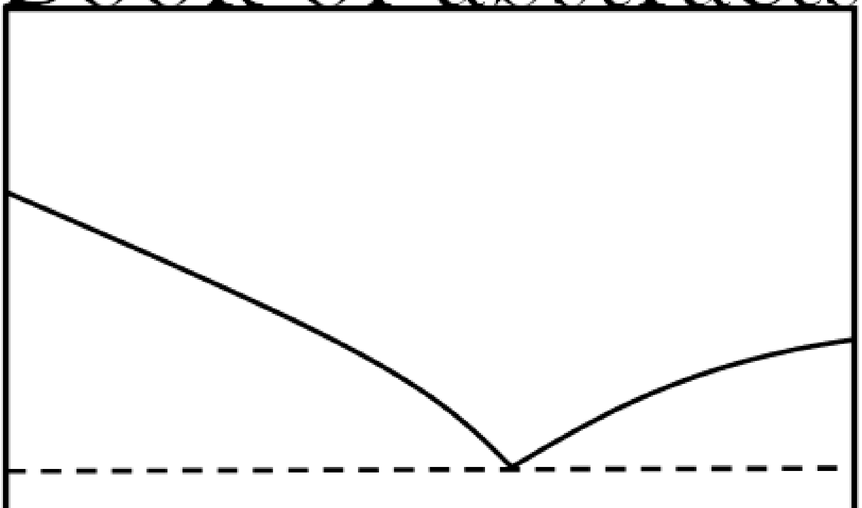
3rd International Meeting on Deep Eutectic Systems

19-22
JUNE
2023
LISBON

Book of abstracts



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Deep Eutectic Systems

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The Organizing Committee of the 3rd International Meeting on Deep Eutectic Systems is very pleased to welcome you back to Lisbon. The Meeting will be held in Colégio Almada Negreiros of Universidade Nova de Lisboa, in the centre of Lisbon, between the 19-22th of June 2023.

Following a second meeting, which was held online, we are happy to meet you all again in person. It is our expectation that this 3rd meeting continues to pave the series of fruitful meetings, which based on previous editions demonstrates the need to have a forum where experts from around the globe gather to discuss the latest developments in deep eutectic systems. From the bases of fundamental knowledge to the latest application developments, it is interesting to see how broad the spectrum of submitted contributions goes.

The organization committee aims to offer a unique opportunity, in an informal environment, to learn on the newest developments and discoveries in this area. This meeting is also a place for sharing knowledge, brainstorm new ideas and where the participants interact, network and build new bridges towards successful collaborations.

We hope that the 3rd IMDES will motivate and inspire you to pursue your work, and we could not finish without thanking you for the opportunity to organize such an interesting and high scientific level meeting.

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Advanced Research on Natural Deep Eutectic Solvents

Guest Editors
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Deadline
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Deadline
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Special Issue

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Program

	19th June	20th June		21st June		22nd June	
9h00		Opening Session		PL2- Samir Mitragotri		PL3- Gabriela Guillena	
9h15		PL1- Sona Raeissi					
9h30							
9h45				OC18- Bagović	Pharma	OC36- Calogera	Extraction
10h00		OC1- Triollo	Fundament.	OC19- Paul		OC37- Cea Klapp	
10h15		OC2- Morineau		OC20- Lomba		OC38- Amusa	
10h30		OC3- van den Bruinhorst		OC21-Oliveira		OC39- Canales	
10h45		Coffee Break/ Poster Session		Coffee Break/ Poster Session		Coffee Break/ Poster Session	
11h00							
11h15		KN1- Leslie Boudesocque-Delaye	Extraction	KN3- Lorenzo Guazzelli	Biotech	KN5- Hemant Kayshap	Fundamentals
11h30							
11h45		OC4- Viñas-Ospino		OC22- Álvarez		OC40- Haghbakhsh	
12h00		OC5- Damjanović		OC23- Gajardo-Parra		OC41- Alhadid	
12h15		OC6- Mezetta		OC24- Craveiro		Closing Session (sponsored by Quinta do Monte Alegre)	
12h30		OC7- Ardeza		OC25- Freitas			
12h45		Lunch		OC26-Lee			
13h00				Lunch			
13h15							
13h30							
13h45							
14h00							
14h15		KN2- Anastasia Detsi	Materials	KN4- Franca Castiglioni	Pharma		
14h30							
14h45		OC8- Teixeira		OC27- Gameiro			
15h00		OC9- Di Pietro		OC28- Joules			
15h15		OC10- Juneja		OC29- Rocha	Extraction		
15h30		OC11- Daskalopoulou		OC30- Yagmur			
15h45		OC12- Edler		OC31- Chagnolleau			
16h00		Coffee Break/ Poster Session 1		Coffee Break/ Poster Session 2			
16h15							
16h30		OC13-Cea-Klapp	Fundamentals	OC32-Vigier	Biotech		
16h45		OC14- Shayestehpour		OC33- Anugwom			
17h00		OC15- Khokhar		OC34- Kovács			
17h15		OC16- Russina		OC35-Bathke			
17h30		OC17- Alencar					
17h45							
18h00	Welcome Cocktail/ Registration	Team Building					
20h00				Gala Dinner			

Registration, Welcome Cocktail and Lunches

Main atrium inside Colégio Almada Negreiros (Level 1)

Team Building activity

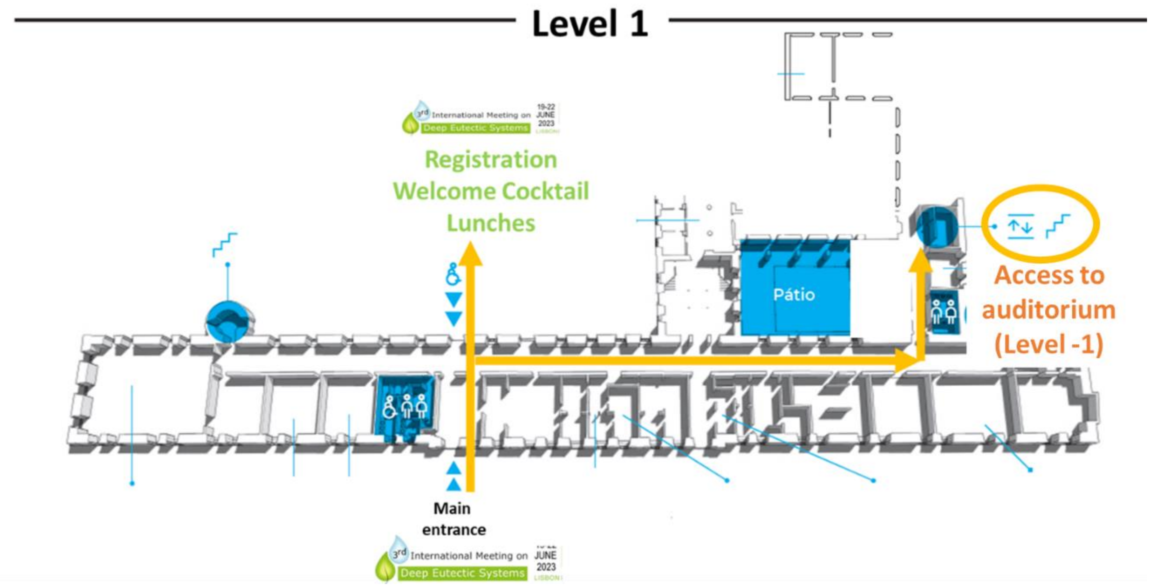
Main Gardens at the entrance of the Colégio Almada Negreiros

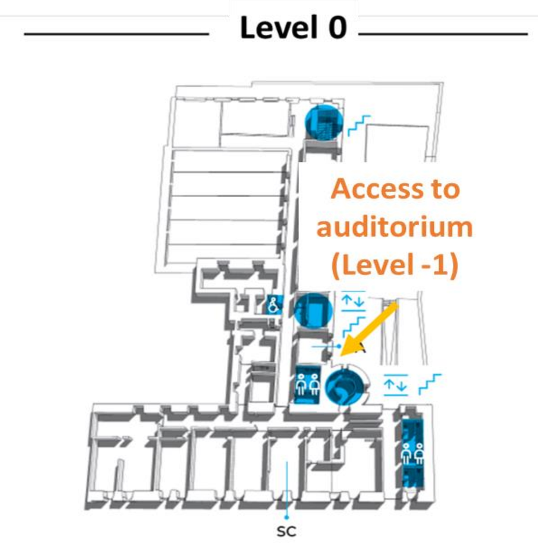
Conference Auditorium, Poster Sessions and Coffee Breaks

Level -1 (accessible by lift or stairs)

Transportation to and from Gala Dinner

Meeting place at the main entrance of Universidade NOVA de Lisboa (Reitoria side)





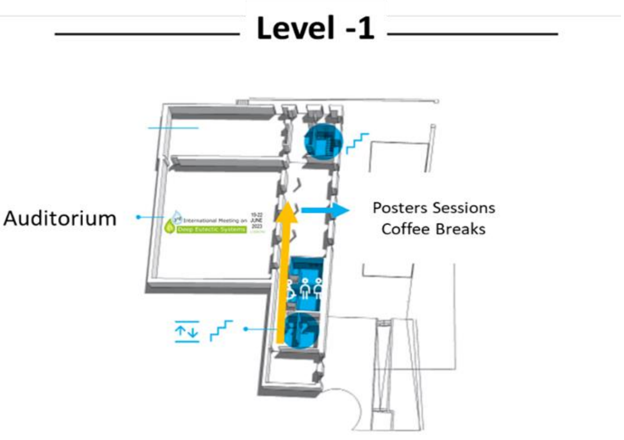


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Table of contents

Poster Session 1 (20th June)

Poster Session 2 (21st June)

PLENARY LECTURES

PL1. Don't Shy Away from Thermodynamics: DES Physical Property Calculations by the Group Contribution Approach

S. Raeissi
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Keywords: physical property, prediction, group contribution, density, viscosity, melting point

The general viewpoint of students and scholars is that thermodynamics is intimidatingly difficult. This is even evidenced by academic articles targeting this exact dilemma, for example: *Difficulties of Students from the Faculty of Science with Regard to Understanding the Concepts of Chemical Thermodynamics* [doi.org/10.1016/j.sbspro.2014.01.223]. Here, effort is made to show that through a specific lens, some of the apparently bewildering and endless pathways of thermodynamics can converge together through a single perspective; that all macroscopic properties are functions of the microscopic structure and its interactions. Understanding this common basis can greatly help in comprehending the many approaches to phase equilibria and physical property estimations. This is because the human brain is far better at understanding complex issues if they are systematically categorized and their common basics are revealed.

With this mindset, this talk attempts to shed light on this common background using very simple language, and by doing so, boost the morale of scholars who dread stepping into the field, despite being well aware that physical properties are often absolute necessities in their research. After all, which brilliant idea can be materialized without accurate property data?

I personally see it as an **academic luxury** that there are numerous routes available to property estimations. Indeed, the varied approaches span from the simple empirical correlations, all the way to sophisticated thermodynamic-based models with extensive calculations. This provides researchers with a spectrum, from which the most suitable approach can be matched to the desired goal, whether it be simplicity, accuracy, possibility of extrapolation, possibility of incorporation into software, etc. There is an answer for all and thermodynamics does not disappoint!

In this study, among the many approaches, I have selected the Group Contribution (GC) approach because I think it has the greatest potential and benefits for the audience of this particular meeting. The GC approach falls in between the very simple blind empirical fits and the elaborate theoretical models, trying to make the best of both worlds through a balance between simplicity and physical background.

However, even more important than its ease of use, is its perfect compatibility as a screening tool for a class of designer solvents, whose envisioned combinations and numbers are practically infinite. The beauty of the GC method for DES researchers is that it requires absolutely no experimental data as input to the model. Therefore, the DES community can envision all sorts of DESs to their hearts desire and check their physical property feasibilities without enduring lab time and expense, thus, eliminating trial and error. In this work, after an attempt to bring down the guards against thermodynamics, a short review is given that introduce the GC models developed specifically for DES physical properties.

PL2. Deep Eutectic Systems for Therapeutic Applications

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Keywords: deep eutectic, ionic liquids, therapeutic applications

Deep Eutectics and Ionic Liquids offer exciting opportunities for several therapeutic applications. Their tunable properties offer control over their design and function. Starting with biocompatible ions, we synthesized a library of deep eutectics/ionic liquids and explored them for various drug delivery applications. Deep eutectics/ionic liquids provided unique advantages including overcoming the biological transport barriers of skin, buccal mucosa, subcutaneous tissue and the intestinal epithelium, among others. At the same time, they also stabilized proteins and nucleic acids, and enabled the delivery of biologics across these barriers. They also provided unique biological functions including adjuvancy towards vaccines and antimicrobial function. I will present an overview of the design features of deep eutectics/ionic liquids and novel biomedical applications enabled by these unique materials.

PL3. Enabling Circular Chemistry by Combining DES as Reaction Media and Haloarcheas for Their Bioremediation

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Keywords: circular chemistry, catalysis, pharmaceuticals, sustainability, bioremediation

Organic compounds, especially pharmaceutical products, must be produced using sustainable methodologies. Using more environmentally benign media such as (DESs) in place of volatile organic compounds (VOCs), [1] has improved the sustainability of organic processes for performing both traditional and novel reactions. A second important aspect to improve sustainability is to develop efficient catalytic transformations as well as waste management.

This lecture will show the results of our research group on the use of DES to carry out organocatalysed processes,[3] transition-metal mediated reactions,[4] and even photocatalysed transformation, with focus in their application of pharmaceutical relevant products. The possibility for the design of catalytic/DES system to perform a new desired transformation and its recycling after the reaction will be highlighted.[5]

The implementation of a new protocol to assess the toxicity of known and new DESs using different bacteria and haloarchaea will be presented.[5] The use of haloarchaeas can be a promising route to easily avoid the release of DES waste in the environment by producing at the same time new compounds of interest, such as carotenoids, showing that DESs can be ideal solvents in the Circular Economy for the Chemical Industry.

[1] D.J. Ramón, G. Guillena, *Deep Eutectic Solvents: Synthesis, Properties, and Applications*, John Wiley & Sons, 2020.

[2] D. A. Alonso, A. Baeza, R. Chinchilla, G. Guillena, I. M. Pastor, D.J: Ramón, *Eur. J. Org. Chem.*, **2016**, 612-632.

[3] D. A. Alonso, S.-J. Burlingham, R. Chinchilla, G. Guillena, D. J. Ramón, M. Tiecco, *Eur. J. Org. Chem.* **2021**, 4065-4071.

[4] X. Marset, G. Guillena, *Molecules* **2022**, *27*, 8445.

[5] X. Marset, J. Torregrosa-Crespo, R. M. Martínez-Espinosa, G. Guillena, D. J. Ramón, *Green Chem.* **2019**, *21*, 4127-4132.

[6] J. Torregrosa-Crespo, X. Marset, G. Guillena, D. J. Ramón, R. M. Martínez-Espinosa, *Sci. Total Environ.* **2020**,*704*, 135382(+8).

KEYNOTE LECTURES

KN1. NaDES for Biomass Valorization: Process Innovation as a Key Point

L. Van Gheluwe[a], S. Odou[a], S. Hilali[a], I. Mike Ardeza[a,b], L. Wils[a] , B. Clément-Larosière[c],
E. Munnier[b], L. Boudesocque-Delaye[a,]*

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Keywords: Natural Deep Eutectic Solvent, extraction process, microalgae, plants, multistep process

NaDES are widely investigated in the field of biomass extraction, for the valorization of metabolites of interest (lipids, pigments, polyphenols). These green solvents are particularly popular for their high solubilization capacity, combined with unprecedented extractive selectivity. If NaDES are extensively used in academic research, paradoxically very few industrial applications have been developed. Indeed, their non-volatile nature, their viscosity and the problems related to their preparation/storage constitute important technological barriers to their dissemination. It thus appears that process innovation is a key area on which to focus research to remove these locks.

In this perspective, we have been working for several years on the development of extractive strategies, taking advantage of the particularities of NaDES with the objective of simplifying and automating the processes.

Thus, different schemes have been developed according to the biomass (wet or dry) and the targeted markets. A first strategy consists in the use of polar and apolar NaDES in a sequential or simultaneous way for the valorization of a wide range of high value-added metabolites. This strategy has allowed to generate, in a reduced number of steps, enriched and purified fractions from Spirulina, *Porphyridium sp*. or *Calendula officinalis*.

Another approach takes advantage of the particular nature of NaDES: the extractive formulation approach. This one-step process, without heating, allows to generate enriched extracts with singular profiles, compared to classical processes using the same NaDES. Moreover, this new approach enables to drastically limit the transfer operations, thus significantly improving the productivity.

KN2. Exploring the Potential of Natural Deep Eutectic Solvents for the Development of Innovative Materials with Enhanced Bioactivity

I. Pitterou[a], A. Tzani[a], A. Malliaraki[a], A. Sklapani [a], C. Fountzoula[b], A. Kriembardis[b],
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Keywords: Natural Deep Eutectic Solvents, hydrogels, biodegradable films, silver nanoparticles

During the last decade, Natural Deep Eutectic Solvents (NADES)-eutectic mixtures formed by two or more naturally occurring components-have been the vehicle for the development of a wide variety of greener processes. One of the most important advantages of NADES is that they can be task-specifically designed in order to suit the target application. The array of potential applications of NADESs spams from organic synthesis, enzyme-catalyzed reactions, extraction processes, drug delivery, CO_2 capture and storage, biocompatible nanosystems and many more. The present lecture will focus on the potential of NADES as well as NADES extracts containing a plethora of bioactive phytochemicals, to effectively act as crosslinking and gelating agents for the formation of biopolymer and protein-based films and hydrogels with enhanced bioactivity and mechanical properties. Another striking feature of task-specifically synthesized NADES and NADES-extracts will be enlightened: their ability to act as reducing and capping agents for the preparation of silver nanoparticles (AgNPs) and their incorporation in alginate hydrogels to produce new materials with antimicrobial activity.

The multifaceted character of NADES can be exploited in many ways. The use of NADES and NADES extracts for the preparation of multifunctional, bioactive materials with advantageous mechanical properties is very promising in the essence that it ensures a green, environmentally friendly yet economically viable access to products promoting green chemistry and engineering and circular economy.

KN3. Deep Eutectic Solvents and Ionic Liquids: Long-lasting Misunderstanding or Possible Future Marriage? An Insight into Their Relationship

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Keywords: deep eutectic solvents, ionic liquids

Deep eutectic solvents (DESs) and ionic liquids (ILs) are two classes of media which have the potential to drive the ecological transition in several different research areas. Although different entities, DESs and ILs share some attractive features, the most astonishing being their designer solvent nature. This denomination is often used to describe the possibility to tailor the properties of these materials for a specific application, which is a unique trait when compared to classical organic solvents.

When first appeared in the literature, DESs were presented, and have then been called this way for quite some time, new ionic liquids. However, the relationship between ILs and DESs deteriorated over time, being DESs called first “kind” of ionic liquids and finally alternative to ionic liquids (Figure 1).

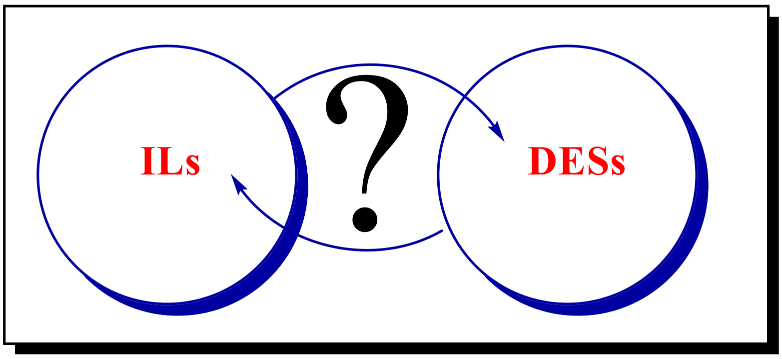

Figure 1. Deep eutectic solvents and ionic liquids: to what extent are they actually related?

Recently, we started to look into the relationship between ILs and DESs, highlighting similarities, clear differences and complementarity in some aspects [1]. Herein, examples will be shown with the aim of underlining pros and cons of both classes of solvents in relevant applications keeping in mind the goal of sustainable development.

[1] J. Afonso, A. Mezzetta, I.M. Marrucho and L. Guazzelli, Green Chem., (2023), 25, 59-105. DOI: 10.1039/D2GC03198A.

KN4. Eutectogels as “Smart” Drug Delivery Systems

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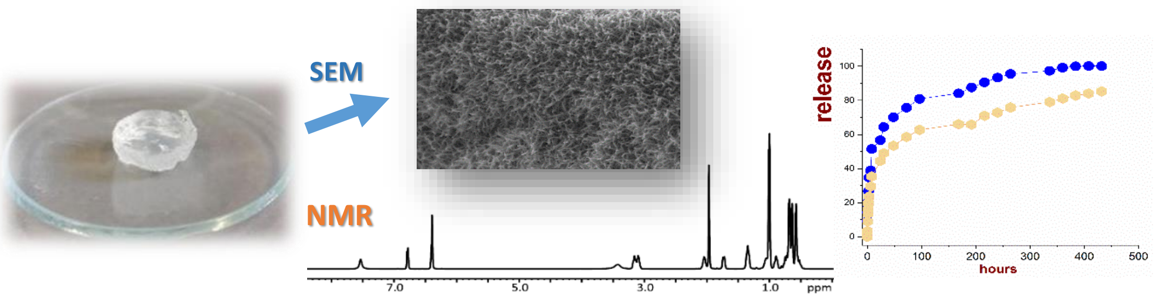
Keywords: eutectogels, drug delivery, diffusion, NMR spectroscopy

Physical eutectogels (Egels) are an emerging class of soft materials with excellent elasticity, thermal and electrochemical stability, non-volatility, and low cost. Due to their physico-chemical properties, these materials are already used for technological devices[1] and biomedical applications[2]. Indeed, they are biologically safe and biodegradable materials. The present study involves design, characterization, and drug-release profiles from novel hydrophobic eutectogels for use as noncovalently cross-linked 3D scaffolds for controlled drug delivery. These easy-to-prepare gels were obtained by gelling nonionic type V DESs consisting of thymol as hydrogen bond donor and menthol as hydrogen bond acceptor. The physico-chemical properties and morphology of single gels and gels loaded with selected drugs were determined by rheology, IR, SEM and diffusion-NMR spectroscopy. The effect of the gelator percentage and drug concentration is also investigated. In our study, we have chosen two small drugs: *i)* ethosuximide a water soluble anticonvulsant drug, and *ii)* dimethyl fumarate, which has low water solubility, used for the treatment of multiple sclerosis. The eutectogel/drug formulations exhibit variable release rates and a final percentage released which depends on the amount of gelator, pH and temperature.



[1] S. Wang, H. Cheng, B. Yao, H. He, L. Zhang, S. Yue, Z. Wang and J. Ouyang *ACS Appl. Mater. Interfaces* **2021**, 13, 20735−20745.

[2] M. B. Bianchi, C. Zhang, E. Catlin, G. Sandri, M. Calderon, E. Larraneta, R. F. Donnelly, M. L. Picchio, A. J. Paredes *Materials Today Bio* **2022**, 17, 100471.

KN5. Microstructure of Deep Eutectic Solvents

A. Malik, M.K. Jha, H.K. Kashyap*
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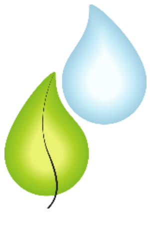
Keywords: DES, hydrophobic, microstructure, molecular dynamics, X-ray scattering

Understanding the molecular level structural landscape of deep eutectic solvents (DESs) helps in optimizing their employment in various applications. Herein, we shall present the results of our molecular dynamics simulations to delineate the microscopic structure of hydrophilic and hydrophobic deep eutectic solvents. We shall discuss about the origin of microstructural ordering in DESs using simulated X-ray scattering structure functions and radial/angular distribution functions. Impact of hydration on the microstructure of DESs willl also be elucidated.



ORAL PRESENTATIONS

OC 1. Supramolecular Cyclodextrin-based DES: From Self-organization to Molecular Recognition

A. Triolo[a,]* S. Fourmentin[b], E. Mangiacapre[c], F. Lo Celso[d], O. Russina[c,*]

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Keywords: cyclodextrin, supramolecular, self-assembly, X-ray scattering, Molecular Dynamics

The progression towards sustainable development recently prompted for the development of novel (so far acknowledged as) DES or Low Melting Mixtures as binary mixtures of host molecules (such as cyclodextrin, CD) and other neutral components, such as levulinic acid [1]. The specific nature of the host component led to the terminology of Supramolecular DES (SUPRA DES), thus highlighting the powerful opportunity of inclusion complex activity of the host component [2]. Presently, also ternary systems composed of stable mixtures of such host molecules (e.g. cucurbituril) and established DES are considered as SUPRADES.

In this presentation, we recollect our recent work focused on these two classes of SUPRADES, by i) exploring the nature of CD solvation in DES and the opportunities offered by this medium [3] and ii) describing structural and solvating features in binary CD-levulinic acid systems.

The nature of interaction of CDs with the other DES components is described as well as the capability of such systems of developing host-guest supramolecular interactions that can efficiently lead to molecular recognition. By the synergy between experimental characterizations and Molecular Dynamics simulations, we provide an atomistic overview over these hierarchical systems, addressing the main features of their macroscopic behaviour.

[1] T. El Achkar, T. Moufawad, S. Ruellan, D. Landy, H. Greige-Gerges, S. Fourmentin, Cyclodextrins: from solute to solvent, Chem. Commun. 56 (2020) 3385–3388
[2] M. Kfoury, D. Landy, S. Fourmentin, Combination of DES and macrocyclic host molecules: Review and perspectives, Curr. Opin. Green Sustain. Chem. 36 (2022) 100630
[3] A. Triolo, F. Lo Celso, O. Russina, Structural Features of β-Cyclodextrin Solvation in the Deep Eutectic Solvent, Reline, J. Phys. Chem. B. 124 (2020) 2652–2660

OC 2. Glassy Dynamics, Ionic Conduction and Dipolar Relaxation of DESs: What Can We Learn from Broadband Dielectric Spectroscopy?

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Keywords: broadband dielectric spectroscopy, glassy dynamics of DES, fundamentals

Broadband dielectric spectroscopy and differential scanning calorimetry are ideal complementary tools to assess the ionic conductivity, dipolar relaxation and glassy dynamics of DESs over an extended range of temperatures and timescales ($10^{-6} – 10^{2}$ s).

We discuss important information that can be obtained from them, based on extensive studies of two prototypical types of deep eutectic solvents, respectively ionic (ethaline) [1], and non-ionic (menthol-thymol) type V DES [2]. For both systems, and for a wide range of composition or hydration levels, crystallization is avoided, thus opening a door to assess the dynamics of the solvents from the normal to the deeply supercooled liquid state.

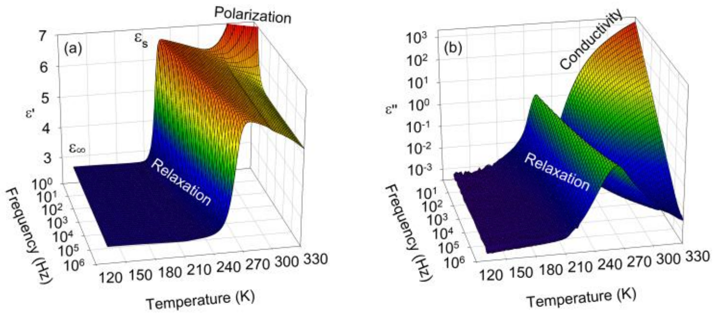

Figure. Complex Dielectric Permittivity of type V DES.

Notably, we address the effect of non-ideal mixing on the solvent dielectric strength and its possible influence on dynamical properties. Moreover, we demonstrate that many salient parameters of the relaxation functions of deeply supercooled DESs, including fragility and non-Debye character all point to the development of dynamic heterogeneities.

Decoupling between rotation and translation dynamics is finally assessed. While it is demonstrated for non-ionic menthol-thymol DES, which strongly supports the heterogeneous nature of the mixture, comparable decoupling is surprisingly only obtained at high water content (DES-in-Water) for ionic DES ethaline, upon actual entry into the biphasic region of the phase diagram.

[1] A. Jani, B. Malfait, D. Morineau, *On the coupling between ionic conduction and dipolar relaxation in deep eutectic solvents: Influence of hydration and glassy dynamics*, J. Chem. Phys. 154 164508 (2021).

[2] C. D'Hondt, D. Morineau, *Dynamics of type V menthol-thymol deep eutectic solvents: Do they reveal non-ideality*? J. Mol. Liquids, 365, 120145 (2022).

OC 3. Defying Decomposition of Archetypal Deep Eutectic Solvent Constituents

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Keywords: thermal decomposition, enthalpy of fusion, solid–liquid equilibria, fast scanning calorimetry

Deep eutectic solvents (DESs) are characterised by large (deep) melting point depressions, which allow them to be used as versatile liquid media over wide temperature and composition ranges [1]. Since eutectic phase behaviour is at the core of DESs, the lack of reliable pure component fusion properties has been identified as a critical obstacle towards the development of novel DESs [2]. Indeed, the fusion properties of various archetypal DES constituents—mainly ammonium salts—are typically experimentally inaccessible because they undergo thermal decomposition before or upon melting [3,4].

