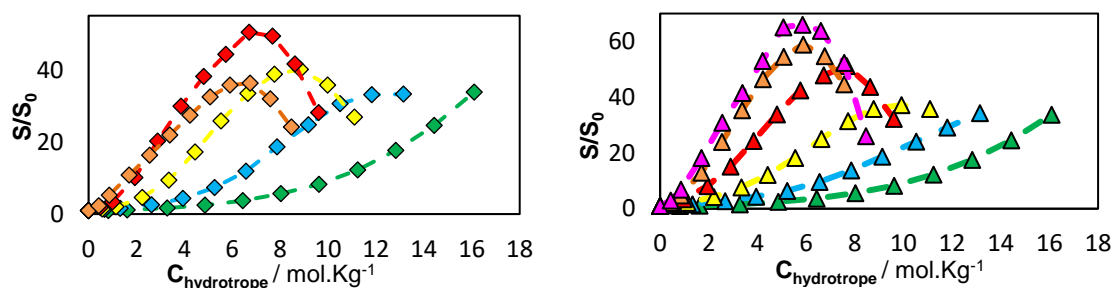
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Alkanediols are a class of di-alcohols widely used in the industry that can provide tunable solvent properties and act as hydrotropes to increase the aqueous solubility of hydrophobic compounds. Inspired by the recently proposed cooperative mechanism of hydrotrope [1], this work studies the impact of apolar volume and polar group position on the performance of hydrotropes. For this purpose, the ability of two different families of alkanediols (1,2-alkanediols and 1,n-alkanediols) to increase the aqueous solubility of syringic acid is investigated. The Setschenow model (low hydrotrope concentration region) shows that the relative position of the hydroxyl groups of the alkanediols does not impact their performance. Instead, their ability to increase the solubility of syringic acid correlates remarkably well with the size of their alkyl chains. However, this is not the case for higher hydrotrope concentrations, where 1,2-alkanediols are found to perform, in general, better than 1,n-alkanediols (Figure 1). These contradictory findings are reconciled using theoretical and experimental techniques, namely the cooperative model of hydrotropy and chemical environment probes (Kamlet-Taft solvatochromic parameter  $\pi^*$  and pyrene polarity scales). It is found that the number of hydrotropes aggregated around a solute molecule does not increase linearly with the apolar volume of the former, reaching a maximum instead. Besides, the results suggest that hydrotrope self-aggregation is more prevalent in 1,n-alkanediols, negatively impacting their performance as hydrotropes. Finally, this work reinforces the idea that hydrotropes should be designed taking into account not only their apolar volume but also their ability to stabilize their self-aggregation in water [2].



**Figure 1.** Relative solubility of syringic acid in aqueous solutions of 1,2-ethanediol  $\blacktriangle$  or  $\blacklozenge$ , 1,2-propanediol  $\blacklozenge$ , 1,2-butanediol  $\blacklozenge$ , 1,2-pentanediol  $\blacklozenge$ , 1,2-hexanediol  $\blacklozenge$ , 1,3-propanediol  $\blacktriangle$ , 1,4-butanediol  $\blacktriangle$ , 1,5-pentanediol  $\blacktriangle$ , 1,6-hexanediol  $\blacktriangle$  and 1,7-heptanediol  $\blacktriangle$  as a function of hydrotrope concentration, at 303.15 K.

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## INSIGHTS INTO THE FORMATION OF (DEEP) EUTECTIC SOLVENTS

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Deep eutectic solvents or systems (DES) have been widely investigated due to their interesting properties and applications, and to the liquefaction and enhanced solubility provided by the decrease of the melting point of the mixture when compared to those of the starting pure constituents [1]. The liquid phase of the mixtures arises due to the melting point depression of the system, which depends on the melting temperature and enthalpy of its components as well as their intermolecular interactions. From a thermodynamics perspective, if such interactions are weak, the systems will behave ideally or even João present positive deviations to thermodynamic ideality, meaning that the interactions between the components of the mixture are less favourable than the interactions found in the pure components individually. The greater the negative deviations to thermodynamic ideality of both components, the greater the melting temperature depression, i.e., the molecular interactions between the components of the mixture are stronger than those found in the liquid phases of the pure substances [2]. The prefix deep should be reserved for such systems, whose components show significant negative deviations from ideality.

Understanding the dominant molecular interactions between the components of eutectic systems is of utmost importance and provides relevant insights on the donor-acceptor interactions that lead to (D)ES formation, helping to design novel mixtures; and data on eutectic systems solid-liquid phase equilibria (SLE) and thus information on the operation window (range of compositions and temperatures) of these systems.

In this context, the purpose of this work is to further explore the interactions between different (D)ES components as molten salts, ionic liquids, terpenes, sugars, carboxylic acids, fatty acids, fatty alcohols, among others, by exploring their SLE phase diagrams. The understanding of the molecular mechanisms behind (D)ES formation allows an informed choice of liquefying agents, i.e., compounds that induce negative deviations to ideality in other solid compounds, originating a liquid mixture and saving time in time-consuming experimental trial and error approaches.

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## SELECTIVE EXTRACTION OF INHIBITORY COMPOUNDS AND SUGARS FROM AQUEOUS MEDIA USING GREEN SOLVENTS

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Nowadays, integrated biorefineries are overcoming the challenges of effective utilization of each component from biomass and improving the efficiency of pretreatment, fermentation and product separation as key to success [1,2]. During the lignocellulosic biomass transformation by biological, chemical or thermochemical treatments different fermentable sugar rich streams are generated [3]. However, inhibitory compounds which negatively influence the fermentation are typically found in these streams [4,5]. In this study, a detoxification method is proposed by selective liquid-liquid extraction of phenolic compounds (phenol, o-cresol, guaiacol, syringol and vanillin) from glucose rich aqueous solutions using green solvents. Specifically, the solvents evaluated herein were three hydrophobic eutectic solvents constituted by the binary mixture of octanoic, decanoic or dodecanoic acid (octanoic: decanoic acid 1:1, octanoic: dodecanoic acid 1:3, decanoic: dodecanoic acid 1:2) and three bio-based solvents (2-methyltetrahydrofuran, cyclopentyl methyl ether and limonene). The extraction efficiencies and selectivities towards phenolic compounds were evaluated from a solution containing 500 mg/L of phenolic compounds and 50 g/L of glucose, as a representative concentration in biorefinery streams. The distribution of the target compounds in each phase after the extraction process was analyzed by HPLC-DAD in the case of phenolic compounds and HPLC-RI for glucose. Finally, the CONductor-like Screening MOdel for Real Solvents (COSMO-RS) method was used to analyze and understand the experimental results obtained by means of excess properties calculations. The results obtained are very promising, as solvents tested can easily extract phenolic compounds but not glucose, which can improve the subsequent sugar fermentation process. In particular, the bio-based solvent cyclopentyl methyl ether provided extraction efficiencies of phenolic compounds above 93 % while that of glucose remained lower than 4 %.

### Acknowledgements:

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## EXPERIMENTAL INVESTIGATION AND THERMODYNAMIC MODELING OF CANNABIDIOL SOLUBILITY IN OILS AND ACID-BASED EUTECTIC SOLVENTS

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Hemp has been used for more than 6000 years as a source of food, fiber, oil, and medicine. From a chemical point of view, the most valuable compounds in hemp are represented by cannabinoids [1]. The cannabinoid market has grown recently, with a wide panel of medicinal and dietary supplement products containing cannabidiol (CBD). This work aims to demonstrate the influence of the fatty acid profile of edible plant-based oils as well as the constituents of the acid-based eutectic solvents on the solubility of CBD. The CBD solubility in various plant-based oils and acid-based eutectic solvents was investigated experimentally. The fatty acid content of ten plant-based oils was analyzed by gas chromatography-mass spectrometry (GC-MS). It was found that CBD solubility is considerably higher in medium-chain triglyceride (MCT) oil—containing only saturated fatty acids—than in oils containing unsaturated fatty acids. The CBD solubility in oils was found to generally increase with increasing the linolenic acid (C18:3  $\omega$ -3) fatty acid content.

The eutectic mixture constituents and ratio were selected based on solid–liquid equilibria calculations. The CBD solubility was significantly higher in acid-based eutectic solvents than in oils. As eutectic system constituents, phenyl and cyclohexyl acids improved the CBD solubility better than linear acids. For eutectic solvents containing acids with similar molecular structures, it was found that the molecular weight of the acid negatively affects the CBD solubility. The CBD solubility data in acid-based eutectic solvents showed that the solution positively deviates from the ideal solution behavior. However, by replacing an acid constituent with L-menthol, a negative deviation from ideal behavior was observed. Consequently, the highest CBD solubility was observed in L-menthol-based eutectic solvents.

