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4èmes Journées Plénières du GDR SolvATE en collaboration avec le GDR Hydrates de gaz

9-10 décembre 2021
Institut Chevreul, Lille

cnrs

GDR Groupement de recherche

SolvATE Solvatation : Avancées Théoriques et Expérimentales

Groupement de recherche

SolvATE Solvatation : Avancées Théoriques et Expérimentales

Groupement de Recherche 2035 SolvATE

Book of Abstract

Lille, 2021

GDR SolvATE 2035: Book of Abstract
Editors: A. Idrissi, A. Juhasz
Front Cover : Marc Fourmentin

Preface

SolvATE is a French network, funded by the Chemistry Institute of the CNRS, joining about forty Laboratories who share an interest in understanding solvation at a molecular level. One of the strengths of this network resides in its multidisciplinarity: theoreticians and experimentalists, chemists, physicists and engineers all expressed a strong motivation in building a playground for new collaborations and exciting projects.

The conference program covers the three main topic of the GDR SolvATE :

1) *Solvents in chemistry; towards a sustainable future*
2) *Solvation and interfaces / surfaces*
3) *Nanoconfined media and Solvation in systems of interest in the biological and pharmaceutical field and for food processing*

and also some topics from the GDR Hydrate de gaz.

Local Organizing Committee

Local Organizing Committee

Natalia Correia
Sophie Fourmentin
François Alexandre Miannay
Ákos György Juhász
Bertrand Chazallon
Frederic Affouard
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Program

4èmes Journées Plénières du GDR SolvATE en partenariat avec le GDR Hydrates de gaz

Le 9 et 10 décembre 2021 – Amphi de l'Institut Chevreul -Lille

09/12/2021 08h30- 12h10 : Solvation and Interfaces/surface, nanoconfined media

08h30-08h50: Welcome

08h50-09h20 Pal Jedlovszky, Eszterházy Károly University, Eger, Hungary
Contribution of the different molecules and moieties to the surface tension in aqueous surfactant solutions

09h20-09h40 Denis Morineau, IPR, Université de Rennes 1, France
Confining deep eutectic solvents in nanopores: insight into thermodynamics and chemical activity

09h40-10h00 Richard Asamoah Opoku, PhLAM, Université de Lille, France
Relativistic quantum embedding calculations of halogenated species adsorbed at the air-ice/liquid interface and bulk layer

10h00-10h20 Ari Paavo Seitsonen, ENS Paris, France
Simulation into the solvation and spectroscopic characterisation of 3-hydroxyflavone in various solvents

10h20-10h50 Posters + Coffee Break

10h50-11h10 Florent Real, PhLAM, Université de Lille, France
Nuclear recycling process: the new extracting molecules bring new challenges for molecular modelling

11h10-11h30 Kamalesh Damodaran, CEA Marcoule, France
Deciphering the non-linear impact of Al on chemical durability of silicate glass

11h30-11h50 Porwal Vishal Kumar, LPCT, Université de Lorraine, France
Vibrational properties of organic and biological molecules nanoconfined within layered double hydroxides

11h50-12h10 Alekos Segalina, LPCT, Université de Lorraine, France
Modeling the effect of ionic additives on the energetics of p-type DSSC: the case of Dye-sensitized NiO interface

09/12/2021 14h00-17h30 : Solvents in Chemistry towards a sustainable future

14h00-14h30 Yaocihuatl Medina-Gonzalez, LOF, Université de Bordeaux, France
Solvent Engineering for chemical processes engineering (Video Conference)

14h30-14h50 Emilie Bertrand, IETN, Université de Rennes 1, France
Caractérisation des Solvants Eutectiques Profonds (Deep Eutectic Solvent ou DES) en spectrométrie de masse en mode d'ionisation Cold-Spray (CSI)

14h50-15h10 Corinne Lagrost , ISCR, Université de Rennes 1, France
Polyphenols in Deep Eutectic Solvents. Towards modulation of their antioxidant capacity and long-term stability

15h10-15h30 Agilio Padua, ENS Lyon, France
Solvation in ionic liquids and DES using polarizable simulations

15h30-16h00 Posters + Coffee Break

16h00-16h30 Margarida Costa Gomes, ENS Lyon, France
Reactive separations using porous ionic liquids

16h30-16h50 Carine Michel, ENS Lyon, France
Surface state of heterogenous Ru catalysts in liquid water under gas phase environments

16h50-17h10 Daniel Borgis, ENS Paris, France
Ion-induced long-range orientational correlations in diluted aqueous electrolytes: What do second harmonic scattering experiment measure?