We could overcome this limitation by heating these salts at rates beyond their decomposition kinetics (>1000 K/s) using fast (differential) scanning calorimetry, or F(D)SC. Additionally, we developed experimental strategies that allowed us to study highly hygroscopic components with F(D)SC under dry atmosphere. By coupling FSC with synchrotron X-ray scattering and high-speed microscopy imaging, we provided evidence of melting and recrystallisation for choline chloride, three tetraethylammonium halides, and trimethylglycine (also known as betaine). Finally, we evaluated the enthalpy of fusion of studied compounds with FDSC, which is the missing link to predict the liquid window of their DESs.

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OC 4. Current Approach for Carotenoids Extraction Using Hydrophobic Deep Eutectic Solvents

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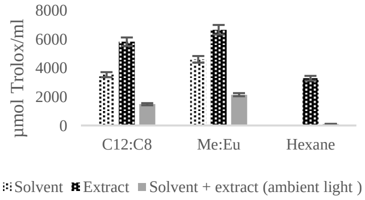
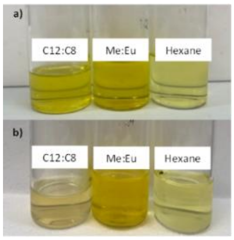
Keywords: hydrophobic deep eutectic solvents, carotenoids, ultrasound assisted extraction, sustainability, antioxidant capacity

Natural carotenoids have a wide range of applications in the food, pharmaceutical, and cosmetic industries as coloring agents and antioxidants. Consequently, industries are more concerned about extracting them from natural resources and by-products. The present research aimed to evaluate the extraction efficiency of carotenoids from orange peel (OP) using Hydrophobic Deep Eutectic Solvents (HDESs) as an efficient alternative to replacing organic solvents. To intensify the extraction process Ultrasound-Assisted Extraction (UAE) was used. OP was obtained from orange fruits (*Citrus sinensis*, Navel cultivar). Two hydrophobic DES were prepared Menthol: Eucalyptol (Me:Eu) and Lauric acid: Octanoic acid (C12 :C8). Extractions were performed using a solid/liquid ratio of 1:10, for 30 min with 50W of ultrasound power at 45°C. The obtained extracts were characterized by total carotenoid content (TC) determined spectrophotometrically at 450nm and the antioxidant capacity was measured using DPPH method. Additionally, the antioxidant and the color stability of HDESs extracts was monitored for 20 days. Finally a Response Surface Methodology (RSM) was adopted to analyze the significance of extraction parameters. Me:Eu showed the highest carotenoid extraction yield (359.3±3.5 mg/100gfw), and also presented high stability during the storage period. HDESs extracts showed higher antioxidant capacity compared to hexane extracts, while Me:Eu extracts showed the lowest color variation (5.9±0.2). Optimal parameters using Me:Eu were an extraction time of 20 min, ultrasonic power of 120 W (60%), and a solvent-to-solid ratio of 20 mL/g reaching a carotenoid content of 573.4 mg/100 g_{fw}. While C12:C8 optimal parameters were 10 min, 80 W (40%), and 10 mL/g, respectively, providing a carotenoid content of 183.7 mg/100 g_{fw}. Overall, the results showed that HDESs can improve carotenoid stability, and combined with the intrinsic safety and edibility of their components makes these extracts appealing for food formulations.





OC 5. Deep Eutectic Solvents for Determination and Recovery of Tartaric Acid from Winery Residues

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Keywords: COSMO-RS, deep eutectic solvents, grape pomace, tartaric acid

The interfacial nanostructure of the three most widely-studied Deep Eutectic Solvents (DESs), choline chloride:urea (ChCl:Urea), choline chloride:ethylene glycol (ChCl:EG), and choline chloride:glycerol (ChCl:Gly) at a Pt(111) electrode has been studied as a function of applied potential and water content up to 50 wt%. Contact mode atomic force microscope (AFM) force-distance curves reveal that for all three DESs, addition of water increases interfacial nanostructure up to ~40 wt%, after which it decreases. This differs starkly from ionic liquids, where addition of small amounts of water rapidly decreases interfacial nanostructure. For the pure DESs, only one interfacial layer is measured at OCP at 0.5 nm, which increases to 3 to 6 layers extending ~ 5 nm from the surface at 40 or 50 wt% water. Application of a potential of ±0.25 V to the Pt electrode for the pure DESs increases the number of near surface layers to 3. However, when water is present the applied potential attenuates the steps in the force curve, which are replaced by a short-range exponential decay. This change was most pronounced for ChCl:EG with 30 wt% or 50 wt% water, so this system was probed using cyclic voltammetry, which confirms the interfacial nanostructure is akin to a salt solution.

Acknowledgments: The work was supported by the European Union through the European regional development fund, Competitiveness and Cohesion 2014-2020 (KK.01.1.1.07.0007.)

OC 6. Valorisation of Food Industry Wastes by Exploiting Natural Deep Eutectic Solvents (NADES)

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Keywords: chestnut shells, cherry pomace, polyphenols, NADES, bio-IL

The agri-food sector annually generates huge amount of waste and by-products, whose disposal provokes serious environmental and economic issues. In this scenario, alongside with the transition towards sustainability and circular economy, the full exploitation of biomass food waste and its recycle into a new chain of value via the development of sustainable and green process are of primary importance [1,2]. In this study, green solvents such as natural deep eutectic solvents (NADESs) and bio based-ionic liquids (bio-ILs) have been employed for the valorization of different food industry wastes (i.e. chestnut shell, cherry pomaces) (Figure 1).

Figure 1. Valorisation process of chestnut shells and cherry pomace.

More in details, choline chloride, betaine or L-proline-based DESs have been investigated for the extraction of polyphenolic compounds, high added value compounds. The composition of extracts was ascertained by HPLC analyses, and the polyphenols content was assessed by colorimetric assays. Then, cholinium glycinate bio-IL has been successfully employed for the fractionation of the lignocellulosic residue obtained after polyphenols extraction. Cellulose enriched material and lignin enriched material were obtained, and the nature of the extracted fractions was confirmed by infrared spectroscopy and thermal gravimetric analysis. Also, the recovery of the NADES and the bio-ILs have also been proven, which make the whole process viable and amenable for large-scale applications.

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OC 7. Eutectic Matrices for Bioactive Compounds Valorization and Formulation: Carotenoids as Case Study

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Keywords: natural deep eutectic solvents, carotenoids, *C. officinalis*, *S. oleracea*, Response Surface Methodology, topical gels

Plants species are well known source of bioactive compounds, is gaining attention from many fields ranging from food to cosmetics. In particular, carotenoids, a class of phytonutrients found in the cells of a wide variety of plants like marigold flower (*C. officinalis*) and spinach leaves (*S. oleracea*) biomasses. It could also be interesting as a natural colorant as it is representing for the yellow, orange, and red pigments of plants.

Recently, our laboratory described the strong potential of Natural Deep Eutectic Solvent (NaDES) to extract and stabilize carotenoids in a liquid medium. The carotenoids concentration was assessed by comparing different eco-extraction technologies such as ultrasound assisted extraction (UAE), microwave assisted extraction (MAE) and an innovative process developed in our lab. During sample preparations, the physicochemical parameters of NaDES enriched with plant extracts play a crucial technique on the ability to retain those highly degradable carotenoids. According to the results obtained, each NaDES has a different selectivity of carotenoids based to their composition. Thus, mid polar glycerol based NaDES showed superior extraction performances of carotenoids of different polarities in all eco-extraction media better than conventional solvents. Response surface methodology (RSM) were adapted in this study for the generation of predictive models to simulate and optimize carotenoids extraction under three different experimental conditions. The box-behnken design was effective to generate the optimized list of conditions for the optimal total carotenoids content (TCC).

These preliminary results are important steps for scale-up purpose involving highly degradable compounds. As carotenoids impart various benefits in cosmetics, understanding the interactions of NaDES-based extracts with the ingredients of the cosmetic formulations for an effective identification of the best preparation approach by doing control studies using topical gels.

OC 8. Impact of DES on Metal-Organic Framework Synthesis and Properties

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Keywords: porous materials, Metal-Organic Frameworks, crystal morphology, DES

Deep Eutectic Solvents (DESs) represent an emerging class of solvents featuring some characteristics of their ionic liquid cousins - low vapor pressure, relatively wide liquid range, non-flammability and the ability to dissolve polar species - along with unique specificities, such as their limited toxicity and an improved biocompatibility [1]. Their use as media for the ionothermal preparation of Metal-Organic Frameworks (MOFs) has been recently explored, showing that not only DESs represent green and less toxic alternatives to solvents commonly used in the synthesis of these porous crystalline materials, but also that they may play different roles in the MOF construction [2]. Aiming at further investigating the potential of DESs for MOF synthesis and their impact on the properties of the materials, we are exploring their use for the preparation of prototypical MOFs as well as of new architectures [3-4]. For example, we have recently reported that the choline chloride/urea (1:2) DES and its analogue based on ethylene-urea can be used for the preparation of Mg-MOF-74 as well as of novel Ca-based MOFs. Interestingly, these mediums were shown to have an impact on the crystal morphology and textural properties, and were demonstrated to allow the preparation of otherwise water-sensitive materials [4]. These results and more recent efforts will be presented in this contribution.

Examples of MOFs prepared in DES [4]

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OC 9. Hydrophobic Eutectics and Eutectogels: A Fertile Playground for Structural and Dynamic Studies

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Keywords: hydrophobic eutectic solvent, eutectogel, intermolecular interactions, diffusion

Hydrophobic non-ionic eutectic solvents (HES) are recently standing out from the crowd of (deep) eutectic solvents, (D)ES [1]. Compared to conventional type III hydrophilic (D)ES, non-ionic HES typically display lower viscosities, are chloride-free, and can be used in applications where even low water contents represent an issue. As a further step, hydrophobic non-ionic eutectogels (HEG) can be prepared from the immobilization of HES in a solid-like scaffold. Here I report on stable and homogeneous gels obtained in a matter of minutes using a low-cost low molecular weight gelator at a very low loading, with a simple one-pot preparation process ranked as "excellent" in the EcoScale metrics [2].

If considerable progress has been achieved in the understanding of intermolecular interactions and mobility within traditional hydrophilic (D)ES, very little is known for HES [3] and even less for HEG [2]. A multidisciplinary approach is applied here combining liquid-state and HRMAS NMR methods with FTIR, thermal and rheological measurements, to shed light into structure and dynamics of both liquid and semi-solid samples. Noteworthy, the liquid-like nature of the hydrophobic mixture is retained upon gelation, and an unexpected increase of the diffusive motion of the HES components is observed under confinement compared to pure HES.

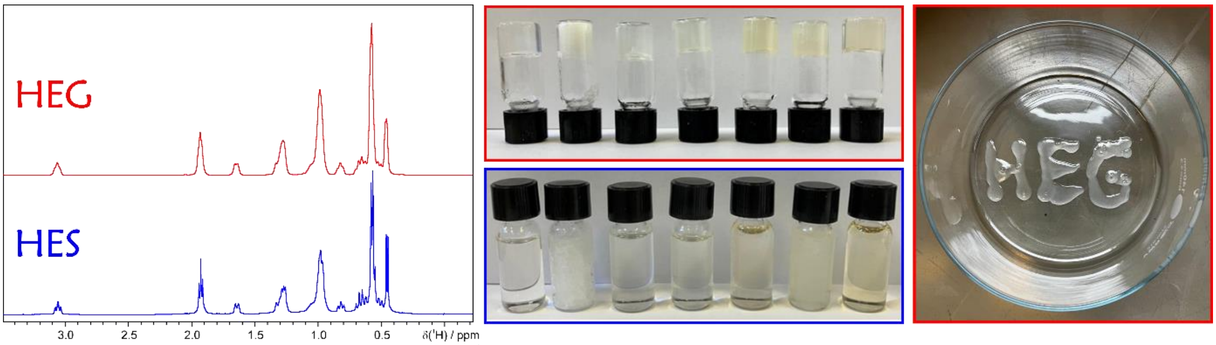

Fig. 1. (a) Liquid-state and HRMAS ^{1}H spectra of a representative HES and HEG, (b) pictures of a selected set of HES (bottom) and HEG (top) ad (c) photograph of a representative HEG.

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OC 10. Classifying Deep Eutectic Solvents for Polymer Solvation via Intramolecular Dimer Formation

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Keywords: deep eutectic solvents, choline chloride, polydimethylsiloxane, good solvent, bad solvent

Deep eutectic solvents (DESs) have emerged as versatile and inexpensive solubilizing media with widely varying physicochemical properties. Establishing characteristics of a novel solvent milieu for polymer dissolution is an important exercise. Assessment of two DESs constituted of H-bond acceptor (HBA) choline chloride (ChCl) and H-bond donors (HBDs) glycerol and urea named ChCl:Gly and ChCl:Urea, respectively, as solvents for polydimethylsiloxane (PDMS) solvation is carried out *via* investigation of intramolecular dimerization by pyrene (Py) end-tagged PDMS of MW 3100 (Py-PDMS-Py) as a fluorescent probe in the temperature range 293.15–363.15 K. The outcomes are compared with those in liquid PDMS of average MW 2000 (PDMS2000) and in glycerol. While the intramolecular dimerization by Py-PDMS-Py happens exclusively in the excited-state in liquid PDMS2000, wavelength-dependent fluorescence excitation spectra along with excited-state intensity decay kinetics reveal presence of ground-state interactions between pyrenyl moieties in ChCl:Gly, ChCl:Urea and glycerol. This leads to the proposition that PDMS prefers to stay in predominantly coiled form in DESs and glycerol as opposed to that in PDMS2000, where PDMS-PDMS contact is maximized leading to the absence of ground-state heterogeneity. Thus, while the liquid PDMS2000 is characterized as a "good" solvent, DESs ChCl:Gly and ChCl:Urea along with glycerol may be designated as "bad" solvents for PDMS dissolution.

OC 11. Redox Properties of Copper Ions in Ionic Liquids and Deep Eutectic Solvents

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Keywords: deep eutectic solvents, ionic liquids, redox potentials, speciation

Deep eutectic solvents (DESs) are mixtures of a hydrogen bond donor (HBD) and acceptor (HBA) and they are widely considered as a cheaper alternative to ionic liquids (ILs). Using oxidising agents, like copper chloride in DESs, sustainable dissolution and recovery of metals is possible. This approach can be considered as a sustainable alternative to mineral acids regarding the recovery of metals from electronic waste (e-waste). However, the redox potential of the oxidizing agent plays a crucial role as it determines whether the oxidation of the target metal will be thermodynamically favorable or not. Redox potential of the oxidising agent depends on its speciation, which in turns depends on the nature of the DES.

Therefore, we investigated the effect of different copper salts on the copper redox properties and speciation as well as the effect of the different solvent anions, using a copper salt in a range of solvents. It was shown that the effect of the solvent anion is much more significant than that of the salt anion on the redox properties. The study of the ionic liquid anion effect showed that copper speciation changes significantly, leading to a greater difference in redox response. Thus, these speciation differences can be used to modify the redox potentials. The effect of the HBD type, present in a DES system, was also investigated and the formal redox potentials of both copper redox couples were plotted as a function of the pKa of the HBD in Figure 1. Speciation was investigated by means of UV-vis spectrophotometry, while the redox potentials were studied using cyclic voltammetry (CV).

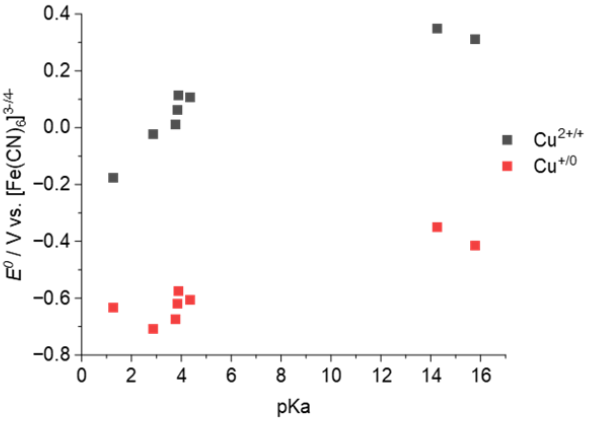

***Fig 1**. Formal redox potentials of $Cu^{+/0}$ and $Cu^{2+/+}$ couples using $[Fe(CN)_6]^{3-/4-}$ as an internal standard and plotted as a function of the pKa of the HBD.*

It was found that the relative redox potentials of the copper redox couples change with the pKa value of the HBD. Increase of the pKa value leads to differences of up to 0.4 V for the $Cu^{+/0}$ and up to 0.6 V for the $Cu^{2+/+}$. The above results were used to select the most effective solvent as well as to ‘‘tune’’ the redox potential to dissolve selectively metals from e-waste, like printed circuit boards and thermoelectric devices.

OC 12. Self-assembly and Mesostructure Formation in Type IV Deep Eutectic Solvents

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Keywords: surfactants, micelles, scattering, pyrolysis, ceria, mesoporous oxides

In our ongoing work we are exploring the formation of micelles in deep eutectic solvents (DES) and their potential applications [1-2]. Previously micelle formation has only been reported in Type III DES, consisting solely of organic species. Here, we have explored the self-assembly of cationic surfactants dodecyl trimethylammonium nitrate/bromide ($C_{12}TANO_3/C_{12}TAB$), anionic surfactant sodium dodecyl sulfate (SDS), and non-ionic surfactants hexaethylene glycol monododecyl ether ($C_{12}EO_6$) and octaethylene glycol monohexadecyl ether ($C_{16}EO_8$) in a Type IV DES comprising the metal salt cerium (III) nitrate hexahydrate, and hydrogen bond donor, urea in the molar ratio 1:3.5 [3]. The cationic and nonionic surfactants form spherical micelles in this solvent, while the anionic surfactant SDS forms highly elongated micelles, due to the polycations present in the DES [4]. The SDS solutions form gels at relatively low concentrations of surfactant, however cationic and nonionic surfactants are soluble at much higher loadings allowing these micelles to be used in a “true liquid crystal templating” approach.

Using $C_{12}TANO_3/C_{12}TAB$, as well as hexadecyltrimethylammonium nitrate/bromide ($C_{16}TANO_3/C_{16}TAB$), or the commercial nonionic surfactant BrijC_{10} (which also has a C-16 tail), in the cerium nitrate:urea DES allows mesoporous cerium oxides to be produced by a solvothermal route. Heating the surfactant solutions at 70 °C causes precipitation of an oxycarbonate phase which can then be calcined to form cerium oxide. The surface area of the oxides produced is dependent on the micellar template used, and the presence or absence of halide ions directly affects the catalytic activity of the ceria in CO oxidation reactions [5].

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OC 13. Surface Tension of Glycol-based Eutectic Solvents in Water

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Keywords: surface tension, DGT, PC-SAFT, Molecular Dynamic

Eutectic solvents, typically called DES, have been studied recently due to their favorable properties for several applications like extraction of biomolecules, bioreactions, and biomass processing, among many others. The applicability of these mixtures composed of a hydrogen bond donor (HBA) and a hydrogen bond acceptor (HBD) has gained attention due to their properties like low vapor pressure, low toxicity, biodegradability, tuneability, etc. Several physicochemical properties have been measured for DES, but surface tension still has a scarce amount of experimental data in the literature with systematic studies in terms of the temperature and different HBA:HBD ratios. However, surface tension data provide significant insights, for instance, on extraction processes for avoiding the presence of emulsions, for evaluating the use of the solvents as lubricants, for permeability applications, etc. In this work, the surface tension of DES based on choline chloride or betaine as the HBA and ethylene glycol, 1,2-propanediol, 1,3-propanediol, and 1,4-butanediol as the HBD were measured at different amount of water. As is shown in Figure 1, experimental results were modeled using the density gradient theory (DGT) coupled to a reliable equation of state like PC-SAFT. Also, molecular dynamics (MD) simulations were performed to provide information at a molecular level of the interfacial behavior.

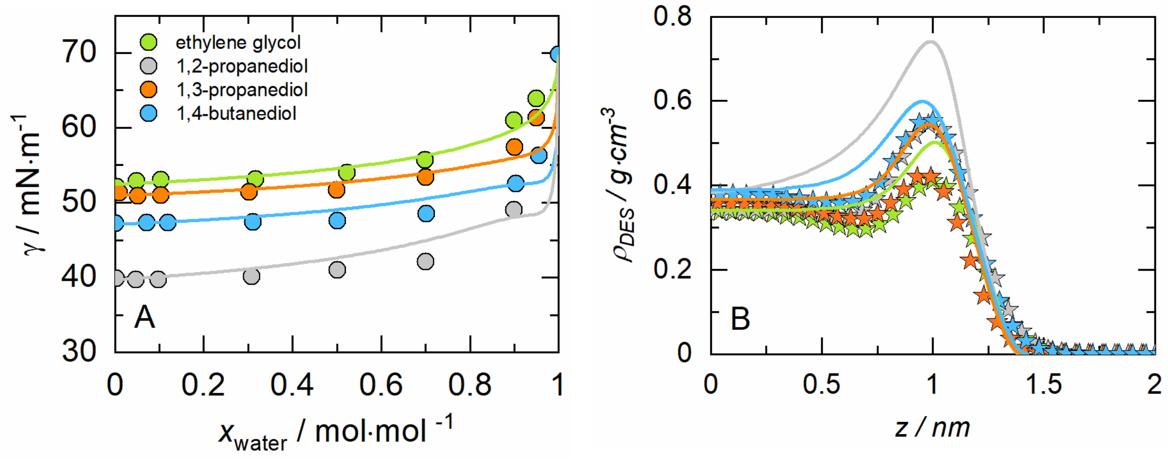

Figure 1. For each DES: ChCl:HBD(1:3) at 40°C: (A) Surface tension at different mole fraction of water and (B) DES density profile at 0.9 mol mol^{-1} of water. Circles: Experimental values, Stars: Molecular Dynamic, Lines: Density Gradient Theory + PC-SAFT.

OC 14. Towards Rational Design of Deep Eutectic Systems: from Empirical Force Fields to Machine Learning Interatomic Potentials

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Keywords: molecular dynamics simulations, polarizable force field, machine learning inter-atomic potentials, computational studies

We will present three studies showing the capabilities and limitations of molecular dynamics (MD) simulations to understand deep eutectic systems (DES) at the molecular scale. Each study differs in the employed model to consider intra- and intermolecular forces.

In the first study, we investigated the influence of urea derivatives as hydrogen bond donors (HBD) on the nonideal mixing of choline-based DESs by a force field model based on scaled atomic charges [1]. We observed a strong correlation between the experimentally reported activity coefficients of choline chloride in these mixtures with coordination numbers of the HBD sites around the chloride anion. The same trend was observed for the calculated derivative of the chemical activities from our MD simulations, further indicating that incorporation of the anion in the hydrogen bond network of the HBD is one of the main driving forces for the observed nonideal eutectic behavior in these mixtures.

In a second study, we developed a polarizable force field model for reline (a choline chloride and urea mixture in a 1:2 ratio). [2] Predicted dynamic properties such as diffusion coefficients and ionic conductivity are in good agreement with experimental values, showing significant improvements over nonpolarizable models. However, the model lacks transferability between different systems since a system-specific damping function for specific interactions of the anion must be introduced. This damping parameter must be fitted to computationally expensive first-principle MD simulations. Thus, it is an overall time-consuming approach to study DESs.

Motivated by our previous experiences, we have investigated the capabilities of machine learning inter-atomic potentials to close the gap between the accuracy of the first-principle methods and the efficiency of the empirical force fields. This enables MD simulations of systems consisting of several thousand atoms on the nanosecond time scales with quantum mechanical accuracy but at a fraction of the computational cost. This facilitates reliable first-principle MD simulations within a few weeks, which are not limited to nonreactive systems.

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OC 15. Investigation of Lanthanide Metal-Based Deep Eutectic Solvents and Their Potential as Solubilizing Media

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Keywords: Deep Eutectic Solvent, viscosity, density, polycyclic aromatic hydrocarbon, self-aggregation

Deep eutectic solvents (DESs) belong to a rapidly growing solvent family and are becoming solubilizing media of prominence in different aspects of science and technology. Lanthanides salt-based DESs represents the type-IV DESs composed of hydrated metal salt such as lanthanum nitrate hexahydrate, cerium nitrate hexahydrate and gadolinium hydrated as ionic constituents and urea as the molecular component. For effective utilization of these neoteric media, assessment of their physicochemical properties is essential. These DESs features high density and lower viscosities in comparison with common and popular type III DESs and other metal based DESs. Density and dynamic viscosities of these DESs were found to decrease with increasing concentration of the molecular counterpart urea and temperature. The temperature dependence of the dynamic viscosity follows Vogel−Fulcher−Tammann (VFT) expression similar to that of common imidazolium ionic liquids. Accompanied with these dynamic physical properties, these DESs also exhibit an unprecedented solute solvation behavior. The unique solute-solvent interactions lead to the excimer formation of a widely recognized polycyclic aromatic hydrocarbon pyrene at very low concentration within these lanthanide-based eutectics. Preferential interaction of the π-cloud of the pyrene with the polycationic species involving lanthanide results in bringing of pyrene molecules together in the vicinity of the urea-water H-bonded nano-domains resulting in pyrene-pyrene aggregations in micromolar concentration regime. We have also employed these nascent DESs for investigating their role in surfactant self-assembly formation. The in-depth multipurpose study of these ionic liquid analogues-lanthanide metal salt-urea DESs will help in establishing them as potential novel solubilizing media in science and technology.

OC 16. Water-based DES: Properties and Opportunities

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Keywords: water; hydrogen bonding; natural; hydrophobic vs hydrophilic; X-ray scattering; Molecular Dynamics

The kaleidoscopic richness of DES formulations prompts for exploring a variety of opportunities towards a sustainable development. The chances offered by DES tunability in design ought to be exploited to decrease the environmental impact associated to their use. In this respect a steady path towards exploitation of natural, sustainable and low cost chemicals to develop a DES can be recognised in the recent literature.

In this scenario, the exploitation of water as the hydrogen bonding donor species in the DES formulation, rather than as a contaminant or an added component to an already existing formulation, is recently attracting great attention.

In this presentation we will report on recent results from our group (as well as other teams) on the use of water as major component on the formation of different hydrophilic [1] as well as hydrophobic DES [2,3].

We will exploit the synergy between experimental characterizations and Molecular Dynamics simulations, to provide an atomistic level overview of series of water-based DES, aiming at extracting common features in the behaviour of the eco-sustainable, natural DES.

We will also show selected examples of the impact of such DES in carbohydrates solvation.

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OC 17. Accurate Description of the Thermophysical Properties of Choline Chloride-Based Deep Eutectic Solvents and Their Aqueous Mixtures using soft-SAFT EoS

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Keywords: Deep Eutectic Solvents, soft-SAFT, effect of water; density, viscosity, activity coefficients

A new generation of designer solvents emerged in the last decade as promising green media for multiple applications: Deep Eutectic Solvents (DESs). These compounds consist of mixtures between hydrogen bond donors and acceptors where, due to the strength of these bonds, at a certain proportion, they have a melting point lower than that of their pure components, as well as lower than that of an ideal liquid mixture. Their highly non-ideal behavior has encouraged the study of these systems from different modeling perspectives, so as to characterize their thermophysical properties and relate them to the nature of the compounds forming the mixture. In this regard, the use of advanced equations of state, such as the soft-SAFT approach, provides an attractive framework for reliable estimates of the physicochemical behavior of DESs, as the hydrogen bonding and other association effects can be explicitly considered in the model. One of the important features to consider is the impact of the presence of water on DESs, as the water content can severely modify its thermodynamic properties of DES and affect its supramolecular structure by a new balance of hydrogen-bonding interactions. In this work, a thermodynamic characterization of several choline chloride-based DESs and their aqueous mixtures has been carried out using the soft-SAFT equation of state by developing accurate transferable and semi-predictive models. A description of the density, viscosity and activity coefficients of aqueous DESs, as also isentropic compressibility and speed of the sound of some pure DESs, is provided and discussed throroughly, comparing with experimental data. This methodology provides a new platform to qualitatively select physicochemical properties of new DES in a quick, efficient and reliable manner.

OC 18. Rationale Design of Deep Eutectic Solvents for Improvement of APIs properties

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Keywords: Therapeutic Deep Eutectic Solvents, solubility, stability, permeability, in vitro cytotoxicity

Therapeutic Deep Eutectic Solvents (THEDES) have become an interesting area of DES application since it is expected that they can contribute to a striking difference on the properties of different APIs. By creating a THEDES, eutectic mixture with an API as one of its compounds, we aim to achieve better APIs solubility, stability, and membrane permeation, while not losing its activity. The first step is applying rational design as an effectual tool that enables a fast screening of thousands of compounds, thus reducing the time and resources spent on *de novo* experiments. In the already well-known world of deep eutectic solvents, where there are over a million possibilities to create one, such a tool makes the crucial first step much easier and faster. Using COSMOtherm program, and selecting DES with the lowest $ln\gamma$ value, which is proportional to solubility, a selection of three hydrophobic and three hydrophilic DES for our API of interest (compound x) was done. The computational selection is experimentally proven by HPLC analysis and a stability test is done for a period of 3 months. Permeability was assessed using PAMPA. The antimicrobial activity of chosen API is monitored by disc diffusion assay on a set of gram-positive and gram-negative bacteria. *In vitro* cytotoxicity is carried out using animal cell culture CaCo-2.