Thermodynamic modeling of the CBD solubility in oils and eutectic solvents provides insights into intermolecular interactions between CBD and the solvent. The predictive thermodynamic model conductor-like screening model for realistic solvation (COSMO-RS) was employed to predict the CBD solubility in the studied oils and eutectic solvents. The oils were modeled as a mixture of fatty acids with a relative content estimated by GC-MS analysis. COSMO-RS calculations were performed using the TZVP and TZVPD\_FINE parametrizations. COSMO-RS predictions for the CBD solubility in oils were found unreliable. However, this could be attributed to the assumption that oils are merely a mixture of fatty acids, whereas various substances can present in reality, such as vitamins and polyphenols. The average absolute deviation (AAD) between experimental and calculated mass-based CBD solubility data in oils is 0.1628, 0.2191, and 0.2332 for the TZVPD\_FINE level, the TZVP level, and the ideal solution model, respectively.

In contrast to COSMO-RS predictions for the CBD solubility in oils, COSMO-RS provides quantitative predictions for the CBD solubility in eutectic solvents at the TZVPD\_FINE level. The AAD between experimental and calculated mass-based CBD solubility data in eutectic solvents is 0.0562, 0.1051, and 0.1320 for the TZVPD\_FINE, the TZVP level, and the ideal solution model, respectively. This work shows that predictive thermodynamic models can be a valuable tool to predict bioactive substances' solubility and design tunable eutectic solvents based on non-toxic and natural substances.

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## REMOVAL OF AZO DYES WITH DEEP EUTECTIC SOLVENT DOPED CHITOSAN BEADS

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The textile industry is one of the main contributors to the generation of wastewater effluents, coming from several wet operations such as pretreatments, dyeing, finishing, coating, and washing. Of these, the main bulk of the emissions by volume come from the dyeing process, which generates complex effluents containing dyes which can be toxic to aquatic life [1,2]. Of all dyes, one of the most widely used chromophore system in textile industry is the azo group  $-N=N-$ . Several families of methods are currently employed for decolorization of textile wastewater streams, mainly biological (enzymatic or bacterial degradation), oxidative (chemical or advanced oxidation) and physical (coagulation, absorption and adsorption) [2]. Of these, physical methods, and concretely adsorption, have the unique advantage of allowing a full recovery of all elements involved in the wastewater treatment process: water, adsorbent, and unspent dye. This allows a circular approach to the treatment and dyeing process. Several substrates have been traditionally employed as adsorbents for dye removal, including activated carbon or vegetal residues [2]. More recently, novel natural and biocompatible substrates, such as chitosan films or beads have been proposed with high decolorization efficiencies [3].

In this work, chitosan based beads doped with Choline Chloride:Urea Deep Eutectic solvent (ChCl:Urea DES) and ChCl:Urea DES with magnetic ferrous oxide (FeO) to remove the selected azo dye Reactive Black 5 (RB5). The adsorbents were physically and chemically characterized by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Their isothermal and kinetic behavior was also studied and fitted to a Langmuir isotherm and a pseudo second order kinetic, revealing a process of monolayer adsorption mediated by electrostatic interactions.

Finally, the proposed system allows for high removal efficiencies of up to 99.53% for RB5.

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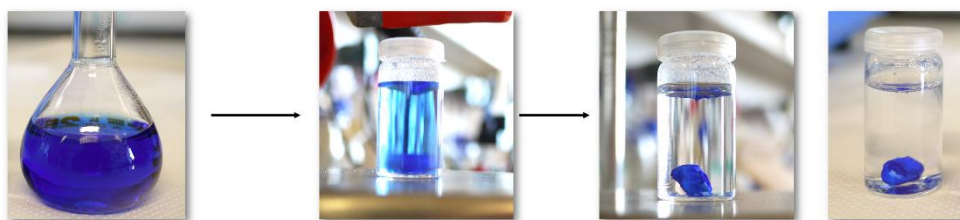
## POLY(IONIC LIQUID)S FOR DYES REMOVAL AGENTS

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Dyes are believed to be used since the Neanderthals, at that time, these dyes were usually extracted from plants, but nowadays more than 1 million tons are annually industrially produced and used mainly by textile industries [1]. One of the major problems concerning the use of dyes is that 10 to 15% are discharged to the environment [2]. PILs have already been explored for the extraction of acid, basic and azo dyes such as bromo phenyl blue, methyl blue, orange II, sunset yellow or amaranth, mainly through the use of imidazolium based PILs [3-4]. This work aims to further evaluate the real potential of PILs as sorbent materials for removal of dyes, direct red 80 and reactive blue 5, from aqueous solutions. For that purpose, poly(diallyldimethylammonium TFSl) was synthesized and subsequently tested as dye adsorbent. Several geometries such as coated stir bar, solid phase extraction cartridge or dispersed powder were explored. The results of the adsorptions are very promising (Figure 1) but this work still needs further studies as well as variable optimization.



**Figure 1.** Representation of RB5 structure and adsorption experiments regarding the PIL and the initial and final aspect of the aqueous dye solution.

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## COMPUTATIONAL MODELLING OF TYPE V DEEP EUTECTIC SOLVENTS

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Type V Deep Eutectic Solvents (DES) are non-ionic liquid mixtures that, through more favourable cross intermolecular interactions, present negative deviations to the ideal thermodynamic behaviour [1]. Since these interactions are normally dominated by hydrogen bonds, it is common to separate the compounds of a DES in either hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) [2]. General DES have been used as a greener option for gas capture, drug delivery, synthesis and catalysis, among other applications [3]. Considered as design solvents, the properties of DESs can be fine tuned to their many applications, however, the overwhelming number of possible HBAs and HBDs combinations makes the trial-and-error experimental approach highly time-consuming and cost-intensive. To overcome this, several modelling techniques must be developed and applied to perform a preliminary selection of the most promising HBA/HBD combinations.

In this work, the capability of two excess Gibbs energy models (UNIFAC [4] and COSMO-RS [5]) and an empirical group contribution methodology (Hou et al. [6]) to predict the eutectic point of several Type V DES is explored. Although both COSMO-RS and UNIFAC are predictive models that estimate the chemical potential of each component in a liquid mixture, COSMO-RS uses quantum chemistry descriptors of molecules while UNIFAC relies on group interaction parameters. These two excess Gibbs energy models allow the calculation of activity coefficients, which quantify the non-ideality of DES. However, the requirement of prior knowledge on the melting properties (temperature and enthalpy) of each pure component is a drawback. Empirical group contribution methodologies overcome this limitation by directly estimating the solid-liquid equilibria diagram, without calculating the activity coefficients, but fail to assess the non-ideality of the mixtures.

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## IONIC LIQUIDS AS ENTRAINERS FOR THE FRACTIONATION OF TERPENE MIXTURES

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Terpenes and their oxygenated derivatives, terpenoids, comprise a family of compounds ubiquitous in nature, found in several single and multicellular organisms, particularly in higher plants [1]. Among the large variety of natural terpenes, those presenting 10-carbon skeletons are called monoterpenes (hydrocarbons) or monoterpenoids (oxygenated), being the major constituents of plant essential oils (EOs) [2]. Besides their pleasant scents, monoterpenoids exhibit relevant biological activity, widely explored in the fragrance, cosmetic, pharmaceutical, and food industries [2,3]. The fractionation and purification of monoterpene and monoterpenoids from their natural matrices are commonly carried out by liquid-liquid extraction or vacuum distillation [4]. In this context, the appropriate selection of the solvent or entrainer plays a key role in designing and optimizing such separation processes.

In the present work, the potentialities of imidazolium and phosphonium ionic liquids (ILs) with different anions (e.g.,  $\text{Cl}^-$ ,  $\text{CH}_3\text{OO}^-$ ,  $\text{PF}_6^-$ ), as separation agents for the fractionation of terpene mixtures are examined. The activity coefficients at infinite dilution ( $\gamma_{13}^\infty$ ) of a large set of monoterpenes and monoterpenoids (including alcohols, ketones, and ethers) in the ILs were determined by inverse gas chromatography in the temperature range of (353.2–458.2) K. From the obtained  $\gamma_{13}^\infty$  data, valuable separation factors (i.e., selectivity, capacity, solvent performance index) were calculated for binary terpene mixtures widely found in EOs, including  $\alpha$ -pinene/ $\beta$ -pinene, limonene/linalool, limonene/carvone, eucalyptol/linalool, and camphor/borneol. Complementary, the predictive COSMO-RS thermodynamic model [5] was applied to describe the separation factors for the studied mixtures.