17h10-17h30 Adriaan van den Bruinhorst, ENS Lyon, France
Thermodynamics of Mixing for Eutectic Solvents: Choline Chloride + Water/Diol

17h30-18h30 Réunion du bureau du GDR

10/12/2021 8h30-11H50 : Solvation in systems with interest in the biological and pharmaceutical field and for food processing

08h30-9h00 Damien Laage, ENS, Paris, France
Aqueous interfaces: dynamics, dielectric properties, and chemical reactivity

09h00-09h20 Emeline Dudognon, UMET, Université de Lille, France
Investigation by Dielectric Relaxation Spectroscopy and Molecular Dynamics simulations of the influence on amorphous Terfenadine dynamics of strongly Hydrogen-bonded water molecules

09h20-09h40 Marie Plazanet, LIPhy, Université Grenoble Alpes, France
Heterogeneous Microscopic Dynamics of Intruded Water in a Superhydrophobic Nanoconfinement: Neutron Scattering and Molecular Modeling

09h40-10h00 Akos Gyorgy Juhasz, LASIRe, Université de Lille, France
Creating three dimensional biopolymer matrices for biomedical purposes

10h00-10h30 Posters + Coffee Break

10h30-10h50 François-Xavier Legrand, Université Paris-Saclay, France
Solvants eutectiques profonds pour le traitement topique de maladies infectieuses : toxicité et perspectives

10h50-11h10 Pierre Fouilloux, AgroSup Dijon, Université Bourgogne Franche-Comté, France
Using low-field NMR relaxometry to reveal slow dynamics and structure in poylgalaturoate hydrogels

11h10-11h30 Luisa Roca Paixao, UMET, Université de Lille, France
When residual water influences the cocrystallization output: the carbamazepine and tartaric acid case

11h30-11h50 Salma Soussi, ICM, Université Bourgogne Franche-Comté, France
Molecular Modeling for Pyrrolidine: Using Computational Chemistry Techniques Associated with Experimental study

10/12/2021 14H00- 16H20 : Recent advances in Gas Hydrates : fundamentals to applications

14h00-14h20 A. Desmedt, ISM, Université de Bordeaux, France
Hydrates de gaz: des recherches allant du génie des procédés à l'astrophysique et aux géosciences en passant par les sciences moléculaires (Video conference)

14h20-14h50 C. Cuadrado-Collados, LMA, University of Alicante, Spain
Methane hydrate formation in the confined space of porous materials for gas storage (Video Conference)

14h50-15h20 M. Ciulla, University G. d'Annunzio of Chieti-Pescara, Chieti, Italy
Some recent advances on technological applications of gas hydrates

15h20-15h40 S. Zafar, PhLAM, Université de Lille, France
CO_2 hydrates as an alternative solution to water desalination and greenhouse gas mitigation

15h40-16h00 B. Chazallon, PhLAM, Université de Lille, France
Gas hydrates: characterization and properties probed by micro-Raman spectroscopy

16h00-16h20 D. Broseta, LFC, Université de Pau et Pays de l'Adour, France
Microscopic observations of gas hydrate growth processes (Video conference)

16h20 Discussion sur les interactions entre les deux GdR et clôture des Journées

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Oral and Poster contributions

Investigation of problems related to the lateral pressure profile

<u>Pál Jedlovszky</u>[1], **Marcello Sega**[2], **Balázs Fábián**[3], **György Hantal**[4]

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[4]*University of Natural Resources and Life Sciences (BOKU), Wien, Austria*

ABSTRACT

The calculation of the lateral pressure profile in computer simulations of anisotropic systems is an important problem in various respects; however, it is not a straightforward task at all. The difficulty stems from the fact that pressure is an inherently non-local quantity, which has to be localized in the profile calculation. Further, if an Ewald summation-based method is used to account for the long range part of the intermolecular interactions, the reciprocal space term of this correction is not pairwise additive. We have proposed an accurate and computationally very efficient way of calculating the profile of the lateral pressure, which can also take into account the reciprocal space term when using the sPME method. Further, this way the lateral pressure can be distributed among the interacting atoms in the system as if it were a pairwise additive quantity. Since the surface tension is the integral over the imbalance of the lateral and normal pressure components, and the latter of them is constant, this method allows us to calculate the contribution of the individual particles, molecules and moieties t the surface tension. In this talk, I present a couple of our recent results in this respect. Using an intrinsic surface analyzing method, such as ITIM, the subsequent molecular layers beneath the liquid-vapor interface can be unambiguously identified. This way, the surface tension contribution of the subsequent molecular layers can be calculated. We have performed such a calculation for the liquid-vapor interface of five molecular systems characterized by markedly different intermolecular interactions, namely CCl4, acetone, acetonitrile, methanol and water. Our results showed that at least 90% of the surface tension comes from the first molecular layer in every case, and in methanol this contribution practically reaches 100%.