OC 19. Quantum Chemical Studies of Deep Eutectic Solvents as Mucus Modulating Agents for Enhanced Drug Delivery

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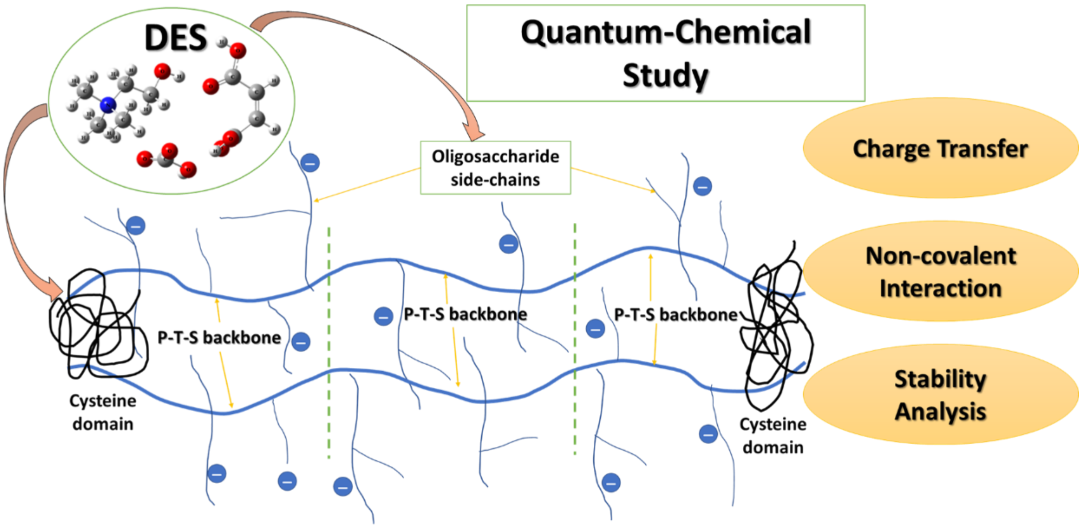
Keywords: DES, mucin, HBA, HBD, diffusivity, drug delivery

Deep Eutectic Solvents (DESs) and Ionic liquids (ILs) have recently been recognized as potential mucus-modulating agents to enable enhanced oral delivery of macromolecular drugs. Present as a lining on epithelial tissues, mucus not only acts as a selective barrier for any kind of pathogen or toxins from entering inside and affecting the internal functioning of the cells, but also acts as a barrier towards effective drug delivery to targeted cells. During disease state, the mucus lining becomes even thicker causing difficulty in drug absorption towards target cells. It has been observed that choline based DESs are able to effectively modulate the physical properties of mucus, like viscosity, to enhance drug penetration through the dense mucus layer along with preserving the chemical composition and integrity of the mucus. This choline-based DESs are safe, biocompatible as well as economic proving to be a promising choice for effective drug delivery agents. Quantum chemical (QC) simulation study of the DES-mucus-drug system, with choline bicarbonate as hydrogen bond acceptor (HBA) and acidic groups like glutamic acid, glycolic acid, maleic acid and malonic acid as hydrogen bond donor (HBD) in the DES, revealed interesting results such as increased diffusivity values of drug through the mucus. The different components present in mucus layer such as the side chain oligosaccharide groups and the disulfide linkage in cysteine domain are found to be interacting with the DES components that facilitates enhanced network of non-covalent interactions along with charge transfer among the DES and the mucin side-chain groups resulting in the reduction of cross-linking among adjacent mucus backbone chains.



OC 20. Solubility Enhancement of Drugs using Deep Eutectic Systems

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Keywords: solubility, deep eutectic systems, active pharmaceutical ingredients

The low solubility of active pharmaceutical ingredients (APIs) in aqueous solvents hinders the formulation of drugs in liquid state. Several methodologies are being used to improve the solubilities of the APIs, being one of them the use of Deep Eutectic Systems (DES). In this work several DES formed by xylitol, fructose, sorbitol and glucose (HBD) and choline chloride as HBA and water have been prepared at different compositions.

The density of these systems has been measured at 25ºC. Results show that density increases as the amount of water decreases. Furthermore, the solubility in these DES of some APIS such as ibuprofen or carvedilol, among others, has been obtained at room temperature. Additionally, the increase in the DES solubility (S) in relation to the solubility of the APIs in water (S0) has been evidenced through the ratio (S/S0). Figure 1, as an example, shows a comparison of experimental solubility values for carvedilol in some DES formed by glucose or sorbitol and choline chloride and water. This trend is the same as observed in solubility of some APIs.

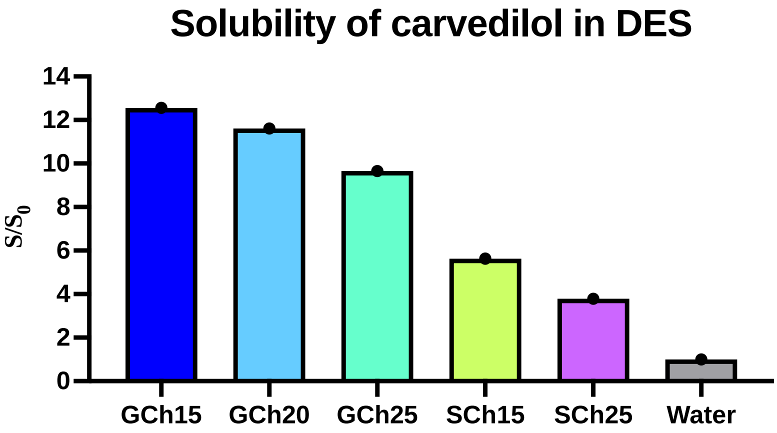

Figure 1. Comparison of the experimental solubility values found for carvedilol in some DES formed by glucose and sorbitol with choline chloride and water.

OC 21. Advances in Unravelling the Specific Cytotoxic Action of THEDES Towards Colorectal Cancer Cells Using a Metabolome Analysis Approach

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Keywords: therapeutic deep eutectic systems, terpenes, NSAIDs, metabolome

In this work the influence of THEDES direct exposure in the endo- and exometabolome of a colorectal cancer in vitro cell line (HT29) is described. This work is part of a wider study to unravel the specific cytotoxic action of THEDES towards cancer cells. The remarkable bioactive properties of DES to help overcoming modern medicine most challenging battles, such as cancer growth and progression, have been continuously reported. Alongside with its tailor-made versatility and compliance with the green chemistry metrics, DES have been pushed forward as potential alternative or complementary therapeutic agents for cancer treatment. In a previous work, we have reported that by allying the cytotoxic properties of terpenes with nonsteroidal anti-inflammatory drugs (NSAID), a THEDES with selective action towards cancer cells (HT29) was obtained. From the results now obtained we were able to see once more that there are significant differences between the control – corresponding to colorectal cancer cells growing in optimal growth conditions – and the cells exposed to the different THEDES used, but this time using a metabolome analysis approach. From these differences we are able to hypothesize that key metabolic pathways, such as those related to catabolism and mostly related to the generation of energy, and anabolism by the influence on amino acids presence, are being influenced by the presence of such THEDES. Thus, with these results we expect to bring an extra layer on the comprehension of what are THEDES specific cytotoxic mechanisms and establish this technology as an innovative approach in the cancer challenge.

Acknowledgements: This work has received funding from the ERC-2016-CoG 725034 and was supported by the Associate Laboratory for Green Chemistry (LAQV) financed by national funds from FCT/MCTES (UIDB/50006/2020). The author acknowledges FCT - Fundação para a Ciência e Tecnologia through Filipe Oliveira's PhD grant 2021.07780.BD.

OC 22. Efficient Eutectic Mixtures for Biocatalysis Reactions. From Waste Oil to Biodiesel

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Keywords: eutectic solvents, waste oil, biocatalysis, circular economy, biodiesel

The concerns expressed in the 2023 Agenda on sustainable development and the compromise between the prevailing philosophy of unlimited economic growth and environmental and social challenges have promoted the concept of a circular economy as a pillar of a more ethical society. With these premises, the efforts to propose sustainable processes are focused on revaluing and minimizing waste. Eutectic mixtures appear as an attractive alternative to offset the ungreenness and environmental impact [1]. In our previous research works we have demonstrated the feasibility of using novel and common eutectic solvents as salting-out agents in extraction strategies [2], lipase-friendly [3] and co-solvents for biocatalysis [4] allowing a step ahead towards a proposal to design sustainable biotechnological processes.

In this work, we report the suitability of using a novel deep eutectic solvent designed with choline dihydrogen phosphate:ethylene glycol (ChDHP:EG) (molar ratio 1:2) both as lipase extractant and coadjuvant in lipase-catalyzed transesterification reaction for biodiesel production from waste oil. The results reveal no harmful effects of ChDHP:EG addition to immobilized lipase B from *Candida antarctica* for catalysis of glycerol-free transesterification reaching close to 90% of FAME conversion. Finally, the reuse of the immobilised lipase was evaluated for several cycles and the absence of biocatalyst deactivation was concluded.

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OC 23. Insights Into Deep Eutectic Solvents Impact on Formate Dehydrogenase Kinetics and Folding Stability

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Keywords: deep eutectic solvents, biocatalysis, kinetics, enyzme stability

Figure 1. (A) Catalytic efficiency of cbFDH under wcosolvent = 0.15 at 298.15 K and (B) ΔB23 cbFDH-cosolvent second virial coefficient obtained by differential scanning fluorometry.
Cosolvents mixtures are an efficient way to modify the kinetics of enzyme-catalyzed reactions without compromising enzyme stability; among them, Deep Eutectic Solvents (DES) have emerged as an exciting media for biocatalytic reactions. DES "tailor-made" nature allows modulating enzyme-cosolvent interactions with compounds of diverse functional groups. In this work, the influence of cosolvents (betaine, glycerol, and sorbitol) and two DES (betaine: glycerol and betaine: sorbitol) in the kinetics of candida boidinii Formate dehydrogenase (cbFDH) was evaluated. The results show a 30% increase in catalytic efficiency in the presence of cosolvents, as shown in Fig. 1A. Further, cbFDH folded-state stability was evaluated using differential scanning fluorimetry, where the cosolvent on cbFDH-substrate dissociation constant, unfolding temperature, unfolding Gibbs energy, and the second virial coefficient were considered. As shown in Fig. 1B, DES presence counteracts betaine negative effect on the protein surface, stabilizing the cbFDH folded-state. This phenomena is futher investigated using cbFDH molecular dynamics simulation in a crowded environment. Understanding cbFDH-cosolvent molecular interactions will help to understand how the environment of proteins changes in the presence of different stimuli. Diverse stabilization mechanisms show the importance of studying cbFDH-cosolvent dynamics toward optimizing biocatalytic processes.

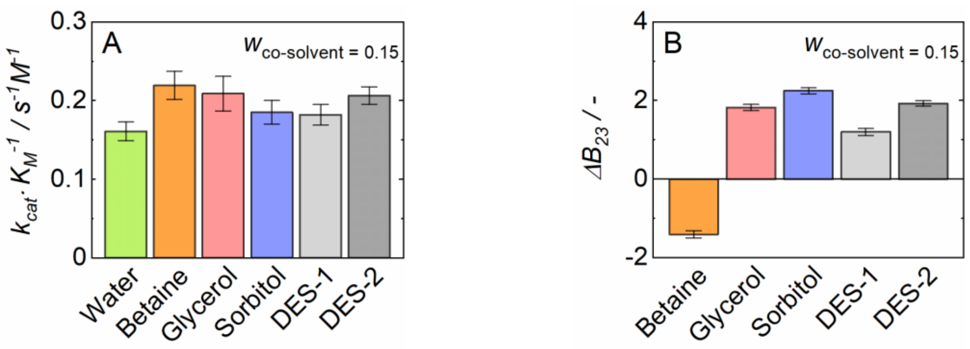

Figure 1. (A) Catalytic efficiency of cbFDH under $w_{cosolvent}$ = 0.15 at 298.15 K and (B) ΔB_{23} cbFDH-cosolvent second virial coefficient obtained by differential scanning fluorometry.

OC 24. Membrane Design using Deep Eutectic Systems for CO_2 Separation Processes

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Keywords: gas separation, membranes, CO_2 solubility, gas separation

CO_2 anthropogenic emissions are responsible for climate changes and the current climate crisis, having a direct impact in our society, economy, and health. It is therefore urgent to find technologies and solutions to deal with this problem. Given that the radical change to zero CO_2 emissions is possible, it is a goal that is still being challenged for economic and political reasons. The most immediate, practical and pragmatic way to diminish CO_2 emissions, is to consider post-combustion capture strategies, that capture and separate CO_2 before its emission into the atmosphere. In the last years, deep eutectic systems (DES) have been considered as potential solvents for CO_2 solubilization and therefore its capture. Various DES have been tested as CO_2 absorbents, such as the ones composed of choline chloride (ChCl) and urea or glycerol, showing high CO_2 solubility [1]. ChCl:urea (1:2) and ChCl with glycols, such as glycerol have been tested for CO_2 absorption. The solubility of CO_2 in DES supported membranes was also determined, exhibiting good selectivity towards CO_2 compared to CH_4 and N_2 [2]. The use of enzymes, such as carbonic anhydrase (CA), can also improve the absorption process of CO_2 in these systems [3]. In this work, different families of DES were studied regarding CO_2 solubility, mainly based in betaine, with different amounts of enzyme CA (0.01 and 0,1 mg/g_{DES}). Also, these DES were supported in a PTFE porous polymeric support, and the permeability of these membranes to different gases such as N_2, CH_4 and CO_2 was determined. The ideal selectivity of the DES supported membranes was determined, yielding very promising results. The results obtained also considered the viscosity of the DES, and the influence of their water content in their properties and on the CA activity. The results obtained show that DES supported membranes are efficient in selective absorption of CO_2 in ideal gas mixtures, especially ChCl based ones, and these membranes have the potential application for biogas upgrading.

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OC 25. Eutectic Mixtures for Enzymatic Catalyzed Reactions

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Keywords: lipase, laccase, NADES (natural deep eutectic solvents), new polymers

The enzymatic synthesis as a green route for producing polymers has proven to have a significant impact on lowering the toxicity and operational costs normally generated by chemical procedures [1-3]. Aiming to design environmental-friendly processes to eliminate, or reduce, the use of toxic chemicals, we propose the use of natural deep eutectic solvents (NADES) as reaction media for lipase and laccase polymeric catalysis. In this sense, several deep eutectic mixtures have been created by combining natural compounds chosen for their origin, low toxicity, and enzyme biocompatibility [4,5]. As a cost-effective and green approach to producing a wide range of esters, lipase-catalyzed esterification in anhydrous media offers a new path. These esters are produced by combining organic acids with alcohols and are used in a wide range of industrial applications [2]. Herein, we use the constituents of NADES as a source of monomers for the synthesis of small polymers through esterification catalyzed by lipase in an anhydrous and solvent-free medium. The work's findings are quite promising, as novel polyesters with a significant degree of polymerization and a high conversion yield were obtained. Another application of NADES as a reaction medium is in the production of new polyphenolic polymers through laccase-catalyzed oxidation. The natural eutectic mixtures acted as laccase stabilizers in the reaction media and assisted the dissolution of phenolic compounds with low water solubility. Catechol and extracts from natural sources were used as substrates to create novel polyphenolic polymers through reactions catalyzed by laccases using NADES as solvent. The synthesis of polymers via lipase or laccase catalyzed polymerizations using NADES, combined with their non-toxicity, low cost, and ease of preparation, sets up these solvents as a greener and cleaner approach for the synthesis of high-value-added products.

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OC 26. Deep Eutectic Solvent-based Preparation of Chitin-based Biomaterials: Effects of Deep Eutectic Solvent on Production and Properties of the Materials

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Keywords: deep eutectic solvent, chitin-glucan complex, chitin-glucan nanofiber, nanofibrillation, esterification

Chitin-glucan complex (CGC), which is a natural bio-copolymer of chitin and glucan covalently bound to each other and is derived from fungal cell wall, has many advantageous properties including biodegradability, biocompatibility, antibacterial activity and high adsorption capacity. Thus, CGC has various potential applications such as drug delivery, wound healing and heavy metal removal. Previously, we used deep eutectic solvents (DESs) to pretreat *Agaricus bisporus*, commonly known as white button mushroom to prepare CGCs for the first time. As a result of diverse combinations of hydrogen-bond donors and acceptors in DESs, CGCs could be prepared to have varying properties and structures. Importantly, certain DESs could help produce CGCs that appeared preferable to further functionalization and application for subsequent biomaterial preparations. It is known that nanofibrillation of chitin enhances homogeneous dispersion of chitin in water and thus expands its utilizations despite its insolubility. Hence, we aimed to prepare chitin-glucan nanofibers (CGNFs) by esterification of CGC using acidic DESs. To this, two potential factors were examined on the nanofibrillation efficiency: pretreatment steps (removal of water-soluble material by hot water treatment, protein removal by alkali treatment and deglucanization by acid treatment) to prepare CGC and acidity of DESs. As a result, hot water treatment and deproteination was sufficiently effective to disintegrate the aggregated mushroom structure and remove alkali-soluble material, respectively; removal of water-soluble glucan by deglucanization did not improve the CGNF production. The resulting CGCs were further treated with a variety of acidic DESs; DESs containing more acidic HBDs yielded higher degrees of esterification, leading to better nanofibrillation. Suspension of the successfully prepared CGNFs displayed high permeability and dispersibility. This study shows that DESs can be applied for efficient preparation of chitin-based biomaterials under relatively mild and ecologically benign conditions.

OC 27. Alternative Media for Ocular Drugs Based on Natural Deep Eutectic

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Keywords: ocular drugs, natural deep eutectic systems, drug delivery, ocular diseases

More than 2 billion people in the world suffer from some type of vision impairment or blindness, and at least half of them have a treatable or preventable condition using proper treatment [1]. Topical eye drops remain the most convenient route for ocular drug administration; but, the physiology of the eye limits their use, especially because most drug is lost to precorneal drainage and only a small portion is absorbed at the nasolacrimal duct, becoming systemically available [2]. Therefore, during the design of an ocular formulation it is important to increase the retention time of the drug in the ocular surface. There are several strategies for this, but in this work we explore for the first time the use of Natural Deep Eutectic Systems (NADES) as a new media for ocular drugs, mainly due to their intrinsic viscosity. Hence, several systems composed of different combinations of sugars, polyols, amino acids, and choline derivatives were prepared. Then, NADES aqueous solutions were characterized in terms of rheological and physicochemical properties. The results obtained showed that NADES solutions have an optimal viscosity profile (0.8 to 1.2 mPa.s). Moreover, other parameters were also within the standard values including osmolarity (412 to 1883 mOsmol), and pH (7.4). Additionally, contact angle and refractive index were determined. Furthermore, the selected systems showed low cytotoxicity towards retinal epithelium cells (ARPE-19 cells).
In summary, NADES have promising physical and chemical properties to be used during the design of ocular formulations.

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OC 28. Characterization of Eutectic Mixtures of Sugars and Sugar-alcohols for Cryopreservation

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Keywords: Natural Deep Eutectic Systems, water activity, molar excess volume, thermal analysis, Raman spectroscopy

Natural Deep Eutectic Systems (NADES) composed of sugar and sugar alcohols have been studied and applied in a variety of biological applications. Understanding their interaction with water across dilution and temperature is inherently important for maximizing the utility of NADES. Herein a wide range of sugar:sugar-alcohol molar ratios were synthesized and characterized by viscosity, molar excess volume, differential scanning calorimetry, water activity, and confocal Raman cryomicroscopy. NADES were found to have greater viscosity, reduced heat of fusion, greater absolute molar excess volume, lower water activity, and stronger hydrogen bonding of water than non-NADES mixtures. This is hypothesized to be due to cumulatively stronger hydrogen bonding interactions between components in pure and diluted NADES with the strongest interactions in the water-rich region. This work provides useful data and further understanding of hydrogen bonding interaction strength for a wide range of molar ratios in pure to well- diluted forms.

OC 29. NADES-based Cork Extractives as Green Ingredients for Cosmetics and Textiles

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Keywords: Cork extractives, cosmetic formulations, dyeing/coloration of cotton fabrics.

A significant increase in the sales of natural goods is being observed, especially in Europe. The cosmetic and textile industries are no exception, and the current trend is to develop environmentally friendly products made from natural ingredients.

Cork is a biodegradable and renewable bioresource. This material is used in a variety of applications due to its unique properties, such as high elasticity, low permeability to liquids, and resistance to microbial activity [1,2]. Due to its abundance and distinct chemical composition, cork, has emerged as the most promising component for the development of new chemical products and materials derived from cork by-products [3]. Cork extracts contain components of interest with special properties including antioxidant, anti-inflammatory, and antibacterial activity, that might improve the effectiveness of cosmetic formulations, currently on the market, and may impart new characteristics to textiles. Freitas et al. produced cork extracts using natural deep eutectic mixtures to design environmentally benign processes to eliminate/reduce the use of toxic chemicals [4]. They also confirmed that physical properties of NADES, like polarity and viscosity, influence greatly the extraction process [5]

Herein, the main goal was to investigate the effect of NADES-based cork extracts on cosmetic formulations and on cotton fabrics dyeing. The extracts improved the antioxidant performance of the cosmetic formulations and no cytotoxic effect was detected. Also, cotton fabrics were efficiently dyed with these cork extracts which conferred to these substrates' antioxidant and antibacterial ability.

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OC 30. Modulation of Spirulina Extraction using Octanoic Acid-Based NaDES with Respect to COSMO-RS Predictions

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Keywords: NaDES, COSMO-RS, microalgae, green chemistry, modulation, selectivity

Microalgae are a growing interest in the field of cosmetics as a natural source of valuable and renewable molecules [1]. Among them, chlorophylls, carotenoids or free fatty acids (FFA) are high-values compounds based on their anti-inflammatory, moisturizing and regulating properties of the skin microbiota [1]. For this purpose, Natural Deep Eutectic Solvents (NaDES) have been studied herein as a sustainable alternative, therefore numerous combinations of NaDES have been tested for investigating their biomass extraction potential. Thermodynamic property prediction tools, such as COSMO-RS, are now widely used to prescreen NaDES potential candidates prior testing them experimentally. During this work, an *in silico* screening of several NaDES combinations with respect to chemicals available in our library has been conducted to modulate the non-polar pigments / FFA selectivity during the Spirulina extraction process. Indeed, this modulation was conducted based on the NaDES, non-polar pigments and FFA sigma profiles to evaluate their potential interactions in solution. Building on this methodology, non-polar NaDES based on a short chain fatty acid, *i.e.* octanoic acid (C8), were selected as promising candidates for FFA extraction. Indeed, C8 is a well-known compound for such a purpose within the objective to modulate its extraction ability when making a NaDES [1]. Thus, the extraction potential of a NaDES exclusively based on carboxylic acids, *e.g.* C8-C10, was compared to those obtained when C8 is associated with rather menthol or 2-phenoxyethanol. Tested NaDES formulations were preselected thanks to COSMOthermX solid-liquid equilibrium (SLE) calculations to localize their eutectic point. DSC measurements of formulated NaDES were then realized to critically evaluate COSMOthermX SLE predictions. During this talk, the implementation of this original method will be assessed along with experimental results to selectively extract high values compounds from Spirulina.

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OC 31. Sustainable Extraction of Perfumery Plants using Deep Eutectic Solvents and Ionic Liquids

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Keywords: essential oil; deep eutectic solvent; ionic liquid; GC-MS/FID analysis

Most industrial extraction processes of perfumery plant rely currently on maceration or hydrodistillation techniques. In the former case, non-sustainable organic solvents such as hexane, heptane, petroleum ether and ethanol are usually employed. Hydrodistillation, on the contrary, rely only on water, but has a high energy consumption related to water evaporation and cooling of vapours generated during the distillation process [1].

In order to propose alternative solutions not relying on organic solvents, and in order to increase the yield in hydrodistillation processes, this work reports extraction of perfumery plant using sustainable solvents, namely deep eutectic solvents (DES) or ionic liquids (IL) combined with hydrodistillation. DES have recently attracted considerable attention due to the fact that they are more eco-friendly, can be non-toxic and exhibit low volatility compared to conventional organic solvents [2]. Such DES can be used as a co-solvent with water in hydrodistillation in order to enhance extraction of volatile compounds, without having traces it in the resulting essential oil.

Therefore, in this study, extraction of volatile compounds from pink pepper (*Schinus molle*) was studied combining maceration using DES based on choline chloride and citric acid, as well as ILs based on cholinium cation, with hydrodistillation. Extraction efficiency was evaluated using gas chromatography coupled with mass spectroscopy and flame ionization detection (GC-MS/FID) which is a reference method to identify and quantify the volatile compounds [3]. The influence of IL and DES structures, with or without a carboxylic acid, on the nature and amount of fragrance compounds extracted is reported ad discussed. In addition, sensory analysis for all essential oils obtained in this study was carried out.

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OC 32. Catalytic Hydrogenation of Xylose using DES as a Solvent

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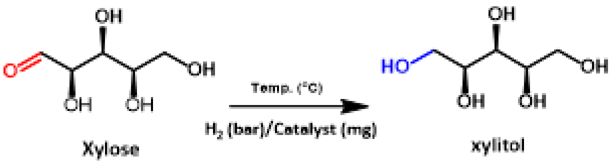
Keywords: hydrogenation, xylose, choline chloride, catalyst

The depletion of fossil carbon resources and increasing concerns on global warming are the major factors that elevated the need to change radically the way we produce, consume and use natural resources. In recent years, renewable resources, particularly lignocellulosic biomass have gained immense attention in sustainable production of fuel and platform chemicals for fossil-free, energy rich and CO_2-neutral chemical industry. In lignocellulosic biomass, a particularly interesting group of molecules derived from carbohydrates fraction are sugar alcohols (i.e. xylitol, galactitol and sorbitol). Sugars alcohols find various application in sugar-free foods and food products as thickeners and sweeteners. For instance, xylitol is a sweetener, which has been commercialized due to its striking properties as high solubility in water, stability upon storage and does not caramelize at elevated temperatures. Xylitol is produced by catalytic hydrogenation of xylose in triphasic batch reactors, where the reagent and catalysts are dispersed in an aqueous medium. Raney Ni catalyst is mainly adopted in such reaction owing to its comparable activity and lower price index to noble metals based catalysts.

We have demonstrated that bimetallic nickel-iron based nanoparticles synthesized by simple one-pot hydrothermal method are active and selective in the hydrogenation of sugars to sugar alcohols. To investigate the catalytic performance of Ni_3Fe_1 bimetallic nanoparticles, hydrogenation reactions were performed in both Deep Eutectic Solvent (DES) and aqueous-phase starting from biomass derived monosaccharides (xylose, mannose, rhamnose, arabinose) (Scheme 1). The comparison of both phase reactions demonstrates that the bimetallic nanocatalyst is three-fold more stable in aqueous phase than in DES-phase reaction but the use of DES allows the increase of the productivity. Analysis of the spent catalyst shows that the deactivation of Ni_3Fe_1 BMNPs is due to the absorption of organic species from DES component at the surface of the catalyst leading to the poisoning of the active sites. The efficient catalytic activity of Ni_3Fe_1 BMNPs is ascribed to the synergistic actions of Ni and Fe bimetallic composition.



Scheme 1. Hydrogenation of D-xylose to xylitol by using Ni_xFe_y bimetallic NPs.

OC 33. Low Temperature Biomass Deconstruction Using a Metal Salt Hydrate Based Deep Eutectic Solvent (DES)

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Keywords: metal salt hydrate, deep eutectic solvent (DES), biomass, low temperature

Deconstruction of lignocellulosic biomass and conversion into biofuels and bioproducts are key routes toward a sustainable bioeconomy, paving the path for economic growth, mitigating climate change, ensuring future energy security and improving human and ecological health. However, attaining scalable biomass conversion is faced with some challenges which include water and power consumption, consolidation of unit operations, utilizing mixed biomass (MB), a sustainable solvent recycling and lignin upgradation. The key point of efficient utilization of lignocelluloses is their disassembly by a simple and mild method and then conversion of the relative fractions to valuable building block molecules, intermediates, or materials. So, molten salt hydrates may be a suitable medium for efficient and direct production of lignin and relative monosaccharides in a one-pot process, especially with various molten salt hydrates by recovery and reutilization. A systematic design of solvent-based deconstruction of biomass, whereby the solvent type acts as a hydrogen bond molecular scissors to realize the room temperature dissolution of cellulose. A metal salt hydrate-based deep eutectic solvent (DES IV) (MSH-DES) that involves metal salt hydrate (as H-bond acceptor) in combination with a H-bond donors is a promising alternative solvent for dissolving cellulose due to its low cost and high H-bond accepting ability. Furthermore, the inclusion of water acts as an essential constituent to regulate the behavior of the ions and the catalytic effect. Herein, we are taking the systematic approach towards a facile, low temperature and quick one-step method to isolate high-purity lignin and degrade cellulose and hemicellulose to relative monosaccharides from lignocellulosic biomass. This process is the basis for efficient conversion of lignocellulose to valuable chemicals and materials. The aim of this work is to demonstrate that MSH-DES could be used as a solvent, which could swell and dissolve cellulose and hemicellulose quickly and completely and at low temperatures. Furthermore, cellulose and hemicelluloses can be hydrolyzed under acidic conditions and isolate lignin as an insoluble residue (IR). In addition, an environmentally friendly and efficient method to recycle and reuse MSH-DES from filtrate will be at the same time be developed.