The results show that ILs with polar anions, such as  $\text{Cl}^-$  and  $\text{CH}_3\text{OO}^-$ , are potential options to fractionate hydrocarbon/alcohol mixtures, such as limonene/linalool. Moreover, the chloride-based ILs also present good performance indices to separate other mixtures with alcohols, such as eucalyptol/linalool and camphor/borneol. On the other hand, the imidazolium  $\text{PF}_6^-$ -based ILs deliver the best performances for fractionating hydrocarbon/ketones mixtures, such as limonene/carvone. Nevertheless, very poor separation factors were obtained for the  $\alpha$ -pinene/ $\beta$ -pinene with all the ILs studied so far, showing that the fractionation of this important mixture found in resins from *Pinus* species is still a challenge. COSMO-RS generally provides similar trends to those obtained from the experimental separation factors, though the model usually delivers underestimated values.

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## ELECTRICAL CONDUCTIVITY MEASURING SYSTEM BASED ON A MULTI-FREQUENCY IMPEDANCE METHODOLOGY

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Electrical conductivity measurements at a fixed frequency are intrinsically affected by the polarization. Although high frequencies diminish the impact of the polarization effect, it raises other problems associated with parasitic effects. Therefore, measuring impedance across a wide range of frequencies is the state-of-the-art procedure.

This work presents the development of a new system for the high precision measurement of electrical conductivity of ionic fluids. The measuring system is based on a Precision LCR meter (20 Hz -500 kHz) from Keysight (model E4980AL) and a commercial electrical conductivity cell, Metrohm (model MTO-6.0908.110) installed in small sample glass vessel (8 mL) as presented in Figure 1. A customized holder (PEEK) of the conductivity cell was designed to insure the vacuum and gas-tight of the sample container. The system is equipped with vacuum/N<sub>2</sub>(g) lines which allows the degassing and atmospheric isolation of the sample. A precision water thermostat bath is used for the temperature control. A dedicated software application was designed for the signal data acquisition and data analysis. The results are evaluated in terms of resistance, reactance, impedance, and phase angle as functions of frequency. The correction for the polarization effect is performed using several extrapolation procedures. The extrapolation is carried by selecting the appropriate frequency range, typically when the reactance contribution is close to its minimum.

The cell constant was experimentally determined by measuring standard aqueous 0.1 and 0.01 molal KCl solutions at different temperatures. The effects of the electrical potential level, N<sub>2</sub>(g) flow and cell immersion depth on the temperature and signal stability were evaluated for KCl solutions and ionic liquids. The accuracy of the apparatus was evaluated by measuring a series of reference ILs.



**Figure 1.** Representation of the measuring system and data treatment.

## IMPACT OF SILICATE ON THE SOLUBILITY AND AQUEOUS SPECIATION OF U(VI) IN ALKALINE TO HYPERALKALINE SYSTEMS

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Uranium is the main element in the nuclear fuel cycle and accordingly contributes with a very large inventory to nuclear waste. In the reducing conditions expected to develop in deep underground repositories, uranium will mostly prevail in the +IV oxidation state. However, in alkaline to hyperalkaline conditions, the stability field of U(VI) expands and the redox borderline between U(VI) and U(IV) is shifted to significantly reducing conditions, *i.e.*  $(pe + pH) \approx 2-3$ .

Silicon (in the form of silicates) is the most abundant element in the earth's crust and is a relevant component in mineral phases found in different host rocks (*e.g.* clay rock, granite / crystalline rock). Silicate is also one of the main components of cement, which is widely used for construction purposes and for the stabilization of the waste especially in repositories for low and intermediate level waste (L/ILW). The solubility limit imposed by amorphous silica, SiO<sub>2</sub>(am), limits the concentration of dissolved Si to  $\approx 2$  mM from acidic to weakly alkaline conditions. Above pH  $\approx 9$ , the subsequent formation of anionic species like SiO(OH)<sub>3</sub><sup>-</sup> and SiO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup> leads to a significant increase in the solubility of SiO<sub>2</sub>(am). The enhanced Si concentration together with the predominance of anionic silicate species may compete with U(VI) hydrolysis and accordingly may result in the formation of U(VI)-SiO<sub>4</sub> complexes potentially increasing solubility. In spite of the relevance of hyperalkaline systems in cementitious environments, most of the available studies investigating U(VI)-SiO<sub>4</sub> complexes have focused on acidic conditions. Consequently, the NEA-TDB reviews select only thermodynamic data for the complex UO<sub>2</sub>SiO(OH)<sub>3</sub><sup>+</sup>, which forms predominantly in acidic to near-neutral pH conditions [1,2]. The present study aims at obtaining a better description of the U(VI)-SiO<sub>4</sub> system in the alkaline to hyperalkaline conditions relevant in cementitious systems using the concepts of established solution thermodynamics. This study extends from dilute to intermediate ionic strength conditions, the latter being representative of Cretaceous argillites in Northern Germany.

All experiments are performed under Ar-atmosphere. The solubility of U(VI) is investigated from undersaturation conditions using a step-wise approach. In a first step, the solubility of synthetic Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) and commercial SiO<sub>2</sub>(am) is separately investigated in 0.1 and 1.0 M NaCl-NaOH solutions with  $8 \leq pH_m \leq 13$  (U) and  $8 \leq pH_m \leq 11.5$  (Si). Three experimental series are defined for the investigation of the U(VI)-SiO<sub>4</sub> interaction in 0.1 and 1.0 M NaCl-NaOH systems: (i) solubility of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) in the presence of SiO<sub>2</sub>(am), with  $8 \leq pH_m \leq 11.5$ ; (ii) solubility of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) in the presence [Si] = constant = 1.5 mM (*i.e.* below solubility limit of SiO<sub>2</sub>(am)) and  $8 \leq pH_m \leq 11.5$ ; (iii) solubility of Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) at pH<sub>m</sub> = constant = 11 and 12 with  $0.1 \text{ mM} \leq [Si] \leq 10 \text{ mM}$  (*i.e.* below solubility limit of SiO<sub>2</sub>(am) for both pH-values). The possible formation of polynuclear silicate species is evaluated using the molybdate method. The initial Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O(cr) and SiO<sub>2</sub>(am) materials and the solid phases of selected samples after completing the solubility experiments are characterized by XRD, SEM-EDS, chemical analysis and TG-DTA. Preliminary results of this on-going study will be presented in this contribution.

### Acknowledgements

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## ACTINIDE COMPLEXATION WITH ORGANIC LIGANDS IN THE WIPP: STATE-OF-THE-ART

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The Waste Isolation Pilot Plant (WIPP) is a transuranic waste repository in operation since 1999 and with predicted closure beyond 2050. It is located in a salt formation which leads to the presence of high ionic-strength environments. The emplaced waste contains high quantities of organic materials that includes organic chelating agents such as acetate, oxalate, citrate and ethylenediaminetetraacetic acid (EDTA); all of them are considered in Performance Assessments exercises [1,2].

The influence of organics on the actinide mobility in such a complex media depends on many factors, including the pH of the system and the role of major metal ions in the brines (such as calcium or magnesium). Although data for simple, binary actinide-organic complexes, can be found in the literature, data for ternary (or quaternary) complexes have only become available in recent years.

Major ions such as calcium or magnesium are expected to compete with the actinides for the complexation with different organics ligands, thus reducing the effective availability of those ligands to complex radionuclides. Some publications [3,4] suggest that the hydroxyl group in the citrate molecule may play a role in the actinide-citrate complexation under alkaline conditions, leading to the formation of An(III)-citrate or An(IV)-citrate species at pH above 8.5. Recent investigations on the EDTA system [5,6] also point out the formation of ternary or quaternary complexes. The identification of Ca-Pu(III)-(OH)-EDTA or Ca-Pu(IV)-(OH)-EDTA indicate that these type of complexes might also influence on the chemistry of both trivalent and tetravalent actinides under WIPP conditions

This work presents a state-of-the-art modeling study of the actinide-citrate and actinide-EDTA systems of relevance for the specific conditions of the WIPP system, taking into account the significant concentrations of sodium, calcium or magnesium in the brines and the complexity of dealing with highly charged species in saline media.