We also calculated the contribution of the two liquid phases to the interfacial tension at the interface of five different organic liquids, i.e., hexane, cyclohexane, hexanol, dichloromethane, and carbon tetrachloride, with water. Our results reveal that the organic component contributes 20-30% to the total interfacial tension, and this result is independent from the temperature, pressure, water model used, and also from the type of the organic molecule as long as it does not interact strongly and, consequently, does not mix in a considerable extent with water. Among the chosen organic liquids, hexanol is the only one that exhibits partial miscibility with water to an extent accessible by computer simulation. We found that this partial miscibility is associated to a negative contribution of the hexanol molecules, and also that of the hexanol-rich mixed phase, to the total interfacial tension, consistent with the tendency of the hexanol molecules to mix with water.

We also considered the liquid-vapor interface of the solutions of five different amphiphilic molecules, representative of anionic, cationic and non-ionic (alcoholic) surfactants in this respect. We found that the headgroups of alcoholic surfactants give a negligible contribution to the surface tension. The opposite is true for ionic surfactants and counterions, whose effect depends on their ‘hardness’ within the Hofmeister series as well as on the sign of their charge, even though there is a large compensation between ions and counterions.

Confining deep eutectic solvents in nanopores: insight into thermodynamics and chemical activity

Benjamin Malfait, Aicha Jani, Denis Morineau

Institute of Physics of Rennes, CNRS-University of Rennes 1, UMR 6251, F-35042 Rennes, France

ABSTRACT

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 have performed, a comprehensive thermodynamic study of the phase behavior of aqueous solutions of the prototypical ethaline (ethylene glycol / choline chloride 2:1) 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.

Extremely deep melting depressions were attained in the confined states, due to the combination of confinement and cryoscopic effects. These phenomena were analyzed quantitatively, based on a recently proposed extended version of the classical Gibbs-Thomson and Raoult thermodynamic approaches [1]. In this framework, the predicted values of the water chemical activity in the confined systems were shown to systematically deviate from those of the bulk counterparts [2]. 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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Relativistic quantum embedding calculations of halogenated species adsorbed at the airice/liquid interface and bulk layer

Richard Asamoah OPOKU[1], Céline TOUBIN[2] and André Severo Pereira GOMES[3]

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ABSTRACT

The interaction of reactive gases at the air-ice/liquid interface and in the bulk has been proposed to play an essential role in activating diverse compounds that have a major impact on geo-chemical cycles, human health, and ozone depletion in the stratosphere [1]. X-ray photoelectron spectroscopy (XPS) [2], serves as a powerful technique to characterize the elemental composition of such interacting species due to its surface sensitivity. Given the existence of complex physico-chemical processes such as adsorption, desorption at the airice/liquid interface, and migration within the bulk matrix, it is important to establish a theoretical framework to determine the electronic properties of these species under different atmospheric conditions. The focus of this work is to construct an embedding methodology employing Density Functional (DFT) and Wave Function Theory (WFT) to model and interpret photoelectron spectra of adsorbed halogenated species at the core level with the highest accuracy possible.

We make use of an embedding approach utilizing full quantum mechanics to divide the system into subunits that will be treated at different levels of theory [3]. The goal is to determine core electron binding energies and the associated solvent-induced shifts in the binding energies for the adsorbed Cl- and I- at interfaces [4] and in the bulk. The core energy shifts are compared to the data derived from the XPS spectra [4].

We show that the use of a fully quantum mechanical embedding method, to treat solutesolvent systems is computationally efficient, yet accurate enough to determine the electronic properties of the solute system (halide ions).