OC 34. Deacetylation of Mannosylerythritol Lipids in Hydrophobic Natural Deep Eutectic Solvents

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Keywords: biosurfactants, Candida antarctica lipase B, deacetylation, deep eutectic solvents, lipase, mannosylerythritol lipids

Mannosylerythritol lipids (MELs) are a promising group of biosurfactants due to their high fermentation yield, self-assembling properties and biological activities. During the fermentation, a mixture of MELs with different level of acylation is formed. From this mixture, the fully deacetylated form (MEL-D) is the most valuable. To decrease the environmental impact of the deacetylation and to exclude toxic contaminants, an enzymatic process with natural deep eutectic solvents (NADES) was developed in this study.

We tested the deacetylation of purified MELs mixture with immobilized Candida antarctica lipase B enzyme and 2-ethylhexanol as co-substrate in 140 hours long reactions. As solvent, we compared four NADES, both hydrophilic (choline chloride-ethylene glycol) and hydrophobic (menthol-octanoic acid, thymol–menthol and thymol–coumarin), and as reference, pure 2-ethylhexanol (the co-substrate) and toluene (a commonly used volatile organic compound). We monitored the change in concentrations of the different MEL compounds by normal phase high performance liquid chromatography coupled with evaporative light scattering detector.

We reached the highest yield of MEL-D in the pure 2-ethylhexanol as solvent. However, the toluene and hydrophobic NADES systems had similar yields after 140 hours. In the hydrophilic NADES no conversion was observed and in menthol–octanoic acid we experienced a side reaction which led to the formation of triacylated MELs. The pathway of the reaction was the same in every system, MEL-A converted into MEL-C and then into MEL-D, while MEL-B directly converted into MEL-D. The main difference between the systems was the speed of turning MEL-A into MEL-C, which also determined the remaining amount of A and C compounds at the end of the reaction in the different solvents.

Our results indicate that deacetylation of MELs mixtures in NADES as solvent is possible with comparable yields to common organic solvents and even to pure co-substrate. Hydrophobic NADES without carboxylic acid compounds facilitate the reaction the best. This method has a lower cost than using pure co-substrate as solvent and is environmentally less harmful than toluene, yet it has comparable yield of the target product.

OC 35. Surfactant Self Assembly in Halogen Free Deep Eutectic Systems

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Deep eutectic solvents (DES) are an emerging class of modern, often “green” solvents, that can be formed by mixing a different components, often quaternary ammonium salts with sugars, metal salts, carboxylic acids, amino acids or alcohols, to create hydrogen bonded room temperature liquids with a decreased melting point in comparison to their components. They can exhibit unique properties and high tailorability, making them interesting in a wide range of fields such as for electrodeposition, synthesis, extraction or for pharmaceutical applications. DES have been found to support the self assembly of a range of amphiphilic molecules, and the type of surfactants and interaction of the surfactant molecule with the solvent components, as well as additives, have been found to influence the size, shape and morphology of the self-assembled structures formed. Research is also being conducted into their application for e.g. templating of mesoporous materials or emulsification for transdermal drug delivery.

Most of the commonly used DES are formed from components that contain halide ions, and are often not be compatible for applications such as in catalysis, where the presence of halide ions can poison the catalyst. Here we present the formation and structures of cationic and non ionic surfactant micelles in glycerol based halogen free DES systems, investigated through small angle neutron scattering. Factors such as DES components and composition, and surfactant head group and tail length will be discussed.

OC 36. Propeline: A New Candidate for Precious Metal Recovery

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Keywords: ionometallurgy, precious metals, electrochemistry

Nowadays, the recovery of precious metals (Ag, Au, Pd...) is mainly carried out using pyro- or hydrometallurgical processes consisting of numerous steps which generate a lot of waste products. In particular, due to the use of toxic compounds e.g cyanides with strong complexing properties, these wastes require additional specific treatments before their disposal. For the sake of greener process, ionometallurgy appears an attractive alternative. Indeed, this route uses ionic solvents with high complexing and conductive properties in addition to being thermally (low volatility) and electrochemically stable (working in a wide range of potential). This last criterion is very important here with the use of a single electrochemical allowing electro-leaching at the anode and electro-deposition at the cathode, to recover precious metals e.g Au, Pd and Ag from electronic waste. Previous work on this subject revealed the effectiveness of 1:2 mixture of choline chloride (ChCl) (hydrogen bond acceptor) with ethylene glycol (EG) (hydrogen bond donor), called ethaline (ET). Thus, from these first encouraging results and to make the process greener, this work focuses on the substitution of EG by propylene glycol (PG) another hydrogen bond donor of similar structure but far less toxic, actually used in cosmetics and pharmaceuticals. The mixture of PG and ChCl is called propeline (PROP). Bulk properties of PROP required in the electrochemical process, density, viscosity, conductivity, electrochemical stability have been determined. Then, PROP and ET were compared when used in the electrochemical cell, indicating comparable performance in the leaching of Au, Ag and Pd. An analytical method for elemental analysis by ICP-OES in leachates was developed for this purpose. Furthermore, metal speciation in the PROP or ET leachates by spectroscopic methods such as UV-Vis, and EXAFS/XANES at SOLEIL facility are very similar. Finally, the electrochemical deposition step was evaluated by the electrochemical determination of kinetic parameters and the diffusion coefficients of the electroactive metal species involved.

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OC 37. Separation of Furfuryl Alcohol from Water using Hydrophobic Deep Eutectic Solvents

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Keywords: hydrophobic DES, furfuryl alcohol, PC-SAFT, Molecular Dynamics

Furfuryl alcohol (FA) is an important organic chemical feedstock, mainly used to produce furan resins with various properties, such as plasticizers, solvents, and rocket fuels. Nevertheless, FA must be separated from the water solution due to its environmental and human health risks. Due to the presence of an azeotrope in the aqueous solution of FA, the separation of FA from water with conventional distillation methods is problematic. Therefore, other strategies for separation have to be used, such as liquid-liquid extraction. In this work, menthol, thymol, and octanoic acid based hydrophobics deep eutectic solvents were investigated to extract furfuryl alcohol from water at 313.15 K and 1 atm. Three DES were used: thymol + octanoic acid (1:2), L-menthol + octanoic acid (1:2), and thymol + menthol (1:1). In addition, the results were complemented with PC-SAFT modeling and MD simulations using the Martini 3 Coarse-Grained force field , as is shown in Figure 1.

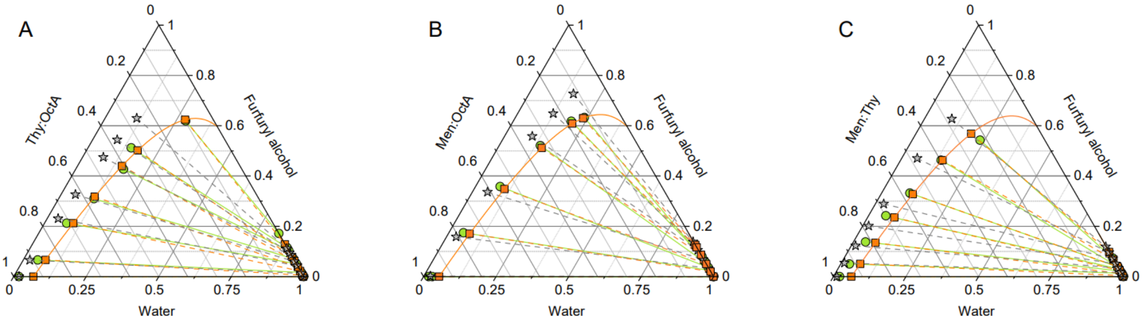

Figure 1: Liquid-liquid phase diagram for the water + furfuryl alcohol + DES systems at 313.15 K and 1 atm. DES: (A) Thymol + Octanoic acid (1:2), (B) L-Menthol + Octanoic acid (1:2) and (C) L-Menthol + Thymol (1:1). Experimental data (●), PC-SAFT (■) and Martini 3 (★).

The experimental determination of liquid-liquid equilibrium (LLE) displays that the selectivity of DESs have values comparable to that found in n-propyl acetate or ethyl acetate and superior to other traditional organic green solvents, such as 1-pentanol and n-butanol. On the other hand, high distribution coefficients were obtained for L-menthol + octanoic acid (1:2) and thymol + menthol (1:1), whereas thymol + octanoic acid (1:2) behaves like the other organic solvents in the literature. The combination of a molecular-based equation of state (i.e., PC-SAFT) and molecular simulation provides an adequate route to model the experimental data in a predictive way.

OC 38. Screening of Acidic Deep Eutectic Solvents for Valuable Metals Extraction from Wasted Lithium-ion Batteries

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Keywords: spent lithium-ion battery, lithium, cobalt, deep eutectic solvents, recovery, COSMO-RS

The large pile-up of spent lithium-ion batteries (LIBs) due to their widespread use in energy storage and electronic devices poses serious environmental risks. Spent LIBs contain heavy metals and toxic chemicals that can pollute land and water bodies. On the other hand, recycling spent LIBs provides additional benefits of recovering valuable metals such as lithium (Li) and cobalt (Co) from the cathode component. As a result, several governments have legislated laws to encourage the recycling of end-of-life LIBs. Among the recycling processes used in valuable metal recovery from spent LIBs, hydrometallurgy is a promising process. However, the use of toxic and harmful solvents in hydrometallurgy is a serious issue. Hence, the search for alternative green solvents is extremely important. Deep eutectic solvent (DES) has been proposed as a viable alternative to conventional solvents for recovering valuable metals from spent LIBs via the hydrometallurgical process. However, effective DES design for metal recovery from spent LIBs is vital to improving this green solvent's potential for industrial applicability. Thus, this study combines DES screening model using the Conductor-like screening model for realistic solvents (COSMO-RS) and experimental evaluation of the solubility of Li and Co in the several DESs. Firstly, several DES starting components are modeled in COSMO-RS to predict their affinity for Li and Co. Based on the screening results, six acidic DESs were synthesized to evaluate their potential for metal recovery from spent LIBs. Among the synthesized DESs, Glycine:Ascorbic:Water-based DES performs best in spent LIB cathode leaching experiments. The ascorbic acid: glycine-based DES showed excellent performance with an extraction efficiency of 97.15% and 82.45 % for Li and Co, respectively, under mild conditions. This enhanced performance of the DES is attributed to the combined reducibility, acidity, and complexation abilities of the DES for valuable metals from the spent LIB.

OC 39. Glycol-based Eutectic Solvents for Separating Methoxyphenols from Aliphatic Solvents

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Keywords: guaiacol, isoeugenol, liquid-liquid equilibrium, choline chloride, glycols

Bio-oil obtained from lignocellulosic biomass pyrolysis is a potential alternative for providing platform chemicals to replace oil derivatives. However, bio-oil is composed of highly oxygenated molecules that require conversion or extraction. Methoxyphenols are bio-oil compounds that are precursors of products typically obtained from crude oil like benzene, toluene, etc. Thus, it is important to understand how to separate the methoxyphenol families from bio-oil for performing their upgrade into value-added products. In this work, the liquid-liquid equilibrium of the mixture composed of guaiacol + n-hexane + ethylene glycol, 1,2-propanediol, or 1,4-butanediol was studied. Also, DES with a molar ratio of 1:4 of choline chloride:glycol was used instead of pure glycol in order to assess the selectivity and distribution ratio of guaiacol when using both types of solvents. Results were modeled using PC-SAFT. Also, the density and viscosity of mixtures composed of guaiacol + glycol and guaiacol + DES were measured and modeled using PC-SAFT and free volume theory, respectively. Results shown in Fig.1 suggest that all the DES improve the selectivity for guaiacol compared with pure glycols. Viscosities of guaiacol + solvent are higher, and excess volumes are more negative when using DES. Models properly represent all the experimental results reported in this work.

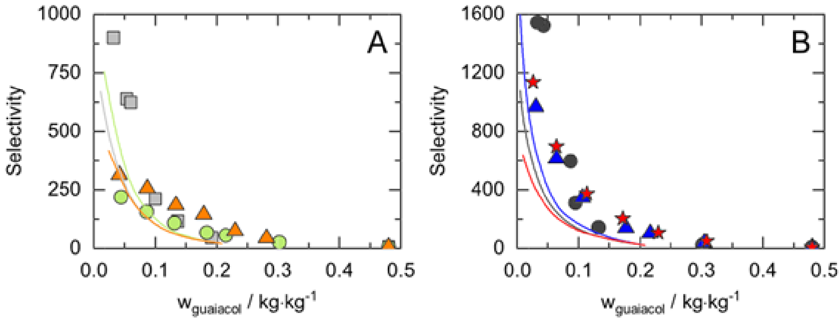

Figure 1. Selectivity of guaiacol in the (A) guaiacol + n-hexane + glycol or (B) guaiacol + n-hexane + glycol-based DES systems at 313.15 K and 101.3 kPa

OC 40. Thermal Conductivity Modelling of Deep Eutectic Solvents by Atomic and Group Contribution Models

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Keywords: DES; green solvent; physical property; modeling; thermal conductivity.

Deep Eutectic Solvents (DESs) are the most recently introduced green solvents by Abbott et al. in 2003 [1]. They showed various interesting properties and applications which lead to being studied significantly by various researchers and scientists. One of their interesting applications is their use as thermal fluids. In addition to their environmental advantages, low cost, and easy preparation, the low melting point for most of them and also high liquid temperature range are the most important characteristics which make them good candidates for use as thermal fluids in various applications. In order to investigate DESs in this field, some physical properties of them should be available. Thermal conductivity is one of those important physical properties. By considering the wide range of various nature DESs and the large number of introduced DESs, it is vital to have a general thermodynamic model for predicting the thermal conductivities of various DESs. Up to now, most of the presented models, are just case-specific and simple ones which are not a good tool for the prediction of the whole DES family. Therefore, it is vital to propose a predictive, general, simple, and accurate model for the prediction of thermal conductivities of various nature DESs. In this study, two predictive atomic and group contribution models have been proposed for this purpose. For the development of those models, a large data bank including 338 data points from 73 various nature DESs has been gathered from open literature and investigated. The developed group and atomic contribution models, in addition to generality and good performances for prediction of thermal conductivities, showed AARD% of 7.65 and 9.52, respectively which show high accuracy of both models.

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OC 41. Design of Deep Eutectic Solvents: A Priori or a Posteriori Information?

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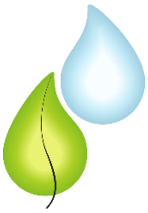
Keywords: solid–liquid equilibria, activity coefficients models, polymorphism, cocrystal

Deep eutectic solvents (DES) design commonly refers to defining the melting temperature of the eutectic mixture at any ratio between the constituents. Solid–liquid equilibrium (SLE) is the principal knowledge to design DES. From a thermodynamic perspective, SLE can be modeled by knowing the pure components melting properties, the liquid phase nonideality, and the type and form of the crystallized solids [1]. Because the liquid phase nonideality, i.e., the intermolecular interactions between unlike molecules, is considered the main characteristic that defines the DES, most SLE in DES studies focus on modeling liquid phase nonideality using thermodynamic models. Accordingly, it becomes widely accepted that the only missing piece of information to predict the phase diagram of DES is the liquid phase nonideality. In recent years, the available data for the SLE phase diagram of eutectic systems have increased significantly, which fueled the interest in using and developing predictive thermodynamic models based on group-contribution, quantum mechanical, or machine learning methods. Data-driven methods are scientifically sound and could provide reliable estimates for the activity coefficients of the components. However, the authors often rely on uncertain experimental SLE data as a training or validation set, unreasonable estimates for the melting properties of thermally unstable substances, and improper modeling of SLE in case of solid–solid transition or cocrystal formation. This work highlights the main challenges in modeling and predicting SLE in DES. First, we review the melting and transition properties of common DES constituents, including their different polymorphs. Second, we present the proper experimental and modeling procedures for obtaining the SLE data. Finally, we discuss the challenges that hinder the development of fully predictive methods for designing DES. We hope this work emphasizes the general requirements to help establish DES designing methods properly.

[1] Alhadid, A.; Jandl, C.; Mokrushina, L.; Minceva, M. *Cryst. Growth Des.* **2022**, *22*, 1933-1942.



POSTER PRESENTATIONS

P 1. Origin of Structural and Dynamic Heterogeneity in DL-menthol based Hydrophobic Deep Eutectic Solvents

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Keywords: hydrophobic deep eutectic solvents, hydrogen bonding, structure function, molecular dynamics

Researchers have recently been inspired to investigate water-immiscible deep eutectic solvents with hydrophobic properties and greener starting materials because of their unique potential applications.[1] Understanding the structure and dynamics of these hydrophobic deep eutectic solvents (HDESs) will help maximize their employment in various potential applications. Herein, we utilized atomistic molecular dynamics simulations to unveil bulk phase morphology and dynamics associated with DL-menthol based HDESs having different alkyl chain lengths of organic acids as hydrogen bond donors. We found evidence of intermediate-range structural ordering in these HDESs through observation of a prepeak in the simulated total X-ray scattering structure function (S(q)s). Following the polarity-based partitioning scheme of total S(q)s, we demonstrated that the prepeak results from the self-segregation of polar groups of DL-menthol and organic acids. The presence of strong intermolecular menthol-menthol, acid-acid, and menthol-acid hydrogen bonding interactions govern the structure of these HDESs.[2] These strong hydrogen bonding interactions are observed between the acid's carbonyl oxygen and the menthol's hydroxyl oxygen with the hydroxyl hydrogen of both acids and menthol, marked by longer hydrogen bond lifetimes. We observe a shorter hydrogen bond lifetime and faster decay rate corresponding to weaker hydrogen bonds between hydroxyl oxygen of acids with hydroxyl hydrogens of menthol and acids. These HDESs exhibited dynamic heterogeneity in the displacements of the DL-menthol and organic acid molecules.[3] As the organic acid's tail length increases, the overall dynamics of HDES become slow. The longer alkyl chain length of acids is more water stable, marked by stronger hydrogen bonding interactions. Thus, lesser HDES will migrate toward the water phase during the extraction process due to slower dynamics, suggesting that increasing the chain length of acid would increase the extraction efficiency, which is also observed experimentally.[4]

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P 2. Enthalpies of Adding Water to Water:NADES Mixtures

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Keywords: NADES, calorimeter, enthalpies, water

Natural Deep Eutectic Solvents are green solvents composed of supramolecular interactions of two or more natural compounds. In these solvents, water plays an essential role in tuning their proprieties; it can be an integral part of the structure or a solvent. In this work, we study the impact of adding water to a previously prepared NADES through isothermal nano-titration calorimetry. Upon adding water to NADES, dual behaviour of the heat flow peak is observed (Figure 1), with a first endothermal step followed by an exothermal. The heat produced by water incorporation into NADES structure and NADES solubilization will be discussed.

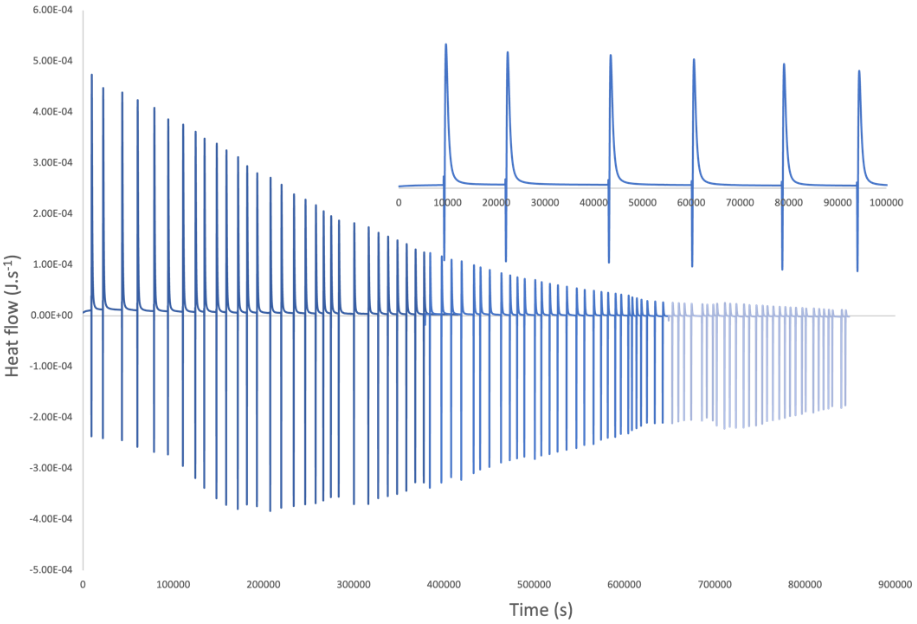

Figure 1. Heat flow variation caused by water addition (10 μL) to.56 mg of Betaine:Urea:Water (1:1:2) NADES.

P 3. In Search of Parameters That Can Help Explain the High Solubility Capacity of Natural Deep Eutectic Systems

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Keywords: NADES, solubility, polarity, dipole moment, Kamlet-Taft parameters, HSPs, ibuprofen

Among the various remarkable features of Natural Deep Eutectic Systems (NADES) such as low-cost preparation, biodegradability, low toxicity, etc., it is also known that many of these formulations, when employed as solvents, exhibit a relatively higher solubilizing character for some organic compounds as Actisve Pharmaceutical Ingredients (APIs)) than pure water. However, the mechanics behind this behaviour is still not well understood. Therefore, this work aimed to explore more about this subject, through the study of ibuprofen´s solubility in various hydrophilic and hydrophobic NADES. This evaluation was carried out through a set of theoretical models (empirical and semi-empirical) that allowed estimating the Hansen Solubility Parameters (HSPs), which is a very useful tool that has been used in many fields, but little explored in those that involve eutectic mixtures. Thus, in summary, in this work, first, the HSPs of selected NADES as well as ibuprofen were predicted using empirical models based on the group contribution method; secondly, the systems were prepared and characterized physicochemically through properties such as viscosity, density, molar volume, dielectric constant, refractive index, dipole moment, surface tension, solvatochromic parameters (polarity and Kamlet-Taft parameters) and FTIR; third, some of these parameters were used to semi-empirically estimate the HSPs, i.e., through their correlations; and, finally, both approaches were validated using the experimental solubility data obtained by the HPLC technique. The results showed that although the models studied were not able to explain the order of solubility found, they proved to be very useful in screening good (hydrophobic) and bad (hydrophilic) solvents for ibuprofen. Furthermore, among all tested models, the empirical one proposed by Hoftyzer and Van Krevelen proved to be the most suitable and recommended for use in the NADES area.

P 4. Modeling the Viscosity of Binary Eutectic Systems at Different Compositions and Temperatures

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Keywords: deep eutectic solvents, mixing rules, solvents design, green solvents, physical property

Deep eutectic solvents (DESs) are considered as promising green alternatives to common organic solvents in various applications. For utilizing DESs in process applications, it is essential to study their viscosity. In this work, the modified Adam-Gibbs (AG) and Vogel-Fulcher-Tammann (VFT) models were combined with 12 mixing rules to calculate the viscosity of 11 L-menthol-based binary eutectic systems (ESs) at various temperatures and compositions. The modified AG and VFT models were adopted to predict the viscosity of pure constituents below their melting temperatures, while the mixing rules were used to estimate the viscosity of ESs. It was found that the VFT model predictions for the viscosity of pure constituents below their melting temperatures were generally higher than those predicted by the modified AG model. Accordingly, when combined with the 12 mixing rules, the modified AG model gave better predictions for the viscosity of ESs than the VFT model. The Grunberg-Nissan mixing rule with one adjustable parameter provided the lowest average absolute relative deviation between the calculated and experimental viscosity. This work shows that the available methods in the literature to model the viscosity of liquid mixtures can be applied to ESs. The key to obtaining satisfying predictions relies on the accurate prediction of the viscosity of pure compounds in their supercool region and the judicious selection of mixing rules.

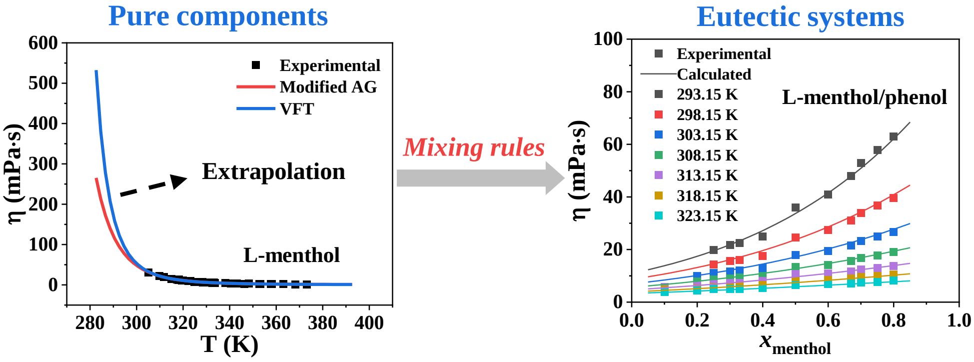

Fig. 1. Proposed viscosity calculation method for ESs.

P 5. Confining Deep Eutectic Solvents in Nanopores: Insight into Thermodynamics and Chemical Activity

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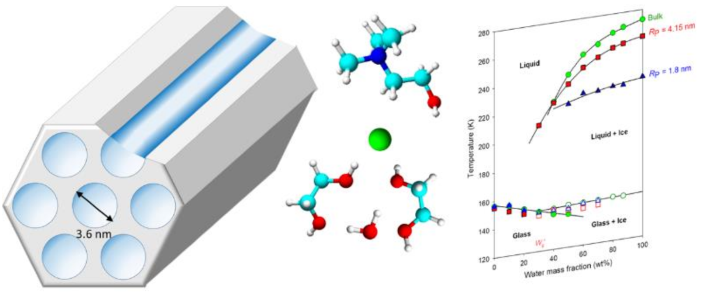
Keywords: DES in nanopores, confinement effects, thermodynamics, fundamentals

For many applications related to catalysis, electrochemistry, gas capture, and energy storage, solvents are not considered as bulk liquid phases but handled at solid interfaces or in mesoporous hosts. However, when they are spatially confined at the nanometer scale, several fundamental properties of liquids considerably differ from those of their bulk counterparts. While the effects of confinement on the physical properties of conventional liquids have been the subject of intense activity over the past two decades, the topic is still in its infancy regarding emerging new classes of alternative solvents.



We present a comprehensive thermodynamic study of the phase behaviour of aqueous solutions of the prototypical ethaline deep eutectic solvent (DES) when confined in well-defined nanochannels of mesotructured porous silica matrices MCM-41 and SBA-15, with pore radii RP = 1.8 nm and 4.15 nm [1]. Extremely deep melting depressions are attained in the confined states, due to the combination of confinement and cryoscopic effects. These phenomena are analysed quantitatively, based on a recently proposed extended version of the classical Gibbs-Thomson and Raoult thermodynamic approaches [1, 2]. In this framework, the predicted values of the water chemical activity in the confined systems are shown to systematically deviate from those of the bulk counterparts [3]. The origin of this striking observation is discussed with respect to thermodynamic anomalies of water in the 'no-man's land' and to the probable existence of specific nanostructures in DES solutions when manipulated in nanochannels or at interfaces with solids.

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P 6. Activity Coefficient Acquisition through Thermodynamics-Informed Active Learning: A Case-Study of Phase Diagram Construction

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Keywords: thermodynamics, machine learning, phase equilibria, Gaussian processes, deep eutectic solvents, acquisition functions

Knowledge on the activity coefficients of all components in a mixture, particularly their composition and temperature dependances, allows for the full determination of a wide range of thermodynamic properties. However, the experimental or computational measurement of activity coefficients is costly, time consuming, and error prone. As such, an intermediate approach is proposed in this work using Gaussian processes (GPs) and active learning. The term "intermediate" is used to signify a model that is not fully predictive (it requires some experimental data for any given system) but not fully correlative either (it requires less data than classical models, while being non-parametric and natively handling experimental uncertainty). The idea behind this strategy is to fit a GP to a limited amount of initial data, compute its standard deviation on a composition/temperature grid, and use a standard-deviation-based metric (known as acquisition function or policy) to select the next points to probe experimentally or computationally.

Active learning had a tremendous impact on the amount of data needed to describe the activity coefficients of the systems studied, which included simple organic mixtures, aqueous solutions of salts, and deep eutectic solvents. This was most beneficial when target-specific workflows were designed to construct VLE and SLE phase diagrams, with many cases requiring as little as a single data point to obtain accurate results. In particular, phase-diagram-targeted active learning was applied to describe the experimental SLE and VLE phase diagrams of deep eutectic solvents, a key step in the design of these novel solvents. Not only was active learning shown to be a valuable tool to minimize the amount of data needed to describe these datasets, but GPs were also shown to be superior to NRTL due to the scarce active-learning-acquired datasets and experimental uncertainty. These results also illustrated the myriad of modifications that can be undertaken to tailor both GP formulations and active learning workflows to specific computational or experimental applications, such as different GP inputs, active learning algorithms, and stopping criteria.