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## SOLUBILITY OF Nd(OH)<sub>3</sub> AM AND Nd(OH)<sub>3</sub> CR IN THE PRESENCE OF CITRATE AND EDTA

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The solubility of An(III), which pertains to Pu(III) and Am/Cm(III), in brine is important in terms of potential release of transuranium elements to the near-field environment as well as performance assessment (PA) models for the WIPP repository. Americium, although present in much smaller quantities (~ 336 kg is potentially WIPP-bound) primarily as Am-241, has a significant impact on release due to its higher activity during the earlier times of repository performance. Lanthanide analogues such as Nd<sup>3+</sup> possess physical and chemical characteristics that allow them to be used to examine the chemical behavior of trivalent actinides [1].

Organic compounds form strong complexes with metals and actinides. The organic compounds addressed in WIPP performance assessment (PA) include EDTA, oxalate, citrate, and acetate. Among them only citrate and EDTA are expected to form strong enough complexes to influence the speciation of actinides and potentially increase actinide concentrations under the expected conditions in the WIPP [2].

Actinide minerals also will have different crystallinities, and the choice of which mineral to represent in the PA will affect the degree of a release. For example, the Am solid phase expected at the WIPP, Am(OH)<sub>3</sub>, can either be amorphous (am) or crystalline (cr) and will dissolve to release soluble Am<sup>3+</sup>. In this work, EDTA and citrate effects on solubility for both amorphous and crystalline phases in brines as a function of two constant ionic strengths (0.1 M and 5 M NaCl) were investigated by an under-saturation approach. In the experiments, commercially available neodymium hydroxide was used as the solid phase. Experiments were equilibrated for over 100 days at an adjusted pC<sub>H+</sub> 7, 9 and 11. The results from the experiments show that Nd (III) solubility higher with crystalline phase and the presence of the organics. These data quantify the effects of WIPP-relevant concentrations of EDTA and Citrate on the solubility of An(III) to challenge the predictions of the WIPP actinide model and inform decisions and recommendations made in the upcoming recertification of the WIPP (CRA-2024).

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## THE PERSPECTIVE OF COOPERATIVE HYDROTROPY ON THE SOLUBILITY IN AQUEOUS SOLUTIONS OF CYRENE

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Dihydrolevoglucosenone, more commonly known as Cyrene, is a novel green solvent produced from cellulose in a two-step process [1-3]. Cyrene is an emerging biobased green solvent that has been shown to have the ability to increase the solubility of hydrophobic substances in water. Even though the water–Cyrene system is an attractive solvent, its applications are hampered by difficulties in the understanding of its solvation mechanism, caused by a delicate chemical equilibrium established between water and Cyrene. Considering that each of these individual species can have a different role (favorable or unfavorable) in the dissolution of a solute, an understanding of this chemical equilibrium is needed to develop the potential of water–Cyrene mixtures for novel applications. This work aims to rationalize the solvent capability of the water–Cyrene system and to establish the mechanisms of solvation through which hydrophobic solutes are dissolved in it. Using the cooperative model of hydrotrophy, it is shown that hydrotrophy is the solubilization mechanism of hydrophobic solutes in the water–Cyrene system, in most of its concentration range. Furthermore, the ketone form of Cyrene is revealed to be the principal hydrotrope of the system, with the diol form acting as a hydrotrope only at low Cyrene concentration. The parameters of the cooperative model, namely, the number of hydrotrope molecules aggregated around the solute and the maximum solubility increase, are shown to be correlated with the hydrophobicity of the solutes quantified by their octanol–water partition coefficient. This result not only supports recent studies on the mechanism of hydrotrophy but also adds a predictive ability to the cooperative model, which is then explored to successfully predict the solubility curves of phthalic acid, aspirin, gallic acid, and vanillin in water–Cyrene mixtures. As such, it is herein shown, for the first time, that a consistent study of solubility for a single hydrotrope, varying only the solutes, allows for the parametrization of the cooperative hydrotrophy model, which can then be used to predict the solubility of any hydrophobic solute in water mixtures of that hydrotrope. In other words, the procedure reported in this work can be perceived as a parametrization procedure for the cooperative hydrotrophy model.

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## EFFECT OF ACTIVATED CARBON PORE SIZE ON THE SORPTION OF AQUEOUS BENZENE SOLUTION

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Adequate availability of clean water has become a global issue due to constant economic and population growth. From an environmental standpoint, systematic removal of harmful contaminants from the environment has become a major concern. Removal of hazardous compounds like BTEX (benzene, toluene, ethylbenzene, and xylene) through adsorption is amongst the most effective strategies for their removal from the environment. BTEX are common industrial pollutants due their ubiquitous presence in petrochemical and solvent blends. Activated carbon is a popular adsorbent material on account of its large micro- and mesoporous volumes and high surface area-to-mass ratio [1]. Its use in removing BTEX compounds from water is an area of active research [2-4]. This contribution employed a factorial approach to whereby the pore size and benzene concentration were varied simultaneously to develop a response surface of the quantity of benzene adsorbed into the activated carbon at ambient temperature.

Atomistic Monte Carlo (MC) [5] molecular simulations in the grand canonical ensemble were used to simulate adsorption of benzene and water from a liquid reservoir into activated carbon pores. Three independent simulations making use of configurational bias [6] were used for each data point. The condensed-phase-optimized molecular potentials for atomistic simulation studies (COMPASS) [7] was used to describe all inter- and intramolecular interactions. Activated carbon was described in terms of the widely used slit pore model [8] wherein the pore size was varied from 1.0 to 2.2 nm. The liquid reservoir comprising benzene in water was maintained at 20 MPa to ensure it remained in a liquid state while not significantly affecting liquid phase equilibria [9], with the Soave-Redlich-Kwong cubic equation of state [10] being employed to compute the chemical potential of both water and benzene in the liquid state over a benzene range of  $10^{-8}$  to  $10^{-5}$  in mole fraction terms (corresponding to a concentration of about 4 to  $4 \times 10^3$   $\mu\text{g/L}$ ).

The results of this study indicate pathways to developing more effective carbonaceous adsorbents for remediating water contaminated with BTEX compounds. By targeting specific pore sizes, the efficacy of environmental clean-up operations employing activated carbon can be improved. The findings of this work help to address the wide challenges raised by pore size profiling.

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## ELECTROCHEMICAL PLATFORM BASED ON NANOSTRUCTURED CARBON ELECTRODE FOR DETERMINATION OF ANTI-INFLAMMATORY DRUGS (NSAID) IN WATER

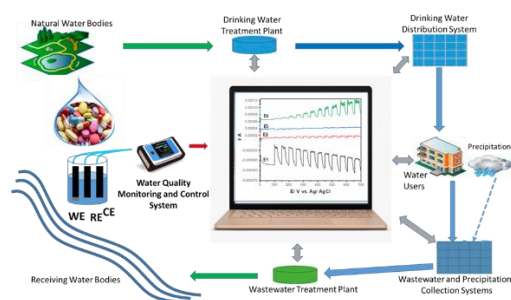
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Nowadays, a growing concern is given by the occurrence of the pharmaceuticals in the water bodies, which exhibits a negative impact on the human health. Many types of pharmaceuticals have been detected with various ranges of concentrations, which requires a continuous development of the advanced analytical method. Electroanalytical methods represent a very promising alternative of the advanced analytical methods due to their simplicity and high performances. An innovative and simple electrochemical approach is proposed in this study for the simultaneous/selective quantification of sodium diclofenac (DCF), naproxen (NPX) and ibuprofen (IBP) from anti-inflammatory drug class in surface water. The platform consists of coupling of amperometric (chronoamperometry and multiple-pulsed amperometry) techniques with graphene-carbon nanotubes (GR-CNT) paste electrode as the working electrode and 0.1 M sodium sulphate as the supporting electrolyte. The operating conditions of chronoamperometry and multiple-pulsed amperometry, selected based on the electrochemical behavior of the GR-CNT in the presence of the anti-inflammatory drugs studied by cyclic voltammetry technique, allowed the simultaneous and selective determination of the specific anti-inflammatory drug. This electrochemical platform was successfully applied in the analysis of pharmaceutical formulations and spiked water samples with the good recoveries. Using nanostructured carbon-based paste electrode, the current work proposes a simple, rapid and advanced alternative platform for sensing anti-inflammatory drugs in water, which can be further developed for a large spectrum of pharmaceuticals considering the simple modification of the paste electrode and different operating conditions/techniques including voltammetric ones, which presents great potential for practical application in screening the water quality in all types of the water bodies (Figure 1).



**Figure 1.** Amperometric responses of GR-CNT paste electrode in the presence of anti-inflammatory drug in water sample.

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## FATTY ACIDS-BASED EUTECTIC SOLVENTS LIQUID MEMBRANES FOR REMOVAL OF SODIUM DICLOFENAC FROM WATER

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Pharmaceuticals have a main role on health and life quality of humans and animals. Nevertheless 30% to 90% of all oral administrated drugs are excreted as active compounds [1], leading the worldwide occurrence of these active compounds and their metabolites in water sources, soils, and biota. As these compounds are designed to have a biological response to small dosages, they are an important threat to public health and ecosystem stability even at low concentration [1]. Additionally, their relative high stability is even more concerning, as the continuous ingestion of small doses can lead to accumulation since the degradation rate is slower than the up taking. On the other hand, conventional wastewater treatment plants (WWTP) are not designed to remove these compounds that enter the environment. Despite the report of diverse cases of life-threatening biological effects of these drugs on wildlife, about 88% of all pharmaceuticals do not have environmental toxicity data [2].

Although the use of eutectic solvents (ES) provides a cheap and efficient solution for the removal of APIs micropollutants [3-4], the toxicity of some of the used compounds and their leaching are drawbacks that need to be overcome to develop a fully sustainable system. The use of all natural compounds like sugars, amino acids, organic acids, choline and urea that exhibit low toxicity and have a high biocompatibility might be the answer for this problem.

In this work, ES based on fatty acids were impregnated on porous membranes by soaking and use to remove sodium diclofenac from water using UV-Vis spectroscopy to quantify the extraction efficiency of the membranes. Experimental parameters such as contact time, number of membranes, pH and initial concentration of pharmaceutical were optimized to achieve a remarkable extraction efficiency 97%. These membranes were re-used over 9 more cycles of extraction without decreasing the efficiency.



**Figure 1.** PVDF membranes impregnated with NADE.

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## **COSMO-RS PREDICTION AND EXPERIMENTAL PHYSICOCHEMICAL CHARACTERIZATIONS OF AQUEOUS SOLUTION OF SUPERBASE IONIC LIQUIDS**

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The increase in global population and well-being drives the growth in demand for textiles products. In parallel, the shortage of land for the expansion of cotton production and the environmental concerns related to cotton and petroleum-based textile materials, are changing the market scenario in favor of wood-based fibers [1]. However, despite the production of high-strength fibers, the solvent systems for today's man-made cellulose fibers are far from ideal since they are based on harmful chemicals. Superbase-based ionic liquids are potential candidates to produce high-performance cellulose fibers while presenting much easy spinnability and good recyclability, than the state-of-the-art ionic liquids [2]. Aiming to gather knowledge to recycle and purify superbase-ILs, in this work the aqueous solutions of two ILs, 7-methyl- 1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate ([mTBDH][OAc]) and 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-eniumacetate, ([mTBNH][OAc]) are characterized by measuring their viscosities, densities, water activities, solvatochromic parameters, solid liquid-equilibria (SLE) and vapor-liquid equilibria (VLE).

All mixtures have higher viscosity and density than water and the values decrease with increasing temperature. The excess molar volumes for all tested mixtures have values less than zero, that is, negative deviations from ideality across the entire composition range. About viscosity, the system [mTBNH][OAc] + water exhibits an atypical behavior, displaying a maximum value of viscosity of 301.52 mPa.s at  $x_{\text{water}} = 0.34$  (293.15 K). This behavior is probably related to the formation of an arrangement that favors the interaction between molecules, limiting mobility and causing increased viscosity.

Regarding the solvatochromic parameters, the data show a slight increase in the polarizability/dipolarity and hydrogen bond donor capability with increasing water concentration. The SLE data of pure ILs and their mixtures with water were determined using differential scanning calorimetry. The higher melting temperature of [mTBDH][OAc] (348.9±0.7 K) compared with [mTBNH][OAc] (287.5±1.8 K) may be explained by the fact that the [mTBNH][OAc] is a mixture of the two isomers. The COSMO-RS was used to predict the SLE and proved to describe the IL-rich mixtures significantly well and suggests that water presents a strong negative deviation to ideality [3]. The water activity coefficients show favorable interactions between ILs and water. In both systems investigated, the boiling temperature of water decreases with increasing water concentration, and negative deviations from ideality are observed, in agreement with the observed maxima for the densities and viscosities. The VLE phase diagram was predicted by using the COSMO-RS which describes the experimental data rather well showing better accuracy at lower pressures. This work presents a set of physicochemical properties that can be used to design the best process to recover and recycle hydrophilic ILs.

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## A THERMOCHEMICAL CONTRIBUTION TO THE STUDY OF THE CONVERSION OF BIOMASS PLATFORM MOLECULES

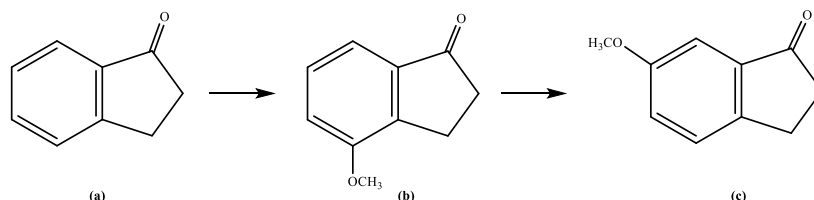
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The production of advanced biofuels by pyrolysis bio-oil upgrading is a topic that has been receiving much attention from both industry and academia in recent years [1,2]. For bio-oil upgrading several processes are involved, namely ketonization and hydrodeoxygenation. To overcome the industrial challenges into the reaction mechanisms leading to advanced biofuels it is require a significant input of accurate thermodynamic data. In this context, our research group is involved in a broad experimental and theoretical study over key polycyclic compounds, namely indanones [3,4].

The present work reports an experimental and computational study of thermodynamic properties of 4-methoxy-1-indanone. The standard molar enthalpy of formation of the compound, in the gaseous phase, at  $T = 298.15$  K, has been derived from the corresponding standard molar energy of combustion and standard molar enthalpy of sublimation, obtained by static-bomb combustion calorimetry and high-temperature Calvet microcalorimetry, respectively. High-level ab initio calculations were also performed to obtain the gas-phase standard molar enthalpy of formation of this compound. Some energetic and structural correlations will be analysed by comparison of the results herein with the ones for related indanone derivatives [4,5].



**Figure 1.** Structural features of 1-indanone (a), 4-methoxy-1-indanone (b) and 6-methoxy-1-indanone (c).

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## **PREDICTION MODELS FOR AROMATIC/ALIPHATIC AND OLEFINIC/ALIPHATIC SEPARATION IN IONIC LIQUIDS**

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Solvents such hexane and heptane are obtained mainly through extraction and fractional distillation operations of refined aliphatic fractions obtained from crude oil. These solvents in turn are used in food, pharmaceutical and polymer industries. With increasing demands and restrictions for higher purity from these markets, it stands crucial for refining companies to invest in processes for the reduction of aromatic and olefinic impurities and thus, remain competitive.

It is then relevant to find a novel and efficient method that can tackle this purification. In this work, the use of Ionic Liquids (ILs) is proposed as extraction solvents that can both remove aromatics and olefins. ILs consist of salts composed of a large organic cation and a smaller organic/inorganic anion that are liquid at temperatures close to room temperature and due to the large number of possible cations and anions combinations, they can be fine-tuned towards a specific application [1]. Yet, due to the large number of available ILs it stands unfeasible to fully study them all, and for this reason, the predictive thermodynamic model COSMO-RS was employed, and validated, to assess ILs with the highest potential for the intended separation, based on partition coefficients and thermodynamic parameters of the species.

With the available data a model correlating the partition coefficients and the IL energies and molecular properties was developed.

From a simple linear model to a more robust multivariable machine learning algorithms were evaluated. While the linear model failed to fit the data from the screening, the machine learning models present good results, having low values for the errors and having a coefficient of determination that reach 90%.

The best results were obtained for ensemble methods, Random Forest and Gradient Boosting, creating a model that can effectively predict the COSMO-RS behavior and allowed to infer the importance of each thermodynamic parameter in the model and system behavior.