P 7. Type V Deep Eutectic Solvents: Design and Applications

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Keywords: green solvents, hydrogen bonding, solid–liquid equilibrium, terpenes, thymol, trioctylphosphine oxide

Unlike types I-IV, the recently proposed type V deep eutectic solvents (DESs) are prepared using solely non-ionic precursors. As such, they typically display lower viscosities than their ionic counterparts, non-negligible vapor pressures (may be advantageous for processes where solvent evaporation is desirable), and are chloride-free. Furthermore, while the design of hydrophobic types I-IV DESs is limited to the use of ions with large apolar volumes, there is ample choice of non-ionic substances that can be used to prepare type V DESs with different degrees of hydrophobicity. Through an in-depth study of solid-liquid equilibria, this work develops guidelines for the design of type V DESs, with emphasis given on how to choose HBD/HBA pairs that maximize the negative non-ideality (and, hence, the melting temperature depression) of the solvent.

The presence of hydrogen bonding in a mixture does not necessarily lead to negative deviations from ideality. As such, DES precursors should be chosen such that their intermolecular interactions when mixed are stronger than those present in their pure liquid phases (hypothetical or not). It is shown that this non-ideality can be achieved by selecting precursors with large polarity asymmetries (compounds possessing strong HBDs or HBAs sites without the ability of establishing strong hydrogen bonding within their pure phases), and the terms asymmetric HBDs (e.g., thymol) and lone HBAs (e.g., trioctylphosphine oxide) are introduced.

The framework developed in this work is particularly useful when trying to liquefy a compound with a desired property (e.g. complexation ability) through DES formation, so that it can be used as a liquid solvent. This target compound may already be an asymmetric HBD or lone HBA, as exemplified by thymol and TOPO, in which case it can be liquefied using a myriad of regular HBDs and HBAs, or may be a regular HBD/HBA, as exemplified by menthol, in which case an asymmetric HBD or lone HBA should be used for its liquefaction. The formation of polymorphs has a negative effect upon the melting temperature depression phenomenon that could be avoided by using molecules with poor crystal packing characteristics, as illustrated by the thymol/menthol system. Finally, thermodynamic models that can be used to screen possible precursors are also discussed.

P 8. Chemical-physical and Structural Properties of Choline Chloride:water systems: the Aquoline DES

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Keywords: water, hydrogen bonding, natural, NMR, X-ray scattering, ab initio Molecular Dynamics

Deep Eutectic Solvents (DESs) are promising eco-friendly solvents for many applications. Among these, Choline Chloride (ChCl)-based DESs have attracted great interest owing to ChCl non-toxicity and low cost. However, their high viscosity and hygroscopicity are significant drawbacks for extensive applications.

In this context, an aqueous mixture of ChCl was recently introduced as an auspicious and low-viscosity Deep Eutectic Solvent. Nevertheless, information regarding the role of water on DES formation is lacking, yet. To contribute to this issue, the behavior of different ChCl:H_2O mixtures at different molar ratios (1:n, with n=2-7, 10, 20) was investigated in terms of different physicochemical properties (density, viscosity and refractive index) and thermal behaviour via DSC measurements, together with NMR analysis and ab initio Molecular Dynamics simulations. DSC has been used to explore the solid-liquid equilibrium and identify the Deep Eutectic nature for ChCl:H_2O 1:4 (termed as *aquoline*). Temperature and composition dependence of density and refractive index were modelled with a master relationship aiming at detecting a general trend. The temperature dependence of the isobaric thermal expansion coefficient α was monitored. Upon increasing water content, an isosbestic temperature was detected, prompting for water-like evolution of hydrogen bonding correlations. NMR analysis and aiMD simulations suggest that ChCl-H_2O interactions lead to "rigid" and local structures that persist with increasing temperature. The formation of a semi-rigid framework related to the high solvation symmetry around chloride and high correlation between this latter and the water molecules. These results have important implications for understanding the role of water in these systems and for improving the design of new sustainable media with suitable properties.

P 9. Evaluation of the Structural Transformations of the System Reline:water by Molecular Dynamics

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Keywords: reline, water, Molecular Dynamics, structural transformations

Deep eutectic solvents (DES) emerged in the last decades as promising green solvent media in many chemical processes and applications where organic solvents are commonly used. A foremost feature of these solvents is the possibility of tailoring their physicochemical properties through the addition of water. The choline chloride-urea binary mixture in the molar ratio (1:2), commonly known as reline, is an archetypal solvent among deep eutectic solvents. Neutron diffraction (ND) and empirical potential structure refinement (EPSR) results provided evidence that reline exhibits a peculiar structural transformation upon water addition that manifests in a sudden dewetting of the choline cations at ~51 wt % water and, therefore, a non-monotonic variation of the choline-water and choline-choline coordination. We study, through molecular dynamics (MD), the influence of water on the structure of a choline chloride:urea:water DES (1:2: :□; □ = 0 to 40), to gain additional insight into the molecular source of this peculiar structural transformation. Five different force fields (OPLS-DA, OPLS-DA/Urea, GAFF0.8-PPC, CHARMM36, CHARMM36-SH) were investigated. Our results show that the ND/EPSR non-monotonic behavior of the choline-choline coordination is qualitatively reproduced by those force fields that describe more accurately the dynamics of the DES, namely, the diffusion and viscosity coefficients. The CHARMM36-SH and GAFF0.8-PPC provided the most accurate description of the structure and dynamics of the DES. However, in comparation with experimental results, the apparent increase of the choline-choline coordination at □ > 10 (41 wt %) is associated with the drain of a particular first coordination sphere, rather than with a decrease of the choline-water coordination, as predicted by ND/EPSR. Overall, our simulations predict a smoother transition between a “Water in DES” to a “DES in Water”, where, although the rate of water retention by choline decreases with the water content, there is no evidence of a crossing point where a dewetting occurs, as predicted by ND/EPSR.

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P 10. Analysis of the Formation Mechanism of Choline-based Deep Eutectic Solvents Using Density Functional Theory

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Keywords: density functional theory, deep eutectic solvents, choline, thermodynamic properties, molecular orbital theory

Deep eutectic solvents (DES) are gradually gaining attention in the field of green chemistry as a valuable alternate to ionic liquids. DES comprises of two or more components, out of which at least two have a hydrogen bonding capacity: one hydrogen bond acceptor (HBA) and one hydrogen bond donor (HBD). A detailed computational study on the formation mechanisms of DES provides an insight of their structural and electronic properties, along with creating a molecular-level link between quantum chemistry and chemical engineering thermodynamics. This research article focuses on the effect of the position of HBD during the self-association of various choline based DES components (choline chloride/urea, choline chloride/glycerol, choline chloride/ethylene glycol, choline bromide/urea), performed with the density functional theory methods using B3LYP/6-311+G(d,p) basis set (Gaussian 6.0.16 version).

Varying the position of urea (P1, P2, P3, P4) at a fixed position of choline chloride, the most stable structure was found with P1 (E_{min}=-27608.948485782 eV). With this another urea molecule was attached at various positions to study DES1 (choline chloride/urea molar ratio 1:2, Figure, E_{min}= -33741.68724576 eV) and structure with the minimum energy is considered as the most stable structure. Same procedure is followed for the other DES. Their bond energies and bond lengths are reported. The nature of DES formation is obtained in terms of molecular orbital theory (MOT), ionization potential (I) and electron affinity (A) via Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital (HOMO-LUMO) energy values and gap. Properties like chemical potential (μ), global hardness (η), softness (S), electrophilicity index (ω), electronegativity (X) and properties of thermochemistry such as enthalpy (H) and Gibb's free energy (G) of the DES formation have been reported.

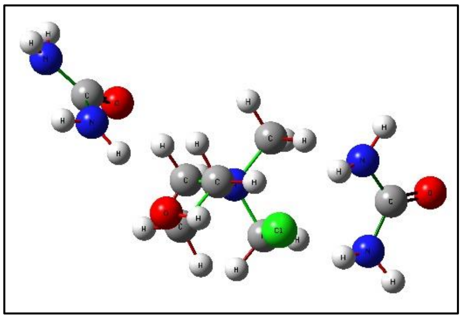

Figure. DES 1 (Choline chloride/urea molar ratio 1:2)

P 11. Effect of Lithium Salt on Fluorescence Quenching in Glycerol: A Comparison with Ionic Liquid/Deep Eutectic Solvent

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Keywords: deep eutectic solvents, choline chloride, urea, glycerol, lithium chloride

It was reported earlier that the addition of LiCl to the deep eutectic solvent (DES) ChCl:Urea (composed of the salt choline chloride and the H-bond donor urea in 1 : 2 molar ratio) and the addition of $LiTf_2N$ [Tf_2N:$(CF_3SO_2)_2N$] to the ionic liquid (IL) [C_2C_1im][Tf_2N] ([C_2C_1im]:1-ethyl-3-methylimidazolium), respectively, results in an increase in the dynamic viscosity of the medium. However, as the concentration of the Li salt is increased, instead of decreasing, the bimolecular quenching rate constant (k_q) for the quenching of pyrene fluorescence by nitromethane is observed to first increase and only then decreases within both media. This unusual initial increase in quenching is hypothesized to be due to structural changes in the DES ChCl:Urea and the IL [C_2C_1im][Tf_2N], respectively, as the Li salt is added. We tested this hypothesis by comparing the physical properties and fluorescence quenching behavior between 1 wt% water in glycerol solution which has similar viscosity to that of the DES ChCl:Urea with the aforementioned DES and IL in the presence of lithium salt as media. In complete contrast, irrespective of the temperature, k_q is found to decrease monotonically with increasing concentration of LiCl within 1 wt% water in glycerol media. These findings therefore highlight the unusual characteristics of ILs and DESs as solubilizing media. The ionic nature of the IL and the high concentration of ions in the DES are deemed responsible for these outcomes.

P 12. Prediction of Viscosities of Deep Eutectic Solvents by Machine Learning + Group Contribution Hybrid Models

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Keywords: DES; green solvent; physical property; artificial intelligence; thermal viscosity

Organic solvents have been of the utmost importance to chemical industries. The widespread use of dangerous, toxic, and highly volatile organic solvents has a long-term effect on the environment and human health. As a result, these industries are looking to increase the sustainability of their manufacturing by emphasizing the switch to environmentally friendly and neoteric solvents. Deep eutectic solvents (DESs), which have appeared as an alternative to ionic liquids (ILs), are one of these neoteric solvents. They are regarded as low volatile, non-flammable, chemically and thermally stable, and biodegradable. DESs' physical and chemical properties can be highly tuned to suit the demands of a specific mission. From chemical engineering and technology, viscosity is a crucial input variable for the efficient and reliable design and optimization of numerous processes. So, developing an accurate, rapid, and user-friendly model is necessary to determine the viscosity of DESs because the present empirical models are inaccurate and experimental methods are costly and time-consuming. This work used a comprehensive and carefully revised DES viscosity databank consisting of 2533 laboratory data points from 305 DESs to properly implement two smart techniques: multi-layer perceptron artificial neural network (MLPANN) and least square support vector machine (LSSVM). To increase model predictability and accuracy and minimize the black-box character of LSSVM and MLPANN approaches, the group contribution (GC) method is also used to create these models. So, these viewpoints are known as MLPANN-GC and LSSVM-GC. The best MLP model structure contains a single hidden layer with ten neurons and a log-sigmoid transfer function. The LSSVM model employed a radial basis function (RBF) kernel and 10-fold cross-validation. The two proposed models consider the dependency of DES viscosity on temperature, molar ratios, and functional groups. The average absolute relative deviations (AARD%) of the suggested MLPANN-GC and LSSVM-GC models for predicting DES viscosity are 9.43% and 6.88%, respectively, which attests to their acceptable accuracy and efficient performance.

P 13. A Computational Modelling Approach for an Ad-hoc Choice of the Optimal DES for Gas Refrigerant Recovery

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Keywords: soft-SAFT; density; viscosity; gas solubility; process design

The use of Deep Eutectic Solvents (DES) as solvent for gas capture and separation is one of its potential applications in the industry. However, although promising results have been achieved at a lab scale, the impressive number of possible entities forming the DES makes recommendable the use of computational tools able to guide the experiments in the design and formulation of optimal combinations, so as to enhance its capacity.

A theoretical robust methodology is presented to thermophysically characterize DESs for gas refrigerant recovery applications. For this purpose, the soft-SAFT equation of state has been used in combination with other modelling tools, such as COSMO-RS. Based either on molecular simulation data or charge analysis distribution, a rational choice of a molecular model and the number of dominating hydrogen bonds is proposed. An individual component approach, where each entity forming the DES is treated as an independent compound, is followed to describe main physicochemical properties of the system. Next, a practical application related to the CO_2 and the refrigerant industry (high global warming potential fluorinated gases) is studied by describing the solubility of these greenhouse gases in different DESs, highlighting the impact of different variables (pressure, temperature) and structural characteristics of the DES (type of HBA, HBD, number of fluorine atoms, etc.) in the results. Finally, variables, such as the selectivity to carry out a gas separation process, are predicted so as to provide a preliminary capture and separation simulation unit with ASPEN.

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P 14. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) Electrospun Nanofibers Containing Natural Deep Eutectic Solvents Exhibiting a 3D Rugose Morphology and Charge Retention Properties

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Keywords: PHA, NADES, electrospinning, air filtration, charge retention, fiber alignment

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a very versatile biobased polyester due to its balanced physical properties, excellent biocompatibility and biodegradability characteristics, and industrial-scale production, which can be further modified with other agents to improve and expand its industrial relevance and application areas. In this sense, the use of natural deep eutectic solvents (NADES) could be a promising approach. NADES is a eutectic mixture of two (or more) components, which consists of hydrogen bond donor and hydrogen bond acceptors. This new kind of solvents present unique physicochemical properties, such as negligible volatility, extensive variety of polarity, liquid state far below 0 ℃, high solubilization and stabilization capacity for a broad range of compounds, high extraction performance, and plasticization properties. Moreover, NADES present relatively low cost, biodegradability, biocompatibility, easy production, nontoxicity, and therefore they represent an alternative to substitute organic or other toxic solvents. Hence, the aim of this study was to investigate the effect of NADES on electrospun PHBV nanofibers for its potential use in air filtration applications. For this, PHBV fibers containing 26% of several NADES were prepared by electrospinning process using a high-throughput Fluidnatek LE-500 pilot line from Bioinicia S.L. (Valencia, Spain). From the different NADES screened, Choline Chloride:Urea:Water was selected, since it was found to produce an interesting and surprising rugose 3D morphology, natural fiber alignment, and charge retention properties. A lasting charge retention profile was observed when NADES containing PHBV fibers were deposited between commercial spunbond materials. Finally, a system consisting of a very thin layer of PHBV/NADES nanofibers sandwiched between two layers of a spunbond non-woven exhibited a substantial improvement in filtration efficiency with a minor increase in pressure drop. The here-developed NADES containing PHBV fibers can be considered as a very interesting and promising sustainable material for, among other applications, air filtration.

P 15. Mixed Micelle Formation by Sodium Dodecylsulfate and Dodecyltrimethylammonium Bromide in Aqueous Ionic Liquid Media

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Keywords: mixed micelles, ionic liquid, surfactant mixture, synergism, antagonism, surfactant aggregation, charge screening

Surfactant self-aggregation within ionic liquid (IL) - based media has been investigated to compare and contrast the role of such media with that of water. Behavior of a surfactant mixture constituting of two surfactants with oppositely charged head groups, namely anionic sodium dodecylsulfate (SDS) and cationic *n*-dodecyltrimethylammonium bromide (DTAB), is assessed in aqueous IL media. Contrary to what is observed in water, it is shown earlier that effective charge screening of the surfactant headgroups by IL ions in a typical IL 1-ethyl-3-methylimidazolium ethylsulfate ([C_2C_1im][$EtSO_4$]) results in formation of (SDS + DTAB) mixed micelles with critical micelle concentrations (CMCs) ranging between those of SDS and DTAB, respectively. The miscibility of (SDS + DTAB) mixture in aqueous [C_2C_1im][$EtSO_4$] reveals that as the content of IL [C_2C_1im][$EtSO_4$] is increased, the miscibility of the surfactant mixture improves indicating increased charge screening involving ions of the IL and the surfactant headgroups. For water mole fraction ω̈;) ≤ 0.90, (SDS + DTAB) surfactant mixture is miscible in aqueous [C_2C_1im][$EtSO_4$] system in all proportions. For 1.00 ≥ ω̈; ≥ 0.90, while synergism persists due to the presence of attractive electrostatic attraction between SDS and DTAB headgroups leading to mixture CMCs below the CMCs of SDS and DTAB, respectively, the extent of synergism diminishes with increase in IL [C_2C_1im][$EtSO_4$] in the solution. For ω̈; = 0.80, the (SDS + DTAB) mixture exhibits CMC values that are closest to the values estimated assuming ideal behavior. For 0.70 ≥ ω̈; ≥ 0.30, the (SDS + DTAB) exhibits antagonistic trend with CMC values higher than those estimated for ideal solution; the antagonistic trend gradually decreases with increase in [C_2C_1im][$EtSO_4$] and again attains close to ideal behavior in neat IL [C_2C_1im][$EtSO_4$]. This trend is subsequently manifested in the composition of the mixed micelles as well as in the net interaction parameter, β. Addition of small proportion of IL to water helps in solubilization of surfactant mixture of oppositely charged surfactants due to effective charge screening of the surfactant headgroups and results in formation of mixed micelles in aqueous IL media over complete composition range.

P 16. Deep Eutectic Solvents and Dilutions There of as Sustainable Electrolytes in Supercapacitors

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Keywords: deep eutectic solvents, electrolytes, supercapacitors

Sustainability is becoming a mandatory aspect to be considered in the preparation of electrolytes for supercapacitors and batteries. Aqueous electrolytes (e.g., salts dissolved in water) have been extensively studied as they are safe, easy to handle and low-cost, but they exhibit a narrow electrochemical stability window (ESW) that limits their practical application. In this context, DESs have attracted attention as electrolytes, as they are environmentally friendly, possess a wide ESW, and exhibit good ionic conductivity, low cost and vapor pressure, and are non-flammable and non-corrosive. However, their high viscosity hinders transport properties, which impedes the high power densities of SC devices. Proper dilution of DES can reduce viscosity and increase conductivity allowing for improved power densities and better device performance.

In this work, we have used DES electrolytes consisting of choline chloride (ChCl) and ethylene glycol (EG) and their respective dilutions in both water and a sulfolane-water eutectic mixture. The dilution of ChCl-2EG (60 wt%) in the sulfonane-water mixture exhibited an electrochemical window of 2.4 V that allowed a high energy density. Interestingly, the power density of this dilution was similar to that of the aqueous dilution while the capacitance retention was better than for both the undiluted eutectic and the aqueous dilution. The results show the potential of DESs diluted in aqueous co-solvent mixtures as sustainable and cost-effective electrolytes for SCs.

P 17. Deep Eutectic Solvents for the Recovery of Metals from the Cathode of Spent Li-ion Batteries

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Keywords: Deep eutectic solvents, spent batteries, metal extraction

With the rapidly growing demand for energy storage by consumer electronics, lithium-ion batteries (LIBs) have become essential in today's society. More recently, the use of LIBs in electric vehicles (to decline the global CO2 emission) and in wind/solar-to-electricity facilities (to mitigate their intermittent power production) is gaining even more relevance within the context of climate change mitigation to achieve the principal international agreements (Kyoto Protocol, Paris Agreement, European Green Deal, and UN Sustainable Development Goals).

This widespread use of LIBs is causing a double effect. On one hand, the production of more LIBs and with larger capacities (the latter needed for the electric vehicle and stationary energy storage markets) results in a significant increase in the consumption of raw materials. On the other hand, this increase in the production of LIBs will lead to the same increase in the disposal of spent batteries with the subsequent risk to the environment due, for example, to the penetration of toxic metals into soils and groundwater.

Recycling (and reuse) offers a solution to both problems by (1) mitigating the shortage caused by mining of the natural ore of metals used in LIBs and (2) dealing harmlessly with the spent LIBs. Moreover, in terms of circular economy, recycling closes the loop by returning materials to the value chain.

The most valuable component of LIBs is the cathode. This work will show an all-DES-based process combining solid-liquid extractions and precipitations for the selective recovery of Li, Co Ni and Mn coming from NMC type cathodes of LIBs. Moreover, the selection of DESs composition (with abundant, of natural origin and biodegradable components) and the operating conditions in the solid-liquid extractions (with low energy consumption and, hence reduced carbon dioxide emissions) will provide some significant eco-friendly features to this process.

P 18. Interfacial Chemical Reactions in Deep Eutectic Solvents

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Recent work on deep eutectic solvents (DES) has demonstrated that these novel liquids can replace volatile organic solvents, which have adverse health and environmental effects, in chemical syntheses. In addition to being inexpensive, non-flammable and non-volatile it has been shown that reactions using organolithium reagents in DES can be carried out at room temperature in air, in the presence of water; conditions that are normally incompatible with polar organometallic compounds. [1, 2] In this work we investigate the role played by choline chloride:glycerol DES in mediating chemoselective alkylation of ketones by RMgX and RLi reagents in air using molecular resolution studies. Liquid neutron diffraction and NMR studies are used to understand the solubility and molecular interactions in ChCl:Gly DES compared to glycerol. These studies along with surface tension and neutron reflectivity measurements suggest an interfacial mechanism whereby the reaction takes place at the DES/non-polar organic interface as the acetophenone substrate is sparingly soluble in the DES and organizes at the DES/non-polar organic interface facilitating the reaction.

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P 19. Deep Eutectic Solvent-based Preparation of Chitin-based Biomaterials: Effects of Deep Eutectic Solvent on Production and Properties of the Materials

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Keywords: deep eutectic solvent, chitin-glucan complex, chitin-glucan nanofiber, nanofibrillation, esterification

Chitin-glucan complex (CGC), which is a natural bio-copolymer of chitin and glucan covalently bound to each other and is derived from fungal cell wall, has many advantageous properties including biodegradability, biocompatibility, antibacterial activity and high adsorption capacity. Thus, CGC has various potential applications such as drug delivery, wound healing and heavy metal removal. Previously, we used deep eutectic solvents (DESs) to pretreat *Agaricus bisporus*, commonly known as white button mushroom to prepare CGCs for the first time. As a result of diverse combinations of hydrogen-bond donors and acceptors in DESs, CGCs could be prepared to have varying properties and structures. Importantly, certain DESs could help produce CGCs that appeared preferable to further functionalization and application for subsequent biomaterial preparations. It is known that nanofibrillation of chitin enhances homogeneous dispersion of chitin in water and thus expands its utilizations despite its insolubility. Hence, we aimed to prepare chitin-glucan nanofibers (CGNFs) by esterification of CGC using acidic DESs. To this, two potential factors were examined on the nanofibrillation efficiency: pretreatment steps (removal of water-soluble material by hot water treatment, protein removal by alkali treatment and deglucanization by acid treatment) to prepare CGC and acidity of DESs. As a result, hot water treatment and deproteination was sufficiently effective to disintegrate the aggregated mushroom structure and remove alkali-soluble material, respectively; removal of water-soluble glucan by deglucanization did not improve the CGNF production. The resulting CGCs were further treated with a variety of acidic DESs; DESs containing more acidic HBDs yielded higher degrees of esterification, leading to better nanofibrillation. Suspension of the successfully prepared CGNFs displayed high permeability and dispersibility. This study shows that DESs can be applied for efficient preparation of chitin-based biomaterials under relatively mild and ecologically benign conditions.

P 20. The Chemical Stability of Common Deep Eutectic Solvents with Oxidizing Agents used in Gold Hydrometallurgy

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Keywords: deep eutectic solvent, oxidizing agent, gold leaching, chemical stability

Deep eutectic solvents (DES) are emerging solutions under intense scrutiny for a large scope of industrial applications including natural product extraction, electrodeposition and metal ore leaching [1]. For gold hydrometallurgy, DES are considered to be a social and environmentally friendly alternative to cyanide-based mixtures and their technical advantages are currently explored compared to other aqueous processes [2]. DES composed of metal-free eutectic mixtures containing a quaternary ammonium salt based on an ionic organic compound such as choline chloride (ChCl) and a non-ionic organic compound such as urea (U), ethylene glycol (EG) or paratoluenesulfonic acid (PTSA) have been used here. However, these common DES cannot leach gold without adding an oxidizing agent. Nevertheless, the addition of either organic or inorganic oxidants can be detrimental to the DES stability. Indeed, gold oxidizing reactions need to occur within the DES electrochemical stability window. To assure this experimentally, the open circuit potential (OCP) has been monitored with a platinum electrode placed in the gold leaching solutions. Supported by infrared and NMR spectra analyses, the chemical stability has been studied for some commonly used DES, such as Ethaline (1 ChCl : 4.85 EG), Reline (1 ChCl : 1 U), p-thaline (1 ChCl : 1 PTSA.H_2O) and Oxaline (1 ChCl : 1 Oxalic acid.2 H_2O), mixed with oxidants usually used in gold hydrometallurgy, such as iodine, iron(III) chloride, nitric acid and some more powerful ones like hydrogen peroxide or cerium(IV) sulfate. Within this study, it was demonstrated that the OCP monitoring was a very useful tool to assure the DES stability during the ageing at a given temperature. For example, an incompatibility between the oxidant and the DES has been observed for Ethaline+$Ce(SO_4)_2$ and Reline+$FeCl_3$ solutions. Complementary steady potential experiments provided additional evidence of the degradation of Oxaline likely to be caused by a reaction of esterification and water loss at 80 °C [3]. Instead, a slight decrease in potential was not necessarily detrimental to the gold leaching ability, as shown by the example with Ethaline+I_2 mixture. Indeed, by following the iodine speciation using the UV-Vis spectroscopy, the presence of I_2Cl^- as the main predominant specie was detected in the ethaline after the iodine addition, whereas an increase of I_3^- amount was recorded during the solution ageing. This specie has a lower potential but improves the gold leaching.

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P 21. Electrolytes for Supercapacitors Based on Deep Eutectic Solvents Obtained from Aqueous Salts Hydrates

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Keywords: aqueous salts hydrates, eutectics, electrolytes, supercapacitors

Water-in-salts (WISs) electrolytes have paved the way for developing the next generation of supercapacitors (SCs) with wide electrochemical operating windows. However, the high viscosity of super-concentrated WISs electrolytes weakens the electrochemistry performance of SCs, such as specific capacitance and cyclability, which are crucial for expanding the application of SCs. Furthermore, the electrochemical performance of SCs containing WISs electrolytes is predicted to deeply deteriorate over time if the solvent-salt interactions equilibrium breaks down, resulting in phase separation. Thus, there is an urgent need for electrolytes that are both electrochemically and thermodynamically stable to ensure long-term durability. In this study, we propose a novel type of green and low-cost deep eutectic solvent (DES)-based concentrated electrolytes, composed of different aqueous salts hydrates (e.g., hydrated lithium acetate-LiOAc, hydrated sodium acetate-NaOAc, and potassium acetate-KOAc) dissolved in water/ethylene glycol (EG) solvent mixtures. The tuning the molar ratio among salts and/or between salts and the solvent mixtures allowed improving the capacitance retention to ca. 85% under cycling test at 1.9 V, 4 A/g after 10000 cycles without sacrificing the ionic conductivity. The resulting SCs also exhibited a remarkable specific capacitance and power performance at 0.5 A/g current density (126.83 F/g and 15.74 Wh/kg).

P 22. Sustainable and Straightforward C–H Activation Protocols in Deep Eutectic Solvents

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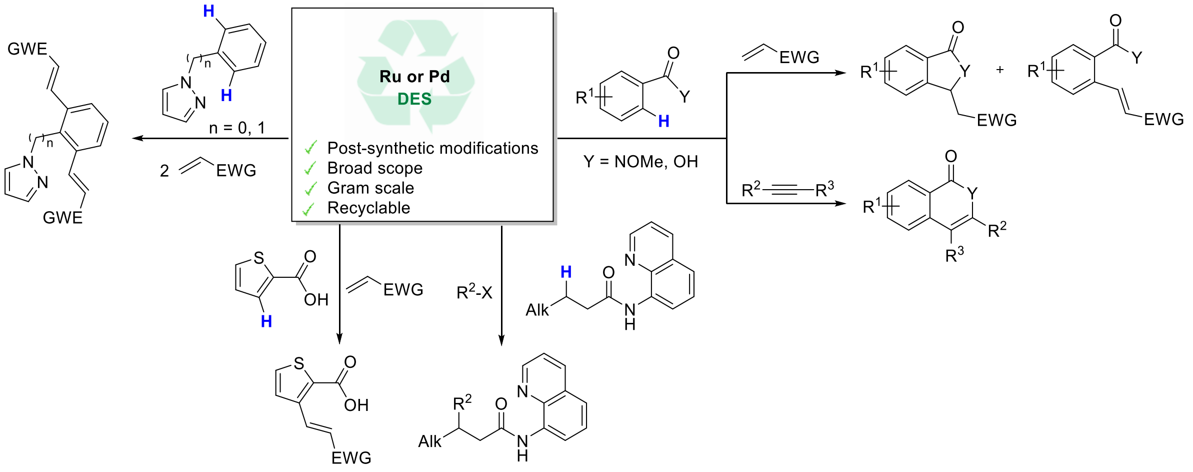
Keywords: C-H activation, deep eutectic solvents, green chemistry, ruthenium, palladium, sustainability

The transition-metal catalysed activation of inert and ubiquitous C-H bonds has emerged as a powerful strategy for the design and development of new synthetic approaches since it allows the use of non-functionalised reagents, providing more straightforward and sustainable protocols for the synthesis of organic compounds.[1] However, its main drawback is the use of toxic and hazardous organic solvents. Hence, the development of benign and environmentally-friendly C-H activation procedures remain in demand. Deep Eutectic Solvents (DESs), emerging sustainable solvents with unique and tuneable properties, have been widely explored recently in a bunch of reactions.[2-4] Herein, this study aims to demonstrate the broad potential of DESs to replace volatile organic solvents, since versatile and efficient methodologies for ruthenium-catalysed C_{sp2}-H activation and palladium-catalysed C_{sp3}-H activation reactions have been developed for the first time in DESs. A wide range of substrates were used obtaining promising results (Scheme 1). Also, it was possible to recycle the reaction medium and the catalyst, to perform the reaction at gram scale and to carry out post-synthetic modifications in DESs.