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## METHYLIMIDAZOLIUM-BASED IONIC LIQUIDS AS SEPARATION AGENTS FOR FUEL PROCESSING

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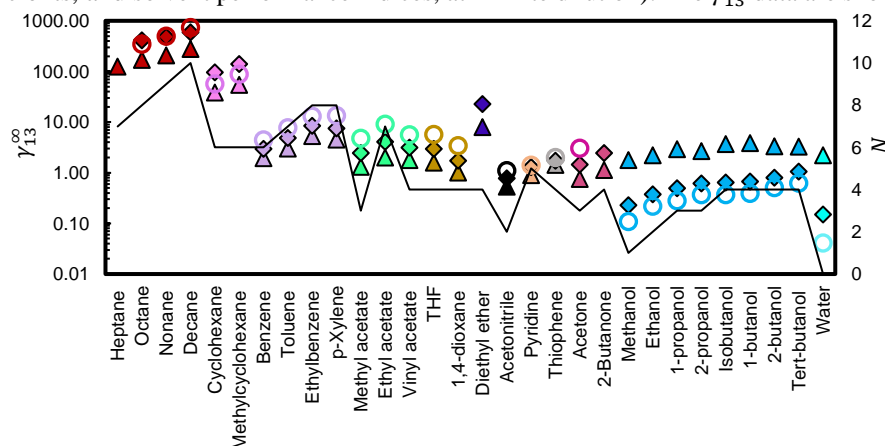
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The desulfurization and denitrification of fuels, the removal of aromatic hydrocarbons from aliphatics, and the separation of azeotropic mixtures are important separations problems in the chemical industry. In this work, the potentiality of using two ionic liquids (IL), [C<sub>4</sub>mim][PF<sub>6</sub>] (1-butyl-3-methylimidazolium hexafluorophosphate) and [C<sub>4</sub>mim]Cl (1-butyl-3-methylimidazolium chloride), as separation agents was investigated. Therefore, the activity coefficients at infinite dilution  $\gamma_{13}^{\infty}$  of 29 organic solutes (alkanes, cycloalkanes, ketones, ethers, aromatic hydrocarbons, esters, alcohols) and water were measured, by inverse gas chromatography, in the temperature range (333.15–383.15) K, in pure [C<sub>4</sub>mim][PF<sub>6</sub>] and in the equimolar mixture of [C<sub>4</sub>mim][PF<sub>6</sub>] and [C<sub>4</sub>mim]Cl. Similar data in pure [C<sub>4</sub>mim]Cl are already available in the literature [1]. The designer character of IL was explored by selecting two IL with a common cation, but different anions, to see the effect of changing the concentration of the anion on the activity coefficients of the solutes and derived properties (excess partial molar properties, selectivities, capacities, gas-liquid partition coefficients, and solvent performance indices, at infinite dilution). The  $\gamma_{13}^{\infty}$  data are shown in Figure 1.



**Figure 1.** Infinite dilution activity coefficients ( $\gamma_{13}^{\infty}$ ) of organic solutes, and water at 353.2 K: measured in this work in [C<sub>4</sub>mim][PF<sub>6</sub>] ( $\Delta$ ) and [C<sub>4</sub>mim][PF<sub>6</sub>]/[C<sub>4</sub>mim]Cl equimolar mixture ( $\diamond$ ); in [C<sub>4</sub>mim]Cl ( $\circ$ ) [1].

In general, the capacities of the nonpolar and polar aprotic solutes are higher in the more apolar [C<sub>4</sub>mim][PF<sub>6</sub>] and the lowest in [C<sub>4</sub>mim]Cl, with intermediate values for the equimolar IL mixture. For alcohols and water, the opposite trend was observed. The results obtained show that the studied IL are among the solvents having the best performance indices, when compared to other methylimidazolium-based IL, for the separation of several model mixtures (octane/benzene, cyclohexane/benzene, octane/thiophene, and octane/pyridine), providing important insights on the use of alternative solvents for the removal of aromatics from aliphatic hydrocarbons and the removal of contaminants from fuels.

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## **HYDROTROPIC EFFECT IN THE PRESENCE OF ELECTROLYTES: COMPETITION BETWEEN SOLUTE SALTING-OUT AND SALT-INDUCED HYDROTROPE AGGREGATION**

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Water solubility enhancement is a long-standing challenge in a multitude of chemistry-related fields [1]. Hydrotrophy is a simple and efficient method to improve the solubility of hydrophobic molecules in aqueous media. However, the mechanism behind this phenomenon has been controversial, and is not yet fully understood. There is yet insufficient knowledge in both the hydrotropic properties of ILs as well as how the salting of hydrotropic solutions of ILs influences the solubility of hydrophobic compounds. The study of this subject could translate in a better understanding of the hydrotropic solubilization mechanism, of the IL behaviour in heavily electrostatic charged environments, and in the design of novel applications for ILs as solvent media and hydrotropes. Hence, we use here different approaches to further the understanding of the characteristics of hydrotrope-solute interactions and to establish the effect of inorganic cations on the behaviour of hydrotropic solutions doped with their chloride salts. Vanillin, a phenolic compound with natural antioxidant and anti-inflammatory properties was chosen as the solute [2-4]. The IL 1-butyl-3-methylimidazolium chloride ([C4mim]Cl) was selected as the hydrotrope as its properties are extensively characterised and is a known hydrotrope for vanillin [5]. Matching the IL anion with the anion of the chosen salts to dope IL solutions, allowed to focus on the study of the effect of the salt cations on hydrotrophy. Thus, herein we investigate the influence of the addition of different chloride salts on the solubility of vanillin in aqueous solutions of [C4mim]Cl and characterize the local environment of the solute and hydrotrope both with and without the presence of additional salts. The results obtained show that the addition of chloride salts hinders vanillin solubility by promoting the hydrotrope aggregation at a nuanced rate but generally dependent on the added salt cation valence. Hydrophobic interactions were found to be central to the aggregation of the hydrotrope around the solute, which seems to drive hydrotrophy. Hydrotrope-solute interactions presented a degree of site-specificity that was lost with salt addition. Pre-existing hydrotrope aggregation prior to solute addition is shown to be detrimental to the hydrotropic effect, seemingly confirming solute-induced clustering of the hydrotrope to be the predominant mechanism of hydrotrophy.

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## SOLUBILITIES OF AMINO ACIDS IN AQUEOUS SOLUTIONS OF SALTS COMPOSED OF DIVALENT CATIONS

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Knowledge of the solubility of proteins in aqueous electrolyte solutions is central to understanding biochemical processes and controlling solution behavior in many scientific and industrial applications [1,2]. Owing to the complexity of proteins [3,4], to simplify the difficulty of obtaining reliable and consistent quantitative solubility data [5], amino acids (AA) and small peptides can be used as model compounds. Although many studies have been published, these are mainly concerned with systems containing monovalent ions, and a lack of data on the solubility of amino acids in aqueous electrolyte solutions containing divalent cations is still on demand.

In this work, the solubility measurement of glycine, L-leucine, L-phenylalanine, and L-aspartic acid in aqueous solutions of  $MgCl_2$ ,  $Mg(NO_3)_2$ ,  $CaCl_2$ , or  $Ca(NO_3)_2$  was carried out up to a salt molality of 2 mol/kg at 298.2 K. The isothermal analytical method was used combined with the refractive index measurements for composition analysis guaranteeing good accuracy. To check the amino acids speciation in the saturated solutions, besides solubility, the pH of the saturated solutions was also measured at 298.2 K. The pure solid compounds as received from the supplier as well as the solids settled in equilibrium with the saturated solution, after vacuum filtration and drying, were analyzed by powder and single crystal X-ray diffraction, to examine any changes in the crystallographic form of the amino acids, that might impact the salting effects.

All salts induced a salting-in effect with a higher magnitude for those containing the  $Ca^{2+}$  cation. The nitrate anions also showed stronger binding with the AAs, thus increasing their relative solubility more than the chloride anions. In particular, calcium nitrate induces an increase in the amino acid solubility from 2.4 (glycine) to 4.6 fold (L-aspartic acid) compared to the corresponding value in water. Amino acid solubility data in aqueous  $MgCl_2$  and  $CaCl_2$  solutions collected from the open literature were combined with that from this work, allowing us to analyze the relations between the amino acid structure and the salting-in magnitude.