Scheme 1

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P 23. Thermophysical Characteristics of Phosphonium Eutectic Nanofluid Based on MWCNT: A New Heat Transfer Media for Solar Desalination System

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Keywords: DES, nanofluid, thermal conductivity, stability

In this work, a thermal medium is created by combining a hydrogen bond donor (HBD) salt, ethylene glycol, with a hydrogen bond acceptor (HBA) salt, methyltriphenylphosphonium bromide (MTPB), at a molar ratio of 1:4. Thereafter, 0.02 wt % Multi-Walled Carbon Nanotube (MWCNT) was dispersed in the base fluid and produced a nanofluid with a diameter of 10–30 nm. A Field Emission Scanning Electron Microscope (FESEM) and a Field Emission Transmission Electron Microscope were used to analyse the structure and morphology of MWCNT before dispersion (FETEM). The crystallinity and functional groups were assessed using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Powder Diffraction (XRD). Zeta potential tests and visual inspection were utilized to assess the synthesised nanofluid's stability. The density, viscosity, thermal conductivity, and specific heat of nanofluids were measured over the temperature range of 25°C to 85°C. Based on the experimental results, viscosity and density decrease as temperature rises. On the other hand, it was shown that the specific heat and thermal conductivity of the nanofluid increased as the temperature goes up. The nanoluid was predestined to be a sustainable heat transfer medium for solar desalination systems after all the thermophysical parameters were compared with the commercially available heat transfer fluid THERMINOL VP-3. The penultimate section compared and verified the thermal conductivity of nanofluid data using molecular dynamic modelling.

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P 24. Eutectogels as Drud Delivery Systems: An NMR Study

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Keywords: HR-MAS NMR, small molecules

Physically crosslinked gels are formed due to non-covalent interactions, such as hydrogen bond, electrostatic forces and van der Waals interactions. The design of drug delivery systems based on physical gels have gained growing attention as the gelation process often occurs under mild conditions and in absence of chemical crosslinking agents. Deep Eutectic Solvents (DESs) are an emerging class of sustainable materials formed by two or more components linked by a strong hydrogen bonding network and used in different applications [1]. The use of DESs as drug delivery systems is related to the possibility of developing DES-based gels, called “eutectogels”, which can deliver a loaded drug in a controlled way [2]. Here we present the synthesis and characterization of supramolecular eutectogels loaded with active pharmaceutical ingredients at different concentrations. The final goal is to study the properties of these systems from a microscopic point of view, mainly exploiting ^{1}H High-Resolution Magic Angle Spinning (HR-MAS) NMR technique to investigate drug dynamics in eutectogels. Macroscopic release kinetics experiments have also been performed under different conditions using quantitative NMR. Gels based on non-ionic type V DESs have been prepared, using thymol as hydrogen bond donor and menthol as hydrogen bond acceptor. In our study, we chose ethosuximide (a water-soluble anticonvulsant) as a model loading drug. Experimental data clearly indicate that molecular mobility in gel systems is not influenced by concentration changes and is always lower than the diffusion observed in aqueous solution. Macroscopic release clearly shows how these systems can be used for controlled drug delivery over long periods of time.

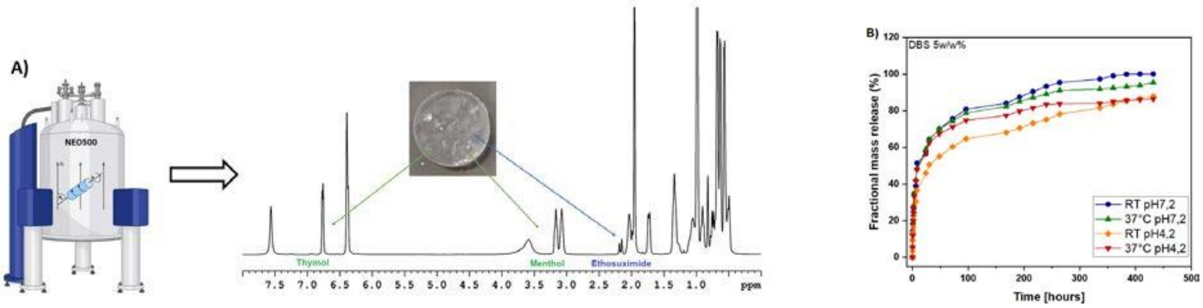

Fig.1: A) schematic representation of HR-MAS NMR, B) Macroscopic release kinetic curves

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P 25. One Step $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ Cathode Active Material Recovery from Ethaline: Leaching, Co-precipitation, Annealing and Successful Reuse as Cathodic Material

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Keywords: Li-ion battery, recycling, deep eutectic solvent

The growth of the Li-ion batteries (LIB) market and the associated economies of scale have made possible the optimization of the production processes and significantly contributed to the reduction of the manufacturing costs. As a consequence, and facing the growing demand, developed countries will inevitably be confronted in the near future with huge quantities of waste LIBs (around 700k tons by 2035, against 15k tons currently) [1]. The development of efficient and environmentally friendly recycling processes is therefore a major challenge for the energy transition. This work processes a highly efficient way for the $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) cathode active material recycling by leaching in a choline chloride/ethylene glycol (ethaline) deep eutectic solvent, with a liquid/solid mass ratio of 50, that was doped with HCl. The addition of the latter at 4 molar equivalents with respect to the metallic contents allows to leach quantitatively and quickly metals at 80 °C. Co-precipitation performed using 0.2 M Li_2CO_3 is achieved with 99% efficiency. The recovered mixed carbonate was mixed with lithium carbonate and was then transformed into the oxide form by thermal annealing. The degree of transformation was monitored using *in situ* X-ray diffraction, allowing to optimize the synthesis of the expected crystalline structure for battery application (900°C). In a final step the NMC recycled material has been tested in battery condition (LP30 electrolyte, lithium metal anode). The poor energy consuming and quick recovery process allows to restore more than 85% of the initial capacity (i.e. 150 $mAh.g^{-1}$) with a coulombic efficiency greater than 99%. At 0.2C during 100 cycles.

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P 26. Study of the Skin and Gastrointestinal Membrane Permeability of Ascorbic Acid in Fourteen Different NADES

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Keywords: PAMPA, NADES, ascorbic acid

Ascorbic acid is an important vitamin with antioxidant capacity. This molecule is thermolabile and easily degraded, the way it passes the biological membranes could be useful to extrapolate to other bioactive compounds. The PAMPA test (Parallel Artificial Membrane Permeability Assay) is used as a screening test to predict passive human absorption.

In this case, the aim of this study is to analyze ascorbic acid skin and gastrointestinal membrane permeability in fourteen different natural deep eutectic solvents (NADES) for the gastrointestinal test, and five for the skin test, due to chlorine chloride is not allowed to be used in cosmetics.

In this test, ascorbic acid standard (0.2mg/ml) was added to fourteen different NADES, and a hydrophobic PVDF Multi Screen Permeability Plate Assembly with 96-well filtration plate (Merk, Millipore, MA, USA) was used as a carrier of the artificial membrane and as the receptor plate. The filter material was coated with 15 µl of solution (L-α-phosphatidylcholine, 1% dodecane m/v). The donor plate was placed onto the receptor place, which had previously been filled with 200 µl of phosphate buffer solution pH 5.5 (for simulating the large intestine segment) and phosphate buffered saline pH 7.4 (for simulation of the human skin). 125 µl of the sample was added to each well of the donor plate and incubated in darkness for 6h at room temperature. After incubation, the concentration of ascorbic acid in the receiving and donor plates was determined by HPLC-UV.

Results show that, choline chloride:lactic acid (5.87 $x10^{-6}$ ± 1.71 $x10^{-6}$ cm/s), choline chloride:glycerol (4.47 $x10^{-6}$ ± 1.01 $x10^{-6}$ cm/s), and proline:malic acid (4.25 $x10^{-6}$ ± 1.25 $x10^{-6}$ cm/s), were the three NADES that had the higher permeability kinetic for the gastrointestinal test, and malic acid:glucose (MA:Glu) (8.51 $x10^{-6}$ ± 7.60 $x10^{-6}$ cm/s) and beatine:malic acid (7.90 $x10^{-6}$± 1.12 $x10^{-6}$ cm/s) for the skin test. Those who had a lower speed in the gastrointestinal test were MA:Glu (1.29 $x10^{-7}$ ± 3.99 $x10^{-8}$ cm/s) and lactic acid:glucosa (LA:Glu) (1.01 $x10^{-5}$ ± 3.85 $x10^{-7}$ cm/s), and for the skin test were LA:Glu (1.65 $x10^{-5}$ ± 1,54 $x10^{-6}$ cm/s) and betaine:citric acid (1.83 $x10^{-5}$ ± 3.28 $x10^{-6}$ cm/s).

In conclusion, ascorbic acid's membrane permeability kinetics depends on the type of NADES used, and also the NADES do not pass the membranes studied, which is interesting to use these solvents in food products and cosmetics in a near future.

P 27. Membrane-assisted Nanoemulsification: Fundamentals and Biomedical Applications of Hydrophobic Deep Eutectic Solvents Based Nanoemulsions

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Hydrophobic deep eutectic solvents (DESs) are a recent class of designer green solvents, alternative to ionic liquids, offering low cost and negligible toxicity. To potentiate bio-based applications, wherein polar media is encountered, the low solubility of these hydrophobic solvents in water was tackled by dispersing them as nanoemulsions using energy-efficient membrane emulsification technique [1].

DES-in-water nanoemulsions were produced sustainably using Nuclepore track-etched isoporous polycarbonate membranes with varied pore sizes. Under optimum conditions, monodispersed and stable nanoemulsions of 39.0±0.4 nm was formulated using an 80 nm pore size membrane. A detour from the principles of *direct membrane emulsification* was witnessed as the membrane pore size did not control, rather assisted in the formulation of DES-in-water nanoemulsions. Accordingly, a new technique was introduced: **membrane-assisted nanoemulsification**.

To further explore the phenomenon of membrane-assisted nanoemulsification, laser-drilled microengineered membranes of 9µm isopores were fabricated and tested. Interestingly, menthol/decanoic acid-based (58.7±0.4 nm sized) and menthol/thymol-based (81.2±0.9 nm sized) hydrophobic therapeutic DESs-in-water nanoemulsions were produced [1,2]. Unique observations such as self-assembly of hydrophobic DESs into nano-droplets, reduced interfacial tension (7.5 $\mathrm{mN.m^{-1}}$) between water and DES, and the hydrophobic DESs wetting behaviour to both hydrophilic and hydrophobic membrane surfaces were witnessed. Along with Tween 80 as a surfactant, the DESs serving as co-surfactants to further stabilise the nanoemulsions were hypothesised and a dimensionless analysis was explored to describe the behaviour of fluids.

From the application perspective, antimicrobial and *in-vitro* drug delivery applications were unravelled. In contrast to DESs or their individual components, the optimised DES-in-water nanoemulsions exhibited increased bioavailability and enhanced synergetic antimicrobial effects against *Escherichia coli, Staphylococcus aureus* and superior potency against *Cutibacterium acnes* (acne inducing bacteria). Furthermore, as hydrophobic DES demonstrated enhanced drug solubilisation capabilities, the drug-loaded DES was encapsulated into nanoemulsions and drug release studies were performed. Lastly, cytotoxicity studies of the nanoemulsions against human cell lines validated its potential for biomedical applications.

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P 28. Increasing the Solubility of Active Pharmaceutical Ingredients Using Deep 3utectic Systems

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Keywords: DES, THEDES, bioavailability, solubility

Deep Eutectic Systems (DES) can be defined as a mixture of two or more compounds, where at least one is a hydrogen bond donor and the other a hydrogen bond acceptor. The decrease in melting point of the mixture to be lower of the melting point of each compound is one important physical-chemical characteristic of a DES [1,2]. When we mix a pharmaceutical ingredient into the mixture with the intuition to increase its solubility and permeability we therapeutic deep eutectic system (THEDES) [3]. THEDES appear as an alternative method for improving the oral bioavailability of certain drugs classified according to the Biopharmaceutical Classification System (BCS) as class II (low solubility, high permeability), III (high solubility, low permeability) or IV (low solubility, low permeability) [4]. In this work, we tested four different drugs, described with low solubility, kindly provided by the pharmaceutical industry, and explored the possibility to increase their solubility using different DES. The solubility of the drug in DES was compared with its solubility in PBS. The results demonstrate an increase of at least 9 times the solubility of 4 different drugs when dissolved with a specific DES compared with solubility in PBS. In which concerns the permeability, the extremely complex structure of drugs can explain the not-so-impressive results obtained. The promising results reinforce the role of DES as the potential technology to increase drug's bioavailability.

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P 29. Broccoli Extracts Obtained Using Deep Eutectic Solvents with Potential Antiproliferative Activity

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Keywords: broccoli, bioactive compounds, antiproliferative activity, antioxidant activity

Due to the high waste and loss of human consumable food, there is the need to find alternatives to take advantage of this food excess in order to achieve a sustainable food system. One of the vegetables most misused is broccoli (*Brassica oleracera L. var. italica*), since around two-thirds of the edible parts of the plant are wasted [1]. A way to valorise broccoli waste is to extract valuable bioactive compounds for pharmaceutical applications, since the broccoli are rich in phenolic acids, flavonoids, carotenoids and glucosinolates, which present anti-oxidant, anti-inflammatory and anticancer activities [1,2]. There are different techniques to extract bioactive compounds that use organic solvents, such as methanol, ethanol and acetone. However, these compounds are toxic for the environment [3]. Therefore, the aim of this work was to find greener alternatives like the use of Deep Eutectic Solvents (DES), to extract bioactive compounds from broccoli, and analyse the potential antiproliferative activity of the extracts. Since, cancer remains a major health problem worldwide, with colorectal cancer (CRC) being the third most incident and one of the most lethal [4].

The results obtained for the extraction with DES were compared with the controls (conventional extraction with ethanol:water (1:1) and methanol:water (3:2)). Additionally, the antioxidant and antiproliferative activities against colorectal cancer cells were also explored in this work.

The preliminary results obtained with hydrophilic DES, seem to show that less phenolic compounds are extracted compared with conventional extractions. Moreover, the extracts presented low antioxidant activity and the antiproliferative capacity was greater with the control extracts obtained. However, in terms of antiproliferative activity, the use of hydrophobic DES seem to be an alternative approach to be able to extract the sulforaphane (a bioactive compound, with cancer preventive potential, obtained from the metabolization of one glucosinolate [3]), since it is an hydrophobic compound. Additionally, in this way, the overall bioactivity of the extracts can increase and be an alternative to take advantage of broccolis waste.

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P 30. Design and Characterisation of Gels and Films Based on Biopolymers for Transdermal Drug Delivery Using Deep Eutectic Systems

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Keywords: deep eutectic systems, solubility, drug delivery, active pharmaceutical ingredients, bioavailability

Enhancing the therapeutic efficiency of existing drugs is one the main contemporary endeavours of the pharmaceutical industry, since most of the commercialised drugs display poor water solubility, hindering their efficiency and bioavailability [1]. Developing novel delivery systems for the current active pharmaceutical ingredients (APIs) is therefore of great importance, not only to overcome some limitations of solid formulations, associated with polymorphism, toxicity, and low bioavailability, but also from a sustainability point of view, since it avoids the need of costly research and clinical trials for new therapeutic molecules. In this regard, deep eutectic systems (DES) have emerged as promising alternative solvents since they are versatile and tuneable mixtures, that can be prepared from natural and abundant components [2]. DES have been reported to be able to dissolve some APIs or to function with the API itself as a component of the eutectic mixture [1,3,4] Recently, new strategies consisting in the addition of a polymeric matrix have been devised, were the polymer acts as a support [3]. In this work, a transdermal drug delivery method was considered to administrate model drugs, such as ibuprofen, diclofenac and lidocaine. Two DES, composed of Lactic Acid: Glucose: H2O (5:1:3) and Citric Acid: L-proline: H2O (1:2:6), have demonstrated the capacity to significantly enhance the solubility of the anaesthetic drug lidocaine, demonstrating a 98- and 36-fold increase, respectively, in comparison with the reported solubility values in water [5]. Our current work aims to combine these DES with natural polymers, such as gelatine and chitosan, to obtain biopolymeric films, capable to function as transdermal delivery systems.

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P 31. Sustainability of the preparation and application of THEDES

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Keywords: design, deep eutectic solvent, poor aqueous solubility, scalability

The design of deep eutectic solvents (DESs) for drug preparation and formulation is an increasing area of R&D, since the proper selection of DES could result in solubility-enhancing formulation of active pharmaceutical ingredient (API). It is estimated that more than 40% of new drug candidates are lipophilic and have poor aqueous solubility, therefore novel approaches in drug formulation are crucial for achieving better bioavailability of poorly soluble drugs. Therapeutic Deep Eutectic Solvents (THEDES) are a relatively new subclass of DESs, where eutectic mixture is formed with an API as one of its compounds, to achieve better solubility, permeability and stability, while retaining its activity. Such outcomes are proven scientifically for different types of APIs, but sustainability and scalability of such formulations have yet to be resolved. Sustainability should be addressed with regard to: low toxicity, good biodegradability, renewable sourcing and low cost, with emphasis on specific demands for pharmaceutical applications. Cost analysis method should be done considering the required purity of forming compounds, as well as applied volumes and dosage, to make a proper decision on possible pharmaceutical application of THEDES. Such a comprehensive approach is the goal of our ongoing research which will hopefully shed new light and encourage the adoption of THEDES in the real sector.

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P 32. Extending the Shelf-life of Red Blood Cells Using Natural Deep Eutectic Systems

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Keywords: red cell concentrate, natural deep eutectic systems, shelf-life extension, blood, preservation

According to the World Health Organization (WHO), in 2018, over 118 million blood donations were collected worldwide. The collected blood can be used for “whole blood” transfusion, or processed to separate its various components, namely red cell concentrate (RCC), platelet concentrate, plasma, etc. RCC are prepared by removing the plasma from the whole blood and substituting it by an additive solution. According to Instituto Português do Sangue da Transplantação (IPST, IP), the shelf-life of RCC is currently 42 days, using a saline-adenine-glucose-mannitol (SAGM) solution as additive. The addition of this solution, and proper storage of RCC (0 to 4 °C), allows for less deterioration of erythrocytes, which decreases the occurrence of post-transfusion complications. Due to their biocompatible characteristics, natural deep eutectic systems (NADES), have been successfully applied in biomedical applications, such as, increasing the solubility of drugs, acting as cryoprotectant agents and even presenting anti-cancer properties. In this work, NADES, composed of sugars, amino acids, polyols, and organic acids, were tested as additive solutions for the storage of RCC. The main goal was to develop a media in which the storage of RCC can be extended beyond the standard 42 days. Preliminary studies show that most NADES studied present no haemolytic activity, while those containing acids in their composition induce clotting of the concentrates. Moreover, the NADES with higher ratios of glycerol induced higher percentages of haemolysis. The standard SAGM solution was substituted by NADES solutions and the RCC were stored under refrigerated conditions. Samples were collected at pre-determined time points to assess haemolysis extent, glucose, and lactates content, and erythrocytes morphology. The results obtained so far show that NADES are suitable candidates as additive solutions to further extend the shelf-life of RCC.

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P 33. A Novel Aerogel from a Collagen-NADES Extract for Potential Topical Biomedical Applications

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Keywords: marine waste valorisation, natural deep eutectic solvent (NADES), blue sharkskin collagen, aerogel porous materials, biomedical applications

Integrating natural deep eutectic solvents (NADES) extraction technologies to recover collagen from marine waste sources is an ongoing topic in our laboratory. Besides being structural elements of the extracellular matrix of human tissues, these biomolecules have numerous properties such as gelation capacity, biocompatibility, and antibacterial activity. This work aimed to develop new porous material from a collagen-NADES extract and perform solid-state characterization. To obtain the aerogels, collagen-NADES extract was gelled under 4°C, converted into alcogel through solvent exchange, and dried with supercritical CO_2. The morphology was studied by Scanning Electron Microscopy, whereas the specific surface area and the pore volume were obtained through Brunauer–Emmett–Teller and Barrett-Joyner-Halenda methods, respectively. The resulting aerogel was light-weight, with a sponge-like structure, a relatively dense meso to microporous network and a specific surface area of 224 m^2/g, specific pore volume of 1.19 cm^3/g and a pore radius of 13.8 nm. Collagen structural integrity was studied by discontinuous electrophoresis, Fourier transformed infrared spectroscopy and circular dichroism. This work demonstrated that a novel aerogel was successfully obtained through supercritical drying of a collagen-NADES gelled extract, revealing a high specific surface area and pore volume material and no impact of the aerogel production process on collagen structure. Future works evolve to evaluate the material's mechanical behaviour, biocompatibility and bioactivity, exploiting the attractive properties of aerogels, collagen and NADES for potential biomedical applications.

P 34. Ecotoxicity of Glycerol-derived Deep Eutectic Systems Using Palaemon Varians as a Biological Model

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Keywords: deep eutectic systems, ecotoxicology, Palaemon variance, biomarkers

Deep eutectic systems (DESs) have been gaining attention as a “green” alternative to traditional organic solvents due to their potential advantages such as lower toxicity, lower flammability, and greater biodegradability. The ecotoxicity of DES depends on the specific components and ratios of the mixture, therefore it is important to evaluate the ecotoxicity of each DES to ensure its environmental safety. Toxicological studies on this type of solvent are scarce, therefore the main aim of this work is to evaluate the ecotoxicity of DES formed by choline chloride (ChCl) as hydrogen bond acceptor (HBA) and glycerol-derived monoethers, with ethyl, methyl, propyl and butyl radicals as hydrogen bond donors (HBD) using the shrimp *Palaemon varians* as biological model and measuring the oxidative stress biomarkers after exposure to compounds. The hypothesis of this study is that "the DES under study present low toxicity and are safe and environmentally friendly for further industrial use". The ecotoxicity was assessed by registering the mortality in *P. varians* to determine the concentration at which 50% mortality occurs (LD50) after the exposure to DES and measure the lipid peroxidation (MDA content), the catalase (CAT), Gluthation-S-transferase (GST) activity, superoxide dismutase (SOD) and total antioxidant capacity (TAC) in animals exposed to the different DES as biomarker of oxidative stress. Some of these results are showed in Table 1 and 2.

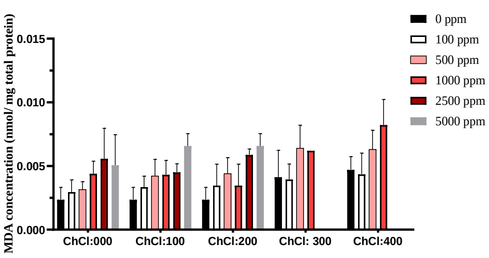

Fig 1. MDA content of tested DES

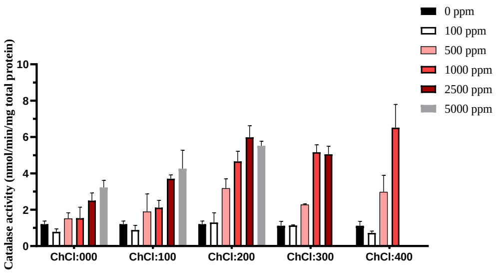

Fig 2. Catalase activity of tested DES

P 35. Selective Extraction of Carotenoids from Novel Bioengineered Algae Using Natural Deep Eutectic Solvents

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Keywords: extraction, carotenoids, algae

Natural Deep Eutectic Solvents (NADES) span a broad polarity range and possess a superior solubilizing ability. Thus, they are suitable green alternative solvents for diverse applications, including solubilization and extraction of compounds. Here we explore the use of NADES for the selective extraction of carotenoids from algae as an alternative to the commonly used organic solvents. NADES were used to extract the carotenoid astaxanthin from the engineered microalgae *Chlamydomonas reinhardtii*, which produces ketocarotenoids including canthaxanthin and astaxanthin in addition to its native carotenoid and chlorophylls. The extracts were analyzed by high-performance liquid chromatography (HPLC). Algal extraction using different NADES yielded colors ranging from light yellow to dark red. Conversely, the extraction using organic solvents, such as *n*-hexane and acetone, produced green color extracts attributed to chlorophylls in addition to other hydrophobic molecules like the carotenoids. The absence of the chlorophylls in the NADES HPLC chromatograms confirmed the selective extraction of carotenoids over chlorophylls. Our results indicate that NADES can be tailored to extract specific groups of carotenoids with much higher selectivity than conventional organic solvents and can be more sustainable alternatives for the selective extraction of valuable biomolecules from algae.

P 36. Development and Optimization of a Green Extraction Process of Greek Wild Rose (*Rosa Canina* L.) Rosehip shells

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Keywords: green extraction, Wild Rose, Natural Deep Eutectic Solvents, experimental design

Rosa canina L. (dog rose or wild rose) is a native shrub of Europe and the Mediterranean region. The hypanthium of rosehip, consists of a rich source of bioactive phytochemicals. Due to their bioactivity, dried rosehips have been traditionally used to treat cough and cold influenza symptoms and have attracted the food and cosmetics industries' interest.

Various solvents have been used for the extraction of phytochemicals from wild rose, however to the best of our knowledge, green solvents such as Natural Deep Eutectic Solvents (NADES) have not been exploited yet. NADES, are mixtures of two or more naturally occurring components that in specific ratios and temperatures show a very low-temperature eutectic point forming a liquid. Their use in extraction processes is advantageous leading to lower extraction time, high extraction yields as well as stabilization of the obtained extracts and protection of the extracted compounds [1-3].

In the present work, the NADES Betaine/Lactic Acid has been used as an extraction medium and the process was optimized by performing Box-Behnken Experimental Design to study the effect of time, Wild rose-to-solvent and %water as a co-solvent along with the NADES. All the extracts were characterized regarding their antioxidant activity as well as their total phenolic and flavonoid content and the optimum extraction parameters were determined. The results of this study were compared to those derived from the conventional extraction using as extraction solvent a hydroethanolic solution. The results showed that the optimum NADES extract was superior to the hydroethanolic extract regarding the total phenolic content (up to 10-fold higher) as well as their total flavonoid content (up to 4-fold higher). Finally, based on our results, the proposed process could be considered as an effective green alternative to the conventional extraction.

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P 37. Innovative Strategy for Aroma Stabilisation Using Green Solvents: Supercritical CO_2 Extracts of *Satureja montana* Dispersed in Natural Deep Eutectic Solvents

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Keywords: aroma, stabilisation, supercritical carbon dioxide, natural deep eutectic solvent

This work investigated the aroma stabilisation approach which uses alternative solvents to provide aroma volatile compounds with long-term stability, more rational use of natural resources, and eliminate solvent waste generation. Volatile compounds isolated using supercritical CO_2 extraction (300 bar, 40 °C, and 4.5h) were dispersed in different betaine- and glycerol-based natural deep eutectic solvents (NADES), and their headspace profile was monitored during 6 months of storage at room temperature. As the control, CO_2 extract stored under the same conditions was used. The plant species *Satureja montana* L., rich in volatile aroma compounds, was selected for research. *S. montana* is a source of oxygenated monoterpenes among which carvacrol (6.38-31.44%), thymol (5.65-23.48%), and thymoquinone (5.88-16.64%) were the most dominant and commercially and pharmacologically most important ones. Oscillations in the headspace profile of the samples were observed, such as the decrease in and/or disappearance of low molecular weight monoterpene hydrocarbons, including *β*-myrcene, ocimene, *α*-phellandrene, *α*-terpinene, *γ*-terpinene, and others. These alterations were most likely caused by evaporation, oxidation, and other chemical changes in components that occur during storage. Chemical transformations of hydrocarbons impacted the oscillations in the content of oxygenated terpenes, hence an increase in certain oxygenated terpenes was noticed. Moreover, in the control, the appearance and the increase in non-terpene components were observed including E,E-hepta-2,4-dienal, γ-butyrolactone, and acetic acid, which represent components that can lead to the development of unwanted odour and smell, changes in the activity of the product, and manifestation of unwanted effects. Considering that the presence of these components was not detected in NADES samples, it can be concluded that the NADES successfully protected *S. montana* volatile components against changes caused by storage and provided stability at room temperature.

Acknowledgements: This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 101003396.