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## SOLID-LIQUID EQUILIBRIA OF ORGANIC ACIDS IN BIO-BASED SOLVENTS

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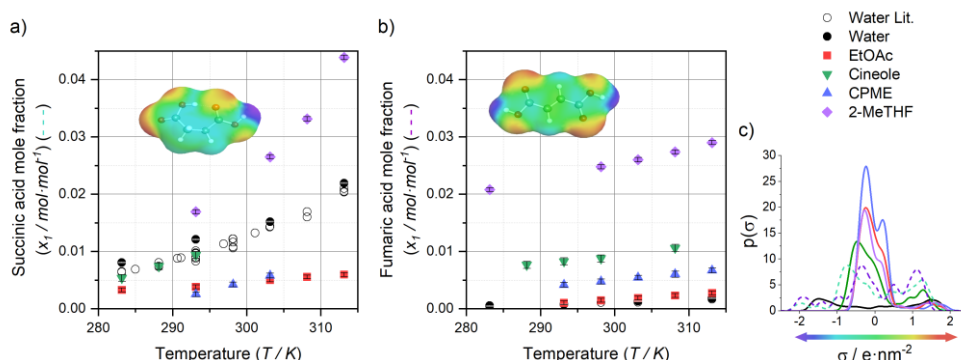
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Succinic acid and fumaric acid have been acknowledged as strategic chemical platforms in the biorefinery industry [1]. To improve the sustainability of their production, alternative green solvents have been proposed and evaluated for liquid-liquid extraction from aqueous fermentation broths. However, fundamental physicochemical properties, such as the solute solubility in the new solvent extraction media, are needed to promote the development of green production routes. In this work, the solid-liquid equilibria of binary systems composed of [organic acid + bio-based solvent] were measured and modelled within a temperature range of [283–313] K. Ethyl acetate, 1,8-cineole, cyclopentyl methyl ether, and 2-methyl tetrahydrofuran were selected as bio-based solvents due to their good extraction performance in the recovery of such organic acids [2]. The measurements were carried out using a gravimetric method and the results (Figure 1.a and Figure 1.b) were correlated with the van't Hoff equation, the modified Apelblat equation, and the Buchowski–Ksiazczak  $\lambda h$  model. Thermodynamic phase equilibria and molecular interactions were modelled from the screening charge density (Figure 1.c) on the molecular surface using COSMO-RS method. Computational results show that the dissolution phenomenon is driven by attractive hydrogen-bonding interactions, which support the experimental solubility trends, both increasing with temperature for all systems.



**Figure 1.** Molecular surface charge density ( $\sigma$ ), experimental, and literature saturated mole fraction organic acids in water and bio-based solvents at temperatures ranging [283 – 313] K: a) Succinic acid; b) Fumaric acid. c)  $\sigma$  – profiles of the bio-based solvents and organic acids studied in this work.

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## SOLVENT SCREENING FOR THE SEPARATION OF NATURAL PHENOLIC COMPOUNDS USING TWO COMPUTATIONAL MODELS

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Phenolic compounds are secondary products from natural metabolic processes that present remarkable antioxidant activity with high-value applications in the pharmaceutical, food, chemical and cosmetics industries [1]. Their isolation and purification can be achieved using Centrifugal Partition Chromatography (CPC), an all-liquid separation technique based on the partition of a solute between two immiscible phases, a stationary and a mobile phase [2]. CPC has as advantages its simplicity, low cost, flexibility and facility to scale up to industrial levels [3]. However, choosing the most appropriate solvent system in CPC is a complex, time-consuming task that requires several partition and solubility data. Computational modelling strategies can be used as a preliminary screening of the solvent systems that provides a suitable partition of the target solutes.

In this work, quercetin, vanillin, ferulic acid and hesperetin were chosen as representative of phenolic compounds that can be found in natural matrices. First, the Conductor-like Screening Model for Real Solvents (COSMO-RS) was applied to estimate the partition coefficients  $K$  (31 data points for all solutes) collected from the literature. An average root mean-square deviation (RMSD) in  $\log(K)$  was obtained of 0.47.

The Abraham solvation model was also used in the prediction of solubility and partition coefficient values. As a first approach, the solute descriptors available in the literature were applied. For ferulic acid, quercetin and hesperetin, it was necessary to re-estimate new solute descriptors, using in the correlation step, a dataset composed by 23 solubility and 12 partition coefficients  $K$  values. An average RMSD of 0.34 and 0.43, in log values, was obtained for the solubility and partition data, respectively. The predictions for all solutes were made for the remaining partition coefficients data, resulting in average RMSD of 0.40.

The COSMO-RS is a fully predictive model that presented a very satisfactory quantitative description of the partition of the target solutes in biphasic systems of different polarity. The Abraham solvation model was also a reliable solvent screening tool, as long as a few sets of solubility and partition data are available to estimate the descriptors. Ongoing work is being carried out to extend these experimental and modelling studies to the solubility of the target phenolic compounds in relevant solvents (e.g. alkanediols and glycerol) in the pharmaceutical and cosmetic areas.

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## ZWITTERIONIC IONIC LIQUIDS AS HYDROTROPES: THE INFLUENCE OF CATIONIC ALKYL CHAINS AND SPACER SIZE ON BIOACTIVE COMPOUNDS SOLUBILITY

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The poor solubility of drug molecules in water is one of the biggest limitations that pharmaceutical industry faces when formulating new pharmaceutical products. The development of new strategies to enhance the solubility of drugs in water has been increasing. Hydrotropy, a molecular phenomenon that consists in the use of hydrotropes to increase the solubility of poorly soluble solutes in aqueous solutions [1], has been widely studied. Still, despite the numerous studies regarding this phenomenon, its mechanism of action is not fully understood [2], and hydrotropes selection is still based on a trial and error approach.

In this work, aqueous solutions of zwitterionic compounds derived from ionic liquids (ZILs) – compounds where the ion pair is covalently tethered – were prepared to investigate their hydrotropic effect and the solubility enhancement of poorly water-soluble compounds. ZILs present chemical properties of high interest and are already widely used in the pharmaceutical industry. Thus, the solubility of two bioactive molecules – vanillin and syringic acid – and one pharmaceutical drug – ibuprofen – in aqueous solutions of sulfobetaine-based ZILs, was determined. The solubility curves of the solutes were determined according to the isothermal shake-flask method [3]. The effect of ZILs cation alkyl side chain length and spacer size between the cationic and anionic groups, were evaluated.

The obtained results demonstrated that ZILs are potential hydrotropes for bioactive solutes and pharmaceutical molecules. These compounds were able to induce considerable increments in water solubility of the studied solutes, when compared to the solubility in pure water. These findings also allowed a better comprehension of the mechanisms behind the hydrotropic effect, that depends not only on the hydrotrope but also on the solute: (1) the hydrotropic effect depends on the alkyl side chain length of ZILs; (2) the influence of the ZILs spacer is not clear and its effect depends on the studied solute; (3) higher hydrotropic effect is observed in solutes with higher octanol-water partition coefficients ( $K_{ow}$ ). Remarkably, ibuprofen, the studied solute with the lowest water solubility, presented the highest solubility enhancement (from mg/L to g/L), demonstrating how the hydrotropic effect induced by ZILs can be of high relevance in the pharmaceutical industry.

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## SOLUBILITY OF H<sub>2</sub>S IN ETHYLENE GLYCOL - BASED SOLVENTS

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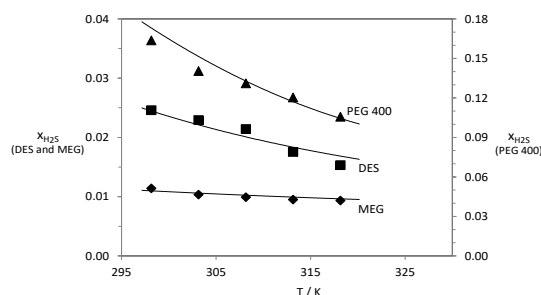
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### Introduction

The physical solubility of H<sub>2</sub>S is a key parameter needed to model the absorption or stripping of the gas in solvents. However, only a few experimental solubility data of H<sub>2</sub>S in solvents, particularly solvents with low vapor pressure and toxicity are found in literature [1,2]. Recently we have determined experimental solubility of H<sub>2</sub>S in ammonium-based ionic liquids [3]. In the present work the experimental data of H<sub>2</sub>S solubility in Ethylene Glycol - Based Solvents (ethylene glycol (MEG), polyethylene glycol (PEG400), and Deep Eutectic Solvents, (choline chloride + MEG in molar ratio 1:2, DES)) were determined using a volumetric method in the temperature range 298 K to 318 K at atmospheric pressure [4]. The data gathered is modelled with the Cubic Plus Association Equation of State (CPA EoS), considering the association schemes four-sites (4C) for hydrogen sulfide and two-sites (2B) for the solvents (MEG, PEG400 and DES).

### Results and Discussion

The results of Figure 1 show that the solubilities for H<sub>2</sub>S increases in the order ethylene MEG < DES < PEG400. The behaviour of the H<sub>2</sub>S solubilities in these solvents indicated that, for MEG and PEG400, the solubilities increase with the size of the solvent which can be related with an higher free volume of the PEG400 compared to the ethylene glycol. The addition of choline chloride to the ethylene glycol, to form a DES, increase the solubility of the H<sub>2</sub>S.