P 38. Regeneration of deep eutectic solvents with tetramethyl oxolane – a bio-derived solvent

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Keywords: deep eutectic solvent, organic solvent, liquid-liquid extraction, biomass delignification

Concerns about the detrimental environmental impact of volatile organic solvents have prompted research into more environmentally friendly alternatives for a variety of processes, including reactions and separations. In light of this, deep eutectic solvents (DESs) have been proposed for biomass delignification as eco-friendly, inexpensive, and high-boiling-point solvents. For any solvent-based process to be sustainable, solvent regeneration is essential. For DESs with low to negligible volatility, and extracted species like lignin that also have low to negligible volatility, distillation cannot be used for regeneration. Liquid-liquid extraction with a much lower boiling solvent is a separation technique that can be used for extraction of lignin and furanics as the main constituents of the stream after DES-delignification.

Contrary to the more well-known solvent, 2-MTHF, which is obtained from sugars, 2,2,5,5-tetramethyl oxolane (TMO), is synthesized from acetylene and acetone. This can be a bio-derived solvent if the acetylene is produced from biogas and acetone using the well-known acetone-butanol-ethanol (ABE) fermentation. Due to its relatively low miscibility with water and the absence of the peroxide production risk associated with other ethers, it is a solvent of interest for potential future industrial applications. This ether seems to be significantly safer than its sterically less populated family members.

We report here the application of TMO in biorefinery liquid-liquid extractions of lignin and furanics from deep eutectic solvent made of lactic acid: choline chloride. The extraction yields for lignin, 5-hydroxymethylfurfural, furfural and lactic acid-solvent mutual miscibility have been studied and will be compared with two other bio-based solvents, 2-MTHF, and guaiacol. TMO is more resistant to lactic acid leaching than 2-MTHF, and it can be recovered and refined using distillation. TMO appears to be a particularly intriguing bio-derived solvent, for which future interest in further uses is possible.

P 39. NADES-US Coupled Extraction of Graševina pomace Polyphenols

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Keywords: Graševina grape pomace, natural deep eutectic solvents, ultrasound-assisted extraction

In many industrial processes, a large used amount of volatile and flammable petroleum-based solvents causes a negative ecological and economic impact. During the past decade, natural deep eutectic solvents (NADES) have been intensively investigated as their substitute. The properties that have gained them the environmentally friendly label are non-volatility (reduced air pollution), non-flammability (process safety), and excellent stability (potential for recycling and reuse). The number of structural combinations encompassed by NADES is tremendous, thus it is possible to design NADES with unique physicochemical properties for a particular purpose such as the design of solvents for the efficient extraction of biologically active compounds. The aim of this work is to prepare ready-to-use extracts rich in biologically active compounds (polyphenols) from wine production waste (Graševina grape pomace) using DES as an extraction solvent coupled with a flow ultrasound reactor.

First, (*i*) the most effective natural eutectic solvent was selected using COSMOtherm software with regard to the polyphenols solubility in NADES and regulations for acceptable NADES-forming compounds in food and cosmetic products. Further, (*ii*) extracts were prepared and optimized on a lab scale. The optimized procedure was (*iii*) scaled up to a two-litter scale in a flow mode for the first time. Finally, (*iv*) the economic evaluation was performed.

Using alternative green technologies for the extraction of bioactive molecules results in a higher yield in a short extraction period with minimized energy consumption.

Acknowledgments: The work was supported by the European Union through the European regional development fund, Competitiveness and Cohesion 2014-2020 (KK.01.1.1.07.0007.)

P 40. Hydrophobic NADES for Trace Metal Removal from Water

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Keywords: NADES, trace metals, metals recovery

Water contamination is a severe threat to human health and the environment. In particular, trace levels of toxic heavy metals are continually released into bodies of water through various human activities, including mining, manufacturing, and agricultural practices. A promising and environmentally friendly option for recovering trace metals from aqueous solutions is the use of hydrophobic NADESs (Natural Deep Eutectic Solvents). NADESs exhibit supramolecular interactions between two or more biodegradable, hydrophobic compounds which can induce the selective transport of metal ions out of the aqueous phase, therefore cleaning the water. This happens because of the affinity between specific functional groups in the NADESs (such as carboxyl) and the metal ions, thereby forming strong coordination complexes. In this work, different hydrophobic NADESs composed of menthol and organic acids were synthesized, characterized, and used for the separation of trace metals from freshwater. The adsorption of these contaminants and their further recovery using NADESs is also discussed.

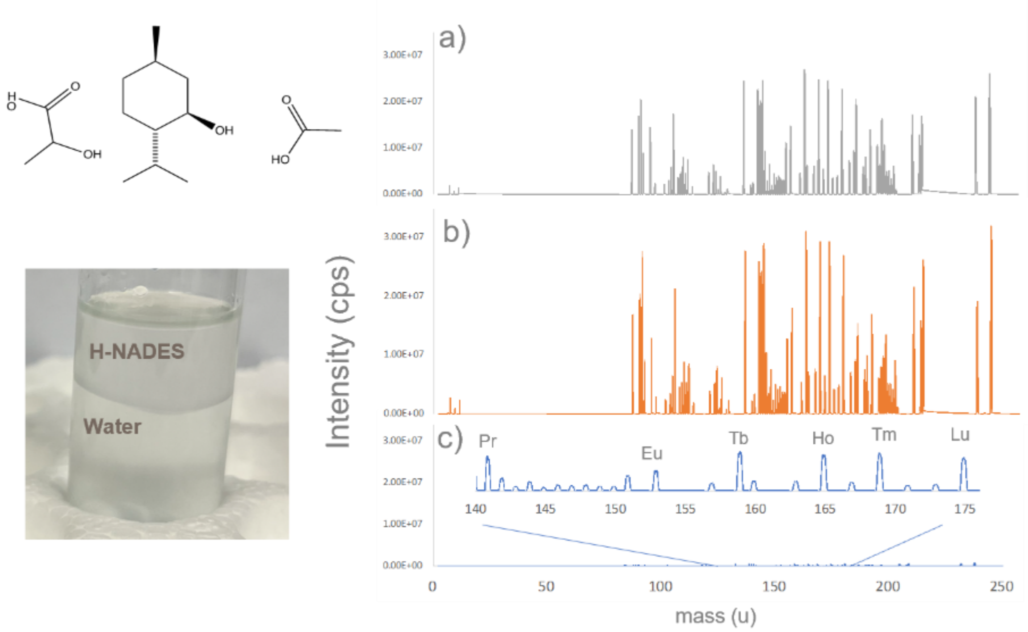

Figure 1: left H-NADES components, and H-NADES:WATERS two-phase solution; right: HR-ICP-MS spectrum of a multielement solution with a concentration of 10 ppb before contact with H-NADES (a), after contact with H-NADES menthol:acetic acid (b) and menthol:lactic acid (c).

P 41. Eutectic Solvents for Inorganic Contaminants Analysis Employing Plasma Sources

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Keywords: green solvents, NADES, sample preparation, ICP OES, ICP-MS

The development of nontoxic and environmentally friendly solvents that can be applied in the sample preparation stage has received increasing research attention in recent decades [1]. Of particular interest is the use of deep eutectic solvents (DES), which have lower melting points than their precursors and offer advantages in terms of solute solubilization, biodegradability, low toxicity, simple preparation, and sustainability. When DES are prepared from natural sources, they are known as natural deep eutectic solvents (NADES) [2]. Both DES and NADES are formed by electrostatic interactions and hydrogen bonding involving donor and acceptor components (HBD and HBA, respectively) [2]. New methods of preparing NADES were developed using microwave radiation and ultrasound, and proved to be fast and efficient [3]. Three different NADES formed by the combinations of citric acid/xylitol/water, malic acid/xylitol/water, and citric acid/malic acid/water, in a molar ratio of 1:1:10, showed applicability for ultrasound-assisted extraction (UAE) of As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, and Zn, with detection employing inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). The methods provided recoveries in the range from 80 to 120% [4]. An evaluation using mixture design for the formation of NADES based on citric acid, xylitol, malic acid, and water was carried out to select the ideal composition of these solvents for elemental extraction applied to environmental samples, prior to determination using plasma techniques. NADES prepared using a ratio of 42:13:45 (% mm^{-1}) for citric acid/xylitol/water and citric acid/malic acid/water were shown to be effective for UAE and microwave-assisted extraction (MAE) of biological tissues and plant material, prior to the determination of As, Cd, Hg, Pb, Se, and V by ICP-MS [5]. Hydrophobic deep eutectic solvents (hDES), obtained using precursors such as acetic acid and DL-menthol, or DL-menthol, pyruvic acid, and acetic acid, have potential for the extraction of Cd and Pb present in soil and sludge samples. The developed solvents showed excellent ability to extract different elemental analytes for determination by plasma source techniques, in addition to complying with the main requirements of green analytical chemistry.

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P 42. Ultrasound-assisted Solid-phase Matrix Dispersion Employing AADES (UA-MSPD/AADES) for As Determination by ICP-MS

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Keywords: green solvents, AADES, UA-MSPD, arsenic

Green analytical chemistry (GAC) has encouraged the development of alternative methods, such as the use of deep eutectic solvents (DES). DES are constituted by the combination of a hydrogen bond donor (HBD) component and a hydrogen bond acceptor (HBA) component, presenting advantages such as low cost, volatility and toxicity[1]. When there is at least one amino acid in the DES composition, amino acid-based deep eutectic solvents (AADES) are obtained[1]. AADES can be used as extraction solvents in the solid phase matrix dispersion method (MSPD), used for solid or semi-solid samples[2]. When AADES as an extraction solvent in MSPD associated with ultrasound assisted extraction (UAE) as a single step procedure, there is potential to develop efficient and environmentally friendly applications. The UA-MSPD/AADES combination was a pioneering approach to determine As in medicinal herbs, as it eliminates the need to synthesize the solvent before starting the extraction. For this, multivariate optimization by Doehlert design (DD) was employed to define the ideal experimental conditions for UA-MSPD using AADES based on β-alanine, citric acid and water (molar ratio 1:2:17)[3]. The effects of temperature, time and sample-solvent ratio were evaluated, and the optimized conditions were 50 °C, 60 min and 10:1 mg mL^{-1}. The accuracy was based on the recovery percentage (95% and 101%), evaluating the certified reference materials. The limits of detection and quantification were 0.039 mg kg^{-1} and 0.130 mg kg^{-1}, respectively. The proposed method was environmentally, scoring 94 points on the Analytical Eco-Scale and 84 points on the RGB 12. Furthermore, when considering the costs of AADES precursors and electricity consumption, UA-MSPD is about 35% cheaper than the conventional method of sample preparation for elemental analysis (MW-AD - Microwave Assisted Acid Digestion), which costs US$ 0.79/sample and US$ 2.22/sample, respectively. UA-MSPD was applied to determine As in commercial medicinal herbs, whose values were within the maximum limit for daily intake established by the World Health Organization (WHO) (0.059 – 0.101 mg kg^{-1}).

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P 43. Deep Eutectic Systems: A Sustainable Approach on the Valorisation of Fruit and Vegetable Wastes

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Keywords: Food waste, extraction, deep eutectic systems, bioactive compounds, antioxidant

Nowadays, one of the major topics and concerns around the world is waste reduction. One of the industries that contributes to the production of large amounts of waste is the agricultural/food industry. For instance, after the harvesting of several types of fruits and vegetables and during their processing, peels, pomace, and seeds are normally wasted. These by-products still have a considerable content in valuable compounds, such as vitamins, proteins, flavonoids, carotenoids, polyphenols, anthocyanins and pigments that have therapeutic potential such as antioxidant, anti-inflammatory and anticancer activities [1,2]. These metabolites have a vast application in different final products such as nutraceutical, cosmetic and even in food products. So, the valorisation of food industry by-products has economic and environmental relevance. This valorisation can be achieved by extracting the bioactive compounds using green solvents such as deep eutectic systems (DES). The main objective of this work was to assess different DES for the extraction of bioactive compounds from food by-products, such as orange peels, grape pomace and apple pomace, and to optimize the extraction conditions (ratio DES/raw material, extraction time, and temperature). Taking this into account, total phenolic content and antioxidant activity were determined in the final DES extract. DES extracts were compared with a conventional extraction method, using an hydroalcoholic mixture as extraction solvent. For instance, DES extracts from orange peels presented contents of total phenolics between 1.5 and 2.5 times more when compared to the conventional extraction, which represents significant improvements in the yield of the extraction. Similar results were observed for the other studied food by-products. In this work, the antioxidant activity was also assessed *in vitro* through the reactive oxygen species assay in HaCat and Caco-2 cell lines, and, finally, the cytotoxicity of the extracts was also evaluated.

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P 44. Green Keratin Extraction from Duck Feathers Using a Deep Eutectic Solvent

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Keywords: extraction, keratin, deep eutectic solvent, biomass valorization

Poultry feathers are an abundant natural material due to the high production of poultry in the world. In the South West of France, more specifically, poultry production is mainly focused on ducks. This duck production generates many co-products, including feathers. Most feathers are usually stored in landfills or buried, which causes environmental problems. Therefore, it is necessary to find a way to enhance this material and provide it with added value. What makes the feather an interesting material is its composition of about 90% protein, mainly keratin. Keratin is known to be an insoluble cysteine-rich protein. It comprises a set of amino acids linked together by peptide bonds, forming a polypeptide chain. The stability of the keratin is made possible by the intramolecular and intermolecular disulfide bonds; thus, these proteins can exist in aggressive environments such as under high temperatures, in solvents, or acidic and basic conditions. The properties of keratin have become crucial for new material creations, and nowadays, the most used extraction methods are based on oxidation, reduction, denaturation, ionic liquids, steam flash explosion, microwave irradiations, and eutectic solvents. The method chosen for this work uses a eutectic solvent because of its non-toxicity, natural origin, and biodegradability. The main goal is to use an eco-friendly process to extract keratin. The choline chloride-urea solvent dissolves the feathers due to its large number of acceptor hydrogen bonds, which breaks the intermolecular and intramolecular hydrogen bonds of keratin. The feathers are mixed with the solvent and heated to dissolve. Once the feathers have dissolved, they are filtered, and the keratin is regenerated by precipitation. The final keratin is obtained after lyophilization. This study is based on the efficiency of the extraction process as a function of various parameters such as temperature, time, and the humidity of feathers, the feather grinding size, and the feathers: solvent ratio. These parameters will be compared regarding yield and the quality of the regenerated keratin. The different keratins were analysed and characterized using thermal analyses: Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and chemical analysis: Fourier transform infrared spectroscopy (FTIR). The size of the keratin molecules obtained was also observed by dynamic light scattering (DLS).

Thereby, the keratin extraction process using a deep eutectic solvent was optimized, and its influence on the structure and properties of regenerated keratin was demonstrated.

P 45. Separation of Terpenoids from Essential Oils Using in Situ Extraction Based on Deep Eutectic Solvents

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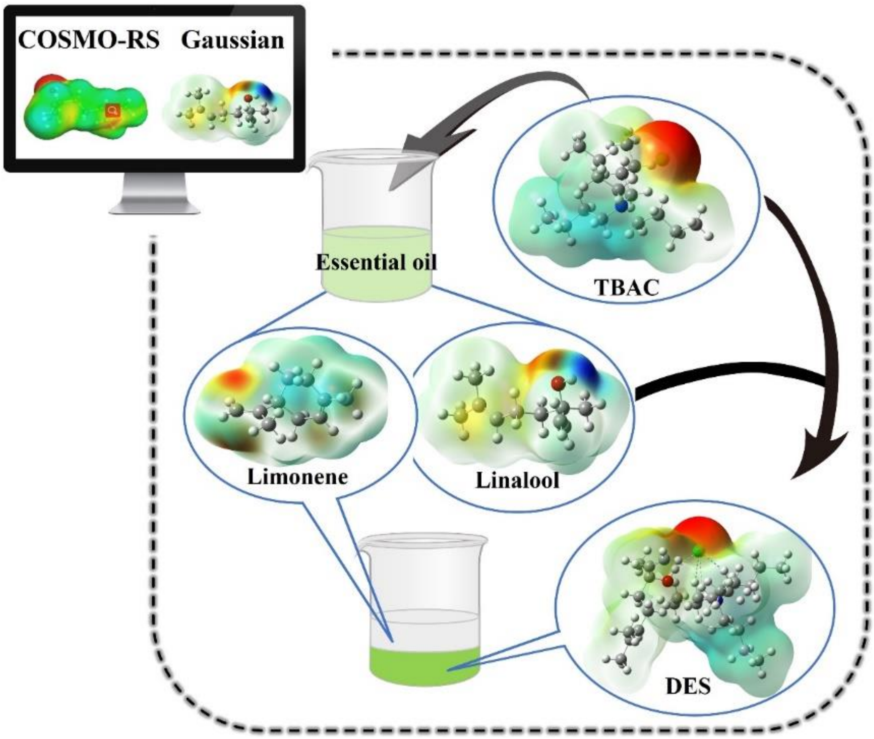
Keywords: deep eutectic solvents, extraction and separation, essential oils

Essential oils are mixtures of volatile compounds isolated from variety, and are used widely in industries. The deterpenation (isolation of terpenes and terpenoids) of essential oils is necessary to improve product quality. This study proposes an extraction method for the separation of terpenes and terpenoids by the way of in situ isolation form. Various quaternary ammonium salts are used to separate terpenoids from crude essential oils by forming deep eutectic solvents (DESs). Tetrabutylammonium chloride (TBAC) which contains suitable ions and symmetry reveals highest terpenoids separation efficiency in the essential oils. The separation mechanism is discussed and the structures of DESs (TBAC/Terpenoids) are proved on COSMO-RS and DFT. Theoretical calculation was used to assess the extraction performance of various TBAC molar ratios, and experimental analysis. The organic solvents and their interactions with terpene revealed n-hexane to be the best organic solvent for recycling DES. Reusable TBAC and high purity terpenoid were obtained through the re-extraction procedure.



P 46. A Sustainable Synthesis of Atenolol in Deep Eutectic Solvents

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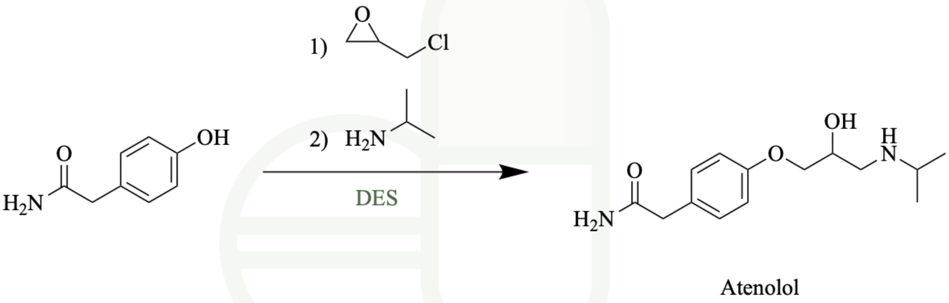
Keywords: deep eutectic solvents, green chemistry, green synthesis, sustainability, atenolol

Pharmaceutical industries have been recognized as major sources of chemical waste because of the huge quantities of solvent which need for the synthesis and purification of active pharmaceutical ingredients [1]. Consequently, synthetic chemists are making considerable efforts to find environmentally friendly solvents in the area of drug development. In this context, deep eutectic solvents (DESs), generally prepared using natural compounds, are emerging as a highly promising category of green solvents that could contribute greatly to the sustainable implementation of green synthesis of pharmaceuticals [2,3].

Atenolol is one of the top five best-selling drugs in the world today used to treat angina, hypertension and to reduce the risk of death after a heart attack. This study discloses an example of a sustainable protocol which can be used to directly synthesize atenolol in DES (Scheme 1).



Scheme 1. *Synthesis of atenolol in deep eutectic solvents*

The traditional synthesis of this drug consists of a two-step process with production of large amount of waste and other by-products to be disposed of. The DES allowed the entire process to be performed avoiding the use of additional bases or catalysts affording atenolol in high overall yields. Furthermore, short reaction times, mild reaction conditions and no chromatography are the main hallmarks of the procedure.

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P 47. Carbon Dioxide Solubility in Type V Deep Eutectic Solvents

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Keywords: type V DES; CO_2 solubility; COSMO-RS; hydrophobic DES

Deep eutectic solvents (DES) are a new class of green solvents that have shown unique properties in several process applications. Carbon dioxide (CO_2) capture is one application that can benefit from DES. Various studies have demonstrated the potential of DESs for CO_2 capture; however, these studies proposed using ionic DESs, which are hygroscopic. Recently, hydrophobic DES based on natural and inexpensive nonionic constituents, also known as type V DES, has attracted much attention [1]. Hydrophobic DESs containing L-menthol possess outstanding properties, such as low viscosity and eutectic temperatures, especially when L-menthol is mixed with phenolic alcohols, such as thymol or carvacrol [2]. This work evaluates nonionic DES containing phenolic alcohols as solvents for CO_2 capture applications [3]. Potential phenolic alcohols and the molar ratio between DES constituents were preselected for experimental investigations based on the conductor-like screening model for realistic solvation (COSMO-RS). CO_2 solubility was experimentally determined in two different DES, namely, L-menthol/thymol in 1:2 molar ratio and thymol/2,6-xylenol in 1:1 molar ratio, at various temperatures and pressures. CO_2 solubility in the studied systems was higher than that reported in the literature for ionic DES and ionic liquids. This study demonstrates that nonionic DES containing phenolic alcohols can be excellent, inexpensive, and simple solvents for CO_2 capture.

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P 48. Exploring Novel Agro-based Deep Eutectic Solvents for Food Packaging Films

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Keywords: hydrophobic deep eutectic solvents, food packaging films, ultrasound emulsification, antioxidant activity

Hydrophobic deep eutectic solvents (DESs) are an emerging class of green solvents, which are economic, tuneable, and environmentally friendly. Synthesis of agro-based hydrophobic functional DESs have been explored in this study by the conventional heating method. For the first time, alcohol-based hydrophobic DESs consisting of thymol and alcohols (hexadecanol, vanillyl alcohol and β–sitosterol) of varying individual melting points have been synthesized, for a range of molar compositions. Along with detailed physicochemical, thermal, and rheological characterization of the DESs synthesized, an EcoScale score of > 95 % re-establishes agro-based DESs as green solvents for their pioneering usage in food packaging.

Hydrophobic DES-in-water emulsions were produced by ultrasound emulsification (750 W, 30min, 1s pulse on/off) technique. The aqueous, continuous phase of the emulsions comprised pectin (biopolymer), glycerol (plasticiser) and Tween 80 (surfactant) and the dispersed phase comprised hydrophobic DESs. Subsequently, the optimized DES-in-water emulsions were cast to form dense membranes at a controlled temperature of 35 °C.

From the application perspective, the antioxidant properties of the synthesized DESs, their individual components and the bio-polymeric membranes were tested by DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate) free radical antioxidant assay. Synergetic effects were witnessed as the antioxidant properties were enhanced in all the DES-based systems tested. The vanillyl alcohol and thymol-based membrane had the highest Trolox equivalent antioxidant capacity of 376.60 µmol Trolox/ml of DES in membrane. Additionally, the films were characterised in terms of optical and mechanical properties, surface hydrophobicity, barrier properties against water vapour, gases (CO_2, O_2) and ultraviolet-visible (UV-vis) radiation. The ongoing studies firmly suggest promising applications of these bio-based films as packaging materials for food products with low water content.

P 49. Comparative Study of Spectrophotometric Methods for Quantification of Chlorogenic Acid in NADES

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Keywords: natural deep eutectic solvents, phenolic compounds, Folin-Ciocalteu, Prussian blue

NADES have become a new way to extract phenolic compounds from different matrices, due to their ability to solubilize both hydrophilic and hydrophobic compounds. The efficiency of this extraction may be evaluated by quantifying the phenolic compounds extracted in the NADES medium. Among the existing methods for the quantification of these compounds, spectrophotometric methods are widely applied in the literature. Due to the nature of NADES (natural deep eutectic solvents), applying spectrophotometric quantification methods presents challenges. The aim of this study was to compare evaluative methods for quantification of chlorogenic acid, a phenolic acid highly soluble in NADES. The methodologies chosen for evaluation and comparison were two redox methodologies applying the Folin-Ciocalteu and Prussian blue reagents. Standard curves of chlorogenic acid were prepared in NADES media of choline chloride:glycerol (1:1) – CC:GL and urea:glycerol (1:1) – U:GL and evaluated by the methods mentioned. It was not possible to quantify chlorogenic acid from the CC:GL curve using the Folin-Ciocalteu reagent, as the equation generated an R^2 lower than 0.9 (Figure 1), making it unreliable to quantify chlorogenic acid in this formulation of NADES. The formation of a yellow precipitate was observed when Folin-Ciocalteu reagent was added to CC:GL samples, without the typical change of color from yellow to blue, indicating that the redox reaction did not occur properly. CC:GL showed higher viscosity than U:GL, that may interfere with the bound between the phenolic compounds and the NADES, making it more difficult for the reaction to occur. The precipitation was also verified in pure choline chloride solution. However, both NADES formulations showed reliable responses by the Prussian blue reagent, although CC:GL has shown lower sensitivity, since the same increase in concentration resulted in a much smaller increase in absorbance.

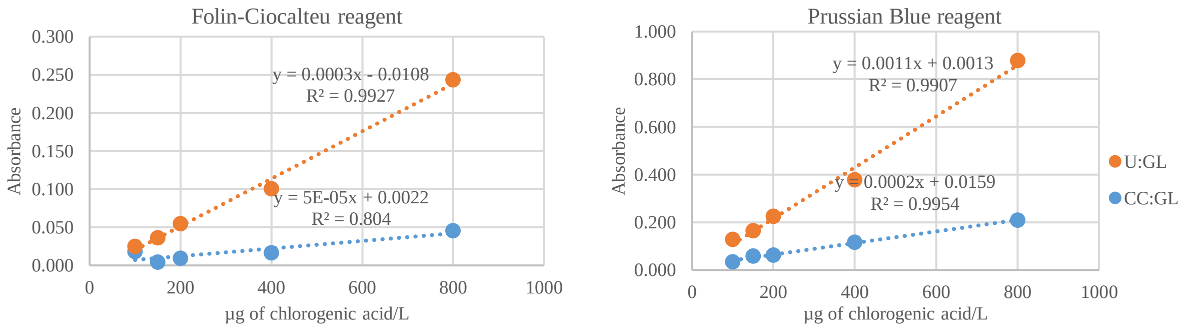

Figure 1. Folin-Ciocalteu and Prussian Blue reagent standard curves of chlorogenic acid

P 50. Antioxidant Activity of NADES Extracts of Sunflower Meal

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Keywords: natural deep eutectic solvents, co-products, DPPH, ABTS, FRAP

Sunflower meal is a co-product of sunflower oil extraction, used mainly in animal feed. It is, however, a material rich in phenolic compounds that may represent up to 4% in dry mass and of which the main components are of the chlorogenic acids family. These compounds have shown antibacterial, anticarcinogenic and antioxidant activities. NADES have been used to extract phenolic compounds due to their ability to extract compounds of different polarities, when compared to organic solvents and water. The aim of this study was to evaluate the antioxidant activity of sunflower meal extracts in NADES media, but also of the pure solvents, in comparison to the hydroethanolic extract. Sunflower meal extracts were prepared in NADES of lactic acid:glucose – LA:G, choline chloride:glycerol – CC:GL, urea:glycerol – U:GL and betaine:lactic acid – B:LA. The concentration of chlorogenic acid was evaluated by a spectrophotometric method using Prussian blue (Table 1) and the antioxidant activity was evaluated by the DPPH, FRAP and ABTS methods. The pure NADES showed significantly lower antioxidant activity than the extracts and it is safe to say that they did not significantly interfere with the reaction of the extracts. Among the extracts the results may be observed in Figure 1. Comparison of Table 1 and Figure 1 indicate that the concentration of chlorogenic acids may not be the only factor affecting antioxidant activity.

Table 1. Chlorogenic acid concentration (mg/L) in different extracts

Ethanol	**LA:G**	**CC:GL**	**U:GL**	**B:LA**
$47{,}2^{b}$	$52{,}5^{a}$	$54{,}9^{a}$	$39{,}0^{c}$	$56{,}9^{a}$

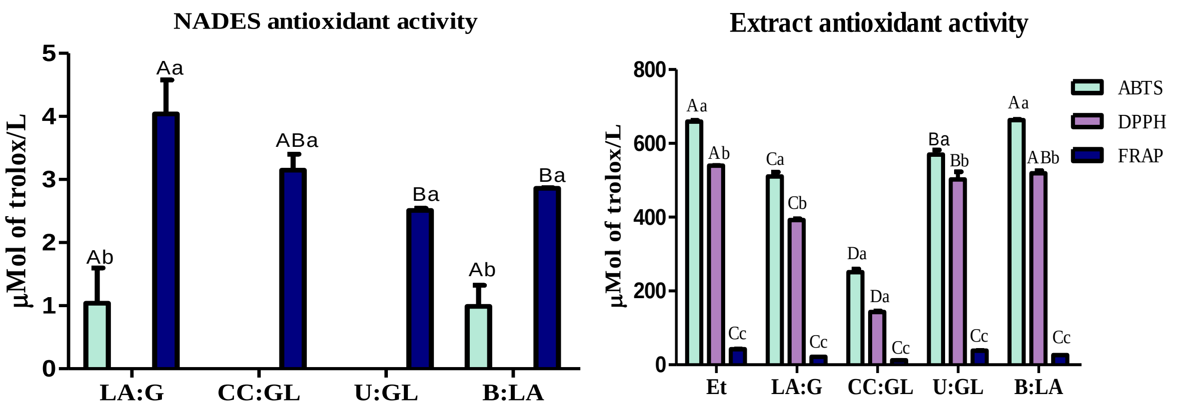

Figure 1. Antioxidant activity in NADES and NADES extracts of sunflower meal. Different capital letters indicate a significant difference in the antioxidant activity between extracts and different lowercase letters indicate a significant difference between the methods.