**Figure 1.** Solubilities,  $x_{H_2S}$  of H<sub>2</sub>S in MEG, PEG400 and Deep Eutectic Solvents (DES) as function of temperature and at atmospheric pressure.

### Conclusions

The solubilities of the H<sub>2</sub>S in ethylene glycol, polyethylene glycol 400, and Deep Eutectic Solvents, (choline chloride + ethylene glycol in molar ratio 1:2), have been determined in the temperature range 298 K to 318 K, at atmospheric pressure. DES, considered as designer and sustainable solvents, can play an important role in the absorption of H<sub>2</sub>S. The CPA EoS model allows a satisfactory description of the solubilities through the ranges of temperature and pressure selected in this work with low average deviations.

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## AQUEOUS BIPHASIC SYSTEM FOR SEPARATION OF SUPER BASE IONIC LIQUIDS

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There is a growing global tendency towards environmental awareness and social concern to develop green and sustainable approaches throughout the textile industry's supply chain. Cellulose has unique structural characteristics, being the most valuable renewable resource available to the textile chain. However, despite the production of high-performance fibers, the solvent systems for artificial cellulose fibers and LYOCCELL viscose fibers are far from ideal once they are based on harmful chemicals [1].

The use of green solvents, as ionic liquids (IL), is one of the sustainable alternatives to producing these fibers. Among the various ILs reported in the literature with the potential to dissolve cellulose, only a small portion has the adequate characteristics to produce regenerated cellulose fibers. 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]) has been identified as a key structure enabling the production of high-performance fibers through the IONCELL-F process. Recently 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-eniumacetate ([mTBNH][OAc]) has also been identified as a promising solvent [2].

Typically, the spinning bath solution undergoes several purification steps to remove particulates and precipitates after fibre spinning. From then onwards, the water is removed to restore IL's solvating power. There are several separation methods available for the removal of water from ILs, such as adsorption, thermal evaporation, membrane processes, aqueous biphasic extraction, and others, however, only a few of these methods are economically viable and can be adopted in the Ioncell process.

The aqueous biphasic extraction (ABE) is based on the formation of aqueous biphasic systems (ABS). The ABS can be formed when two immiscible phases (both water-soluble), for example, polymer/polymer, polymer/salt, salt/salt or salt/alcohol, are brought into contact with each other above the critical concentration at a specific temperature. Thus, in this work, the recovery and purification of ILs from the spinning bath were investigated using aqueous biphasic extraction. The liquid-liquid equilibrium (LLE) data (binodal and tie-lines) were obtained applying a gravimetric method proposed by Merchuk and co-worker [3].

Potassium carbonate ( $K_2CO_3$ ), three alcohols (ethanol, 1-propanol, *tert*-butanol) and 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate ([mTBNH][OAc]) were used. The effects of the alcohols on phase separation were studied. For all aqueous biphasic systems, the increase in temperature promoted a decrease in the slope of tie-lines and did not present a large effect on the binodal curves (biphasic region). The use of  $K_2CO_3$  + 1-propanol system allowed concentrating the IL present in the stirring bath ( $x_{IL} = 20.0$  wt%) obtaining an IL-rich-phase ( $x_{IL} = 45.0$  wt%) and with a small amount of water ( $x_{water} = 7.8$  wt%). The results demonstrate that the ABE separation method can be considered one of the alternative ways to remove water. Still, it also adds another challenge to the recycling process in separating the kosmotropic salt from IL.

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## ENHANCING PHARMACEUTICAL MEDIA SOLUBILITY AND STABILITY BY THERMODYNAMIC MODELING

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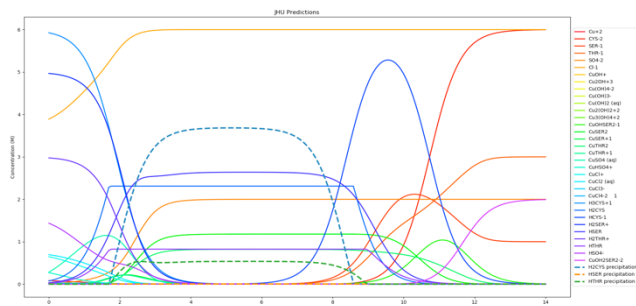
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**Project Description:** It is of vital importance for the pharmaceutical company to understand media solubilities with highly concentrated nutrients and electrolytes. Previously, we had built computational models to predict media component solubility limits from thermodynamic calculations, including activity coefficients. Here, we expanded and improved the thermodynamic model to include long-range ionic interaction to allow calculations of electrolyte and amino acid(AA)-electrolyte complexation solubilities. Using a modified version and expanded databases of a previous model, we added ionic effect to more faithfully characterize the thermodynamic environment of pharmaceutical media. Visual MINTEQ can predict media formulation and trace metal complexation, but it has a limited ionic strength prediction range and the code cannot be incorporated in our UNIFAC thermodynamic model [1]. We incorporated a Visual MINTEQ-like model with our UNIFAC model in a format that can be hosted on the cloud or used in-house. The newly-fitted ionic strength equation would allow calculations to approach nearly 30M, where the extended Debye-Hückel theory used in MINTEQ has a limit of 0.1M. In order to design components that stabilize media formulations, increase AA solubilities and prevent precipitation, we incorporated chemical complexation and speciation equilibrium into our current thermodynamic model, which resulted in a more robust platform to help understand the roles of diverse components on media solubility and complexation.

**Objectives and Methodologies:** 1) Expand the scope and breadth of the short-range UNIFAC solubility model and extend its impact on electrolytes by including the critical ionic interaction effects. 2) Rewrite Visual MINTEQ program so it can become part of a fully integrated thermodynamic software suite. 3) Fitting literature data to regress parameter databases to expand prediction capabilities. 4) Experimentally measure solubilities for compounds of interest using HPLC to validate predictions.

**Results and Interpretation:**



**Figure 1.** Solubility predictions of UNIFAC-chemical complexation model in pharmaceutical media.

The fully integrated software is an extensive effort to predict pharmaceutical media solubilities. The successful prediction of high concentration AAs, electrolytes and formed complexation solubilities would highly benefit process intensification. Precipitation prediction would improve media stability design process.

**Conclusions:** Fully integrated GUI and databases for predicting solubilities and equilibria for both AAs and ionic species in a single software package. This will lead to identifications of novel additives for increasing stability of media formulation and predict precipitation.

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## **SOLUBILITY, LIQUID-LIQUID, VAPOR-LIQUID PHASE EQUILIBRIA AND CRITICAL STATES IN THE SYSTEM WITH BUTYL ACETATE SYNTHESIS REACTION AT 323.15 K**

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Butyl acetate is an important chemical compound which is used as a solvent in various technological processes, e.g. in the production of paints and varnishes. Moreover, quite low freezing point and high value of flash point make butyl acetate promising as an additive to biodiesel fuel enhancing its properties [1]. The common way for the butyl acetate production is esterification reaction but the design of this one needs the information on thermodynamic properties and phase equilibria. First of all, the presence of the heterogeneous area in case of the quaternary reacting mixture acetic acid – butyl alcohol – butyl acetate – water causes the necessity of studying relative disposition of splitting area, chemical equilibrium surface and critical states of liquid-liquid equilibrium (LLE). At the same time, the data about thermodynamic properties and phase equilibria for this quaternary system are fairly incomplete.

In this report we present new results of the study of LLE, vapor-liquid equilibria (VLE) and critical states for the reactive system acetic acid – butyl alcohol – butyl acetate – water at 323.15 K.

The compositions of the coexisting phases for the quaternary system at 323.15 K were determined via gas chromatography. Isothermal titration was applied for investigating of the binodal curve near the critical point. According to the “cloud point” technique, titration end point was fixed visually by the appearance of the second phase. Evaluation of the critical point composition was performed by the specific opalescence in the small area near the critical point. LLE compositions were compared with the data obtained earlier for 308.15 K and 318.15 K [2,3]. A good correlation between all these data was observed.

VLE at 323.15 K was studied for some compositions along the stoichiometric line of the esterification reaction passing through the experimental critical curve using standard equipment for determining VLE - an ebulliometer with the possibility of sampling the vapor phase. Compositions of the coexisting liquid and vapor phases were determined by gas chromatography. These data were used for the estimation of chemical potentials values and the change of chemical affinity during reaction.

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