P 51. Haloarchaea as Molecular Factories: from DESs to the Production of Biotechnological Compounds

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Keywords: deep eutectic solvents; haloarchaea; bioremediation; carotenoids; circular economy

Toxicity of deep eutectic solvents (DESs) has not been accurately studied [1]. On the other hand, halophilic archaea represent one of the most important study models in brine treatment, being able to produce molecules of high biotechnological value such as bioplastics and carotenoids [2]. In this research, the toxicity of four different DESs based on acetylcholine chloride (AcChCl) and choline chloride (ChCl) has been studied. DESs based on AcChCl in combination with acetamide or urea showed a significant drop in pH as the concentration of the DESs in the medium increased. Despite this, growth was slightly higher in AcChCl-based DES cultures compared to ChCl-based ones. The aim of this study was also to evaluate the potential bioremediation of DESs and their relationship with the production of carotenoid pigments. The highest production was obtained with intermediate concentrations of AcChCl-acetamide mixture, (in the presence of 300 mM of DES the production of carotenoids was 15 times higher than the control culture). Differences of bacterioruberin production was also studied between different DESs and concentrations to stablish differences in the pattern of production against toxicity. Furthermore, the possible use of the different DESs as a source of N and C by Hfx. mediterranei cells was studied by means of minimal medium cultures nitrogen and glucose deficient. Thus, the results show that the choline chloride-acetamide and acetylcholine chloride-urea DESs could be consumed, reaching absorbance values at 600 nm wavelengths close to 1. The potential use of haloarchaea for DESs bioremediation show the great interest of this methodology to bioremediate these compounds.

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P 52. Protein Structure and Stability in Hydrated Betaine-based Deep Eutectic Solvents

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Keywords: deep eutectic solvents, ubiquitin, RNA, secondary structure, Molecular Dynamics

Deep eutectic solvents (DESs) are a relatively novel class of green tailor-made solvents, generally comprised of a hydrogen-bond (HB) donor and an HB acceptor, and characterized by a significant depression of the melting point relative to those of the individual components. DESs have attracted much attention due to some of their properties, including, biodegradability, affordability, tunability, and ease of preparation, thus, holding the promise to overcome some of the hindrances of room temperature ionic liquids. DESs have been exploited in multiple applications including biocatalysis and nucleic acid preservation and stabilization. Recent reports have shown that enzymatic activity can be enhanced by using DESs as the reaction media. A pivotal question associated with biological applications concerns the minimum amount of water required to allow biomolecules to maintain their structure and function. Here, the effect of the water content and temperature in the structure of a prototypical globular protein, Ubiquitin, and an RNA tetraloop, GAGA, solvated in betaine-based deep eutectic solvents was probed through molecular dynamics simulations. Optimized force fields for the DES are reported along with a molecular analysis of the structure of the biomolecules in water and in the hydrated and dehydrated DESs.

P 53. Eutectic Mixtures as Efficient Solvent for Microalgae Cell Disruption and Extraction

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Keywords: eutectic mixtures, microalgae, cell disruption, extraction

As a sustainable and economic resource, microalgae has achieved growing attention for the production of various valuable proteins and nutrients. Cell disruption, one of the most crucial steps in production process has been continuously challenged. Being a new generation green solvent, eutectic mixtures have shown great potential as efficient dissolution and extraction media. In this study, effective cell disruption using eutectic mixtures and subsequent tailored purification of high-value fluorescence protein phycoerythrin (PE) from algal biomass was investigated. Firstly, disruption of cell wall compositions by eutectic mixtures was predicted by conductor like screening model for real solvents (COSMO-RS) and then tested on *Porphyridium*. sp. COSMO-RS prediction and microscopic visualization results showed that different eutectic mixtures have significant effects on breakage of the rigid polysaccharide cell wall and release of PE with varying efficiencies. Of note, eutectic mixtures could facilitate the extraction by shortening the time at higher recovery compared to the conventional freeze-thaw method. Further tailored purification based on an aqueous two-phase system coupled with ammonium sulfate precipitation and ultrafiltration could yield PE with fair purity. Thus, the developed method is clearly an efficient and simple, yet eco-friendly approach to producing PE of high commercial value.

P 54. Deep Eutectic System as a Catalytic Medium in the Synthesis of Fuel Additives

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Keywords: levulinic acid, esterification, deep eutectic system, high-pressure carbon dioxide

Biofuels, understood as derived from biomass, are essential to meet fast-growing demand for transportation and alleviate the negative impact of vehicles emissions. Alkyl levulinates can be produced from levulinic acid, one of the top 12 platform chemicals produced from biomass, and have been proposed as both gasoline and diesel additives capable of enhancing fuel quality. Ethyl levulinate, potentially produced from bioethanol, constitutes a particularly attractive high value-added chemical from sustainability point of view.

Conventionally, the Fischer esterification is carried out with strong mineral acid leading to corrosion, environmental pollution, and troublesome catalyst recyclability. Heterogenous catalyst are associated with lower reaction rates, side products or catalyst deactivation. Ionic liquids, although emerged as a green solution, are often characterized by complex preparation, possible toxicity, low biodegradability and high cost limiting their applications to a large extent. In this context, deep eutectic systems (DES) offer a pronounced advantage.

In the undergoing project, several DES are examined as catalyst for the esterification of levulinic acid with ethanol. The influence of process parameters, i.e., temperature, time, alcohol to acid ratio, catalyst loading, on the catalytic activity was studied in a batch mode. The conventional synthetic method was further compared with the process under high-pressure carbon dioxide conditions.

Acknowledgements: This work was supported by the European Union's Horizon 2020 (European Research Council) under grant agreement No ERC-2016-CoG 725034, and by the Fundação para a Ciência e Tecnologia FCT/MCTES projects PTDC/EQU-EPQ/1039/2021 and UIDB/50006/2020 of the Associate Laboratory for Green Chemistry -LAQV. GC-FID data were obtained by the Analysis Laboratory LAQV/Requimte - Chemistry Department, FCT NOVA - Portugal. The authors also thanks to the Croatian Science Foundation Under the project UIP-2017-05-6593.

P 55. Mimicking Nature: Design, Preparation and Applications of Bioinspired Deep Eutectic Solvents

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Keywords: deep eutectic solvents, bioinspired solvents, biological material stabilisation

Observing nature has been one of the most successful ways to find inspiration for solving complex problems through engineering, chemistry and biotechnology. Such nature-inspired design is a multidisciplinary process, and the challenge lies in the identification of the natural function to identify specific applications, as well as to transfer natural concepts into an engineering perspective in the exact same way. In addition, such approach is based on the key idea that nature always functions on a principle of economy and optimal efficiency. Deep Eutectic Solvents (DESs) prepared from naturally derived compounds have been intensively studied as neoteric systems that are expected to provide a natural, cytosol-like environment for various biomolecules, allowing them to show properties and functionality profiles that resemble the ones observed in their natural environment.

Here we report on new two-, three-, and multicomponent eutectic systems directly inspired by the distribution patterns of various metabolites observed across all kingdoms of life, together with their application as storage medium for various biological systems (e.g. proteins, enzymes and cells) and other commercially important molecules of natural origin (e.g. biologically active compounds). Based on the results, these new biorelevant DESs may open up new opportunities for action in diagnosis, monitoring, treatment and manufacture across several research fields and market sectors (Figure 1).

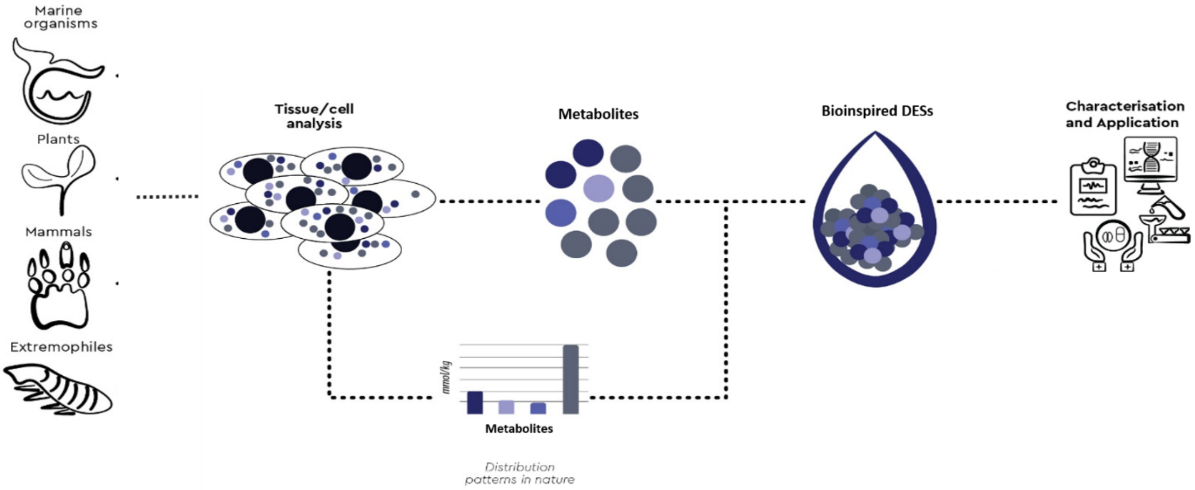

Figure 1. Design, characterisation and application of bioinspired DESs.

P 56. Stabilising Nicotinamide Cofactors in Deep Eutectic Solvents (DES)

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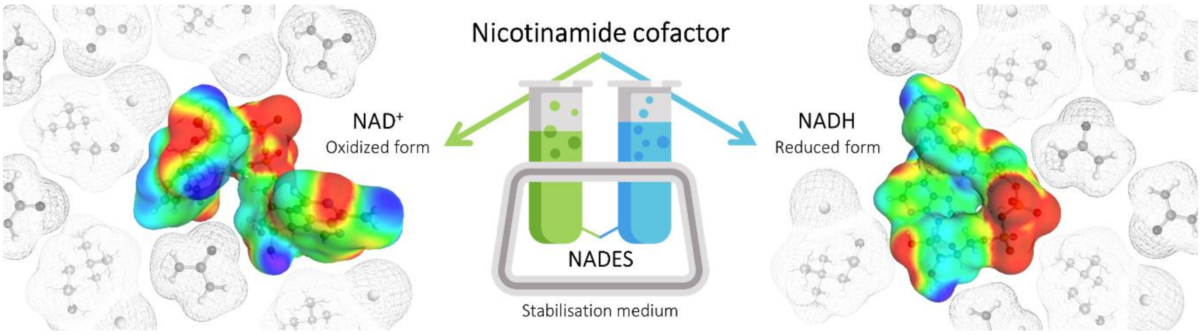
Keywords: DES, nicotinamide cofactors, green chemistry, computational approach

Cofactors are an indispensable part of oxidoreductase-catalyzed reactions, with nicotinamide cofactors NAD$^+$ and NADH being most frequently present. Because they are known for their labile nature and short-term stability, new and fresh stock solutions need to be prepared prior to the reaction, especially when used in biocatalysis. Therefore, finding a solvent that could simultaneously stabilise both cofactor forms in oxidoreductive biocatalytic reactions and minimize their degradation during storage is of great significance.



For that purpose, changes in NAD UV-Vis absorption spectra during the 14-day incubation period in different betaine- and choline-based DES at room temperature were monitored. To decipher the mechanism behind the observed NAD stabilisation, a computational approach was implemented using molecular dynamics (MD) simulations and quantum mechanics (QM) calculations. DES that exhibited the highest stabilisation potential for both cofactor forms were further used in the prolonged cofactor stabilisation and activity studies by using the alcohol dehydrogenase activity assay.
Choline-based DES with urea and ethylene glycol were identified as stabilisers of both cofactor forms. Computational analysis revealed that both cofactors forms change their conformational preference and solvation environment in DES, whose components dominate in their tendency to solvate NAD$^+$ and NADH relative to water. ChCl:U (choline-chloride:urea) showed the excellent capability to stabilise the NAD cofactor during its incubation up to 50 days at 4 °C while preserving the cofactor’s biological functionality. To conclude, ChCl:U was selected as the best NAD liquid storage medium, i.e. a working solution and assay reagent. This study implies that DES should be considered as a solvent for complex redox reactions that require functionality and stability of both the enzyme and the cofactor.

P 57. Accurate Prediction of Carbon Dioxide Capture by Deep Eutectic Solvents using Quantum Chemistry and a Neural Network

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Carbon dioxide (CO2) emissions from fossil fuel combustion are a significant source of greenhouse gas, contributing in a major way to global warming and climate change. Carbon dioxide capture and sequestration are gaining much attention as potential methods for controlling these greenhouse gas emissions. Among the environmentally friendly solvents, deep eutectic solvents (DESs) have demonstrated the potential capability for carbon capture. To establish a theoretical framework for DES activity, thermodynamics modeling, and solubility predictions are significant factors to anticipate and understand the system behavior. Here, we combine the COSMO-RS model with machine learning techniques to predict the solubility of CO2 in various deep eutectic solvents. A comprehensive data set was established comprising 1973 CO2 solubility data points in 132 different DESs at a variety of temperatures, pressures, and DES molar ratios. This data set was then utilized for the further verification and development of the COSMO-RS model. The CO2 solubility (ln(xCO2)) in DESs calculated with the COSMO-RS model differs significantly from the experiment with an average absolute relative deviation (AARD) of 23.4%. A multilinear regression model was developed using the COSMO-RS predicted solubility and a temperature-pressure dependent parameter, which improved the AARD to 12%. Finally, a machine learning model using COSMO-RS-derived features was developed based on an artificial neural network algorithm. The results are in excellent agreement with the experimental CO2 solubilities, with an AARD of only 2.72%. The ML model will be a potentially useful tool for the design and selection of DESs for CO2 capture and utilization.

P 58. Effect of Essential Oil-based Formulation on Biopesticide Activity

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Keywords: biopesticide, emulsion, spray drying, NADES, essential oils, *Bemisia tabaci*

Essential oils (EOs) represent a promising source of biopesticides given their compositional complexity which bestows them high insect specificity and low risk of inducing resistance [1]. However, their use in agriculture remains limited by their rapid degradation, limited duration of effect and non-target toxicity. These issues largely result from the under-optimized methods currently used to formulate EOs, in which their volatile organic compounds (VOCs) are poorly protected [2-4]. In this study we compared pure artemisia and rosemary EOs to EOs formulated in three sustainable, low-cost, and relatively simple manners: as nanoemulsions, atomized powders, or Natural Deep Eutectic Solvents (NADES). 24 h after formulation, the entomotoxicity and phytotoxicity of the formulations was tested on *Bemisia tabaci* infested tomato plants. The identity and relative abundance of VOCs present in all formulations was also assessed 24 h post-preparation using GC-MS and GC-FID. Nanoemulsions proved the most entomotoxic of formulations, followed by NADES and pure EOs, while atomized powders were not significantly more entomotoxic than the control. Unlike other formulations, no phytotoxicity was observed for those based on NADES, and induced particularly high rates of *Bemisia tabaci* mortality when prepared with rosemary EO. Total VOC abundance depended on VOC release kinetics, determined by formulation, which although higher for pure EOs and nanoemulsions, was more gradual for NADES. These results show the importance of EO formulation and the potential for NADES to provide effective, sustained pest control.

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P 59. Innovative Eutectic Systems for Neutralizing Malodorous Compounds

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Keywords: NaDES, volatile malodorous compounds, GC-MS/FID analysis

Urban growth, its related olfactive pollution and increasing social awareness has led to the emergence of an increasing number of complaints due to odour nuisance [1]. Malodorous substances produced by human activities are the cause of significant discomfort, but also health issue such as tension, depression, fatigue and mood disturbance [2]. In order to propose an alternative and sustainable way to commercial deodorizers available, we propose to take advantage of the exceptional solubilizing properties of deep eutectic solvents to develop new odour neutralizing solutions.

To that end, so-called non-ionic DES, or type-V DES [3] were prepared combining natural compounds such as menthol, thymol, eugenol, or terpineol, accordingly, with carboxylic acids, polyols, or coumarin accordingly. The influence of these DES on the volatility of malodorous compounds containing sulphur, nitrogen or oxygen was measured and revealed a significant absorption of these volatile compounds into eutectic solvents.

In addition, DES were formulated in two examples of end-products, namely a cat litter and a perfuming composition. In both cases, the capacity of such eutectic solvents to neutralize fouling smells was demonstrated.

Finally, the olfactive properties of neat eutectic solvents were described by sensory analysis, revealing a masking effect that advantageously complement the neutralizing properties of such solvents.

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P 60. Effective VOC Capture by Hydrophobic Deep Eutectic Solvents Using Static and Dynamic Processes

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Keywords: deep eutectic solvents, biogas upgrading, partition coefficient, absorption capacity, volatile organic compounds, regeneration

We are currently witnessing an increase in biogas production in the context of fossil fuel decline and the future circular economy. Biogas is nowadays considered as an alternative renewable energy. However, raw biogas contains undesirable compounds such as hydrogen sulfide, volatile organic compounds (VOCs) and carbon dioxide (CO_2) that should be removed to upgrade biogas to biomethane to be used as vehicle fuels or injected into the natural gas grid. Biogas upgrading with physical absorbents, such as water and other commercial organic solvents, is simple, efficient and with low energy requirements for regeneration. Also, absorption is an effective method to capture undesirable compounds from biogas.

In this work, the feasibility of biogas upgrading using three hydrophobic DESs, based on fatty acids (C_8:C_{12}, C_9:C_{12} and C_{10}:C_{12}) as well as conventional solvents (glycerol, propylene glycol and propylene carbonate) as absorbent was studied. Nine major volatiles compounds found as biogas impurities were selected (toluene, limonene, pinene octamethylcyclotetrasiloxane, heptane, decene, decane, dichloromethane and methylethylketone) to evaluate the efficiency of these absorbents. The influence of different parameters like temperature, water content and VOC concentration was investigated. To this aim, we determined the vapor–liquid partition coefficient (K) of the VOCs in the studied DESs and conventional solvents. The absorption capacities of the absorbents were also evaluated using a dynamic set-up mimicking an industrial absorption column. This set-up allows the flow rate of VOCs to be modified. Both static and dynamic results are in good agreement.

The results show a decrease in K value for all solvents compared to water, with hydrophobic DESs being the most effective solvents with a K value up to 20000 -fold lower. The obtained results indicate that efficient VOCs absorption can be achieved by the proposed hydrophobic DESs and conventional solvent also providing easy recycling and recovering process.

Acknowledgements: P.V acknowledges the financial support from Dunkerque l'Energie Creative project (PIA3), Starklab and Région Hauts-de-France.

P 61. Use of Deep Eutectic Solvents for Systematic Valorization of Spent Coffee Ground

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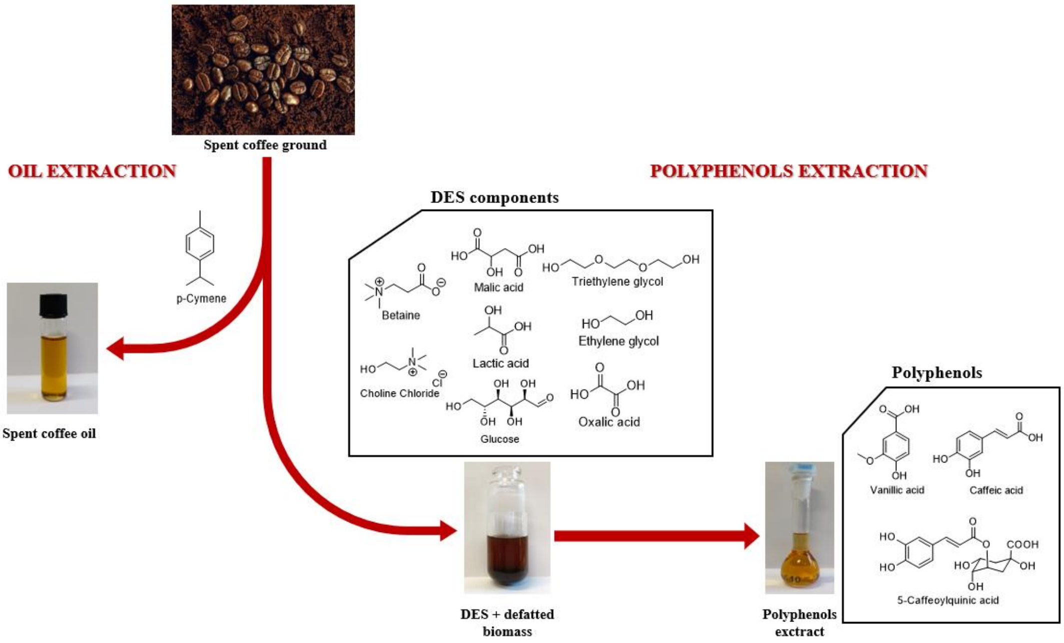
Keywords: deep eutectic solvents, spent coffee ground, biomass valorization

Spent coffee ground (SCG) is the main byproduct obtained from coffee brewing. 65% of coffee beans end up in SCG, hence the amount of waste produced worldwide is massive. It consists of approximately 6 million tons of waste produced every year. In addition, SCG contributes significantly to environmental pollution, since it is a particularly challenging waste to dispose of. Fortunately, due to its unique composition, this biomass could be exploited to obtain different fractions of interest [1,2]. The aim of this work is to realize a completely sustainable study of the biomass. Microwave- and ultrasound-assisted extraction have been employed to reduce the time and energy consumption of the extraction. More in details, SCG has been treated with p-Cymene to extract coffee oil, replacing the use of hexane generally employed to defatting biomass. On the defatted SCG, deep eutectic solvents (DES) have been used to extract coffee polyphenols. For each DES used, different method and time of extraction, temperature and solid/liquid ratio have been tested to evaluate the influence of each variable. Polyphenols content was assessed by Folin-Ciocalteu assay. In addition, DPPH, FRAP and β-Carotene assay were used to evaluate anti-scavenging and antioxidant activity of the extracts. The composition of the extracts was ascertained by HPLC analyses.



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P 62. Experimental Investigation and Thermodynamic Modeling of Cannabidiol Solubility in Plant Oils and Hydrophobic Eutectic Systems

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Keywords: cannabinoids; green solvents; deep eutectic solvents; COSMO-RS; solubility

Cannabidiol (CBD) is one of the most important cannabinoids that can be extracted from the flowers of *Cannabis sativa*. CBD has attracted considerable attention over the past few years due to its several beneficial applications in the pharmaceutical and food industries. Due to CBD's high lipophilicity, it is poorly soluble in water; hence, new hydrophobic solvents are needed for CBD delivery. This study investigated the solubility of CBD in ten plant oils and various systematically designed hydrophobic eutectic systems (ESs) [1]. The molecular weight and structural characteristics of the oils and ES components were found to be related to the solubility of the CBD. CBD was more soluble in medium-chain triglyceride oils than in oils containing long-chain unsaturated fatty acids. Additionally, ESs were found to have a higher level of CBD solubility than oils. The conductor-like screening model for realistic solvents (COSMO-RS) was used to predict the solubility of CBD in oils and ESs. COSMO-RS provided reliable estimates for the CBD solubility in ES. However, the CBD solubility in oils could not be well predicted due to the complex nature of plant oils. This work shows that newly designed green hydrophobic ESs can be explored for CBD extraction from plants as well as CBD delivery in pharmaceutical, cosmeceutical, and nutraceutical products.

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P 63. Fortification of the Biological Activity of Licorice by Frying with Honey, a Natural Deep Eutectic Solvent

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Keywords: natural deep eutectic solvent (NADES), honey, licorice, bioavailability, thermal stability, molecular interactions

Honey was reported to act as a natural deep eutectic solvent (NADES) with a supramolecular structure. Honey-processed licorice has been used since ancient times. Our former study confirmed that honey-processing enhanced the immunomodulatory efficacy, anti-inflammatory efficacy, and hepatoprotective efficacy of licorice. However, it is still unknown why honey-processing can enhance the pharmacological activity of licorice. Therefore, we investigated the synergistic effect of honey on licorice to elucidate the possible potentiation of honey-frying on licorice. Honey increased the total flavonoid and polysaccharide contents in licorice decoction, improved the thermal stability and oral bioavailability of certain pharmacologically active constituents, and augmented their overall pharmacological activities. Similar effects of honey were also observed with a honey analogue GFSH, a NADES made of glucose, fructose, and sucrose with certain amount of water. These synergistic effects of honey are due to the mechanism that honey forms molecular interactions with compounds in licorice. At the meantime, these findings provide theoretical and empirical basis for potential novel applications of honey or other NADESs at augmenting the health-promoting effects of medicinal plants.

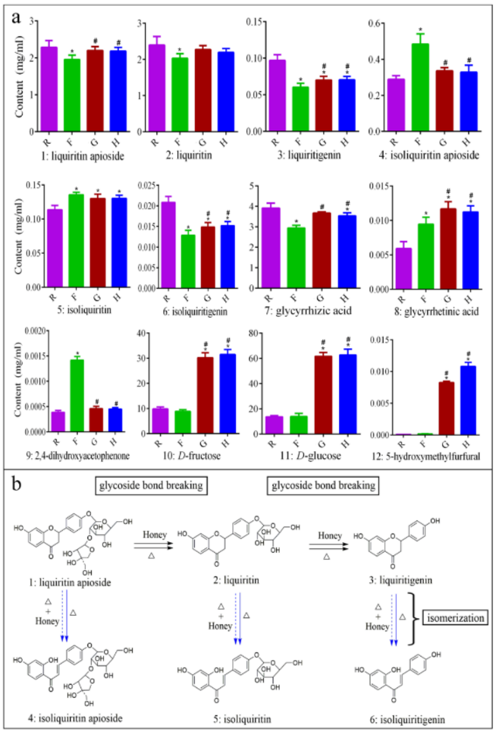

Figure 1. (a) Bar plots of the content of some quality difference markers. (b) Proposed conversion of chemical constituents in licorice caused by heat processing without and with honey or honey analogue (natural deep eutectic solvents, GFSH). (R, raw licorice; F, fried licorice; H, honey-processed licorice; G, GFSH-fried licorice; *n* = 6, * $P < 0.05$ vs R group; # $P < 0.05$ vs F group. Solid line: conversion rate high; dotted line: relatively weak conversion rate;   : heat processing;   + Honey: heat processing with honey)

Reference

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P 64. Evaluation of deep eutectic systems as anti-biofouling agents

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Keywords: antifouling, maritime pollution, ecotoxicity, greener antifouling coatings, bioactive compounds

In current times, sea trade has risen exponentially and with it, a development of sea-based infrastructures. Enacting a major role on the global economy, sea-based industries also deal with a major economic setback, a multitrophic, succession-based, fast-occurring colonization process: biofouling. Consequences include biocorrosion, higher fuel consumption and higher drydock maintenance costs. Current solutions comprise the use of antifouling coatings, however these are based on highly toxic components, such as copper and lead, being progressively outlawed. With an ever-growing concern for marine ecosystems, new, cheap and natural coatings are highly sought-after. One possible alternative is the use of green technology, in the form of natural deep eutectic systems (NADES).

In this work, several NADES were developed, from which Menthol:Oleic acid (1:1) and Thymol:Oleic Acid (1:1), were selected and formally analysed using polarized optical microscopy, having shown to be stable at temperatures close to the melting point of water. Non-target ecotoxicity was assessed on a crustacean model (*Palaemon varians*), showing non-significant alterations to the oxidative stress mechanism and its biomarkers, at tissue level. Anti-biofouling activity was assessed in terms of antimicrobial and antibiofilm activity against *Vibrio parahaemolyticus*, *Vibrio alginolyticus*, *Bacillus subtilis* and *Serratia* sp., quorum sensing on *Chromobacterium violaceum* and microalgae growth inhibition (*Chaetoceros calcitrans*, *Chaetoceros* sp., *Amphora* sp., *Thalassiosira* sp. *Tetraselmis chuii*). Till now, T:OL(1:1), showed the most promising results, with an average IC_{50} = 1.701mg/mL against a panel of marine bacteria, inhibiting the quorum-sensing mechanism of *C. violaceum* at 500µg/disk (>20mm) and the growth capacity of a panel of microalgae at the same concentration (>10mm). While effects were lower compared with using free thymol, this new NADES shows promise for being less toxic than its active component and having a higher degree of miscibility in paint, its future intended application. While M:OL (1:1) had an average IC_{50} = 4.4mg/mL against the studied bacteria, trials with *C. violaceum* and microalgae showed lower activity at 5mg/disk, with inhibition halos ranging from 0-6mm.

Further experiments are being done with medusa polyps to test the anti-settlement activity, ecotoxicity tests on brine shrimps and ocean field trials with NADES-incorporated paint.