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Simulation into the solvation and spectroscopic characterisation of 3-hydroxyflavone in various solvents

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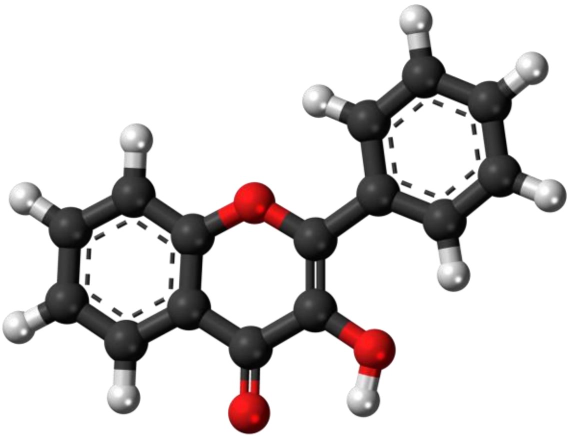
ABSTRACT

Flavones is an important and interesting family of molecules with biological activity. Here we report a computational investigation of the 3-hydroxyflavone in different molecular solvents, and compare to available experimental results. The simulations are conducted with molecular dynamics with the forces acting on the ions from the density functional theory. The solvents are chosen to range apolar and aprotic (carbon tetrachloride, CCl_4) via polar, aprotic (acetonitrile) and polar, protic (methanol) to a polar, "very" protic (trifluoroethanol) molecules. We discuss the various simulated fingerprints that can be obtained from the simulations, including the nuclear magnetic resonance shifts and the optical absorption spectra.



Nuclear recycling process: the new extracting molecules bring new challenges for molecular modelling

FAILALI Abdelmounaim, [1,2] GUILLAUMONT Dominique[1], ACHER Eleonor[1], VALLET Valérie[2], RÉAL Florent[2]

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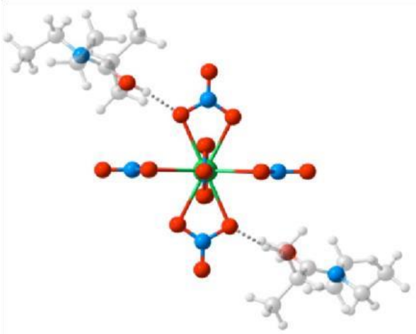
ABSTRACT

In the context of nuclear fuel reprocessing, the recovery and purification of major actinides is achieved using a hydrometallurgical process known as PUREX (Plutonium Uranium Recovering by Extraction). Based on Liquid-Liquid extraction technics, this process requires a specific molecule to extract Pu and U, the Tri-n-butyl phosphate TBP. Monoamides are regarded as alternative family of extraction molecules to TBP, as they are well known for their strong extraction ability of Pu(IV) and U(VI) elements. In addition to this, they show some interesting features, such as the complete incinerability of the solvent degradation products, and a strong dependence of the extraction properties (distribution coefficient and selectivity) on the chemical conditions [1-3].

The strong influence of the structure of amide derivatives on their extraction properties has been demonstrated in several studies in the literature, but not well understood yet. By the use of molecular approach, we propose first to demonstrate at the same time the capability but also the limit of quantum chemistry method to investigate and rationalize the influence of the nature and length of the monoamide alkyl chains on Pu(IV) extraction/complexation [4], and second why larger scale modellings associated to some development of new classical interaction potentials are required [5].



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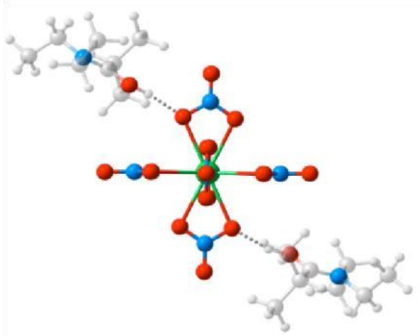

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Deciphering the non-linear impact of Al on chemical durability of silicate glass

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ABSTRACT

The role of Al in aluminosilicate glasses remains somewhat a mystery: at low concentrations, it increases the resistance to hydrolysis of the glass, whereas at high concentrations an opposite effect is observed. To understand the origin of the phenomenon on a fundamental atomistic scale, we performed 577 MD simulations and applied potential mean force (PMF) calculations to estimate the activation barriers for hydrolysis and to statistically correlate them with local structural features of the glass. Models of pure silicate and aluminosilicate glasses are constructed and investigated. PMF simulation results are further validated by the experimental measurements and revealed that Al is very easy to dissociate, but it also increases the glass chemical durability through significantly increasing both the strength of Si and network connectivity of the glass. In contrast, at high Al concentration, preferential dissolution of Al weakens the silicate network, which it supposes to strengthen, and so the glass resistance becomes poor. Through PMF calculations, we evaluated the activation barriers for dissociating bonds around Al as 0.49 eV, which is less than a half of the energy to dissociate bonds around Si in pure silicate (1.22 eV) and around Si in aluminosilicate glass (1.34 eV), all these energy differences being statistically significant. Molecular structural level investigation revealed that Si with Al as a second neighbour in the glass network has a significantly higher activation energy for dissociation than Si in pure silicate glass. The proposed approach opens the way to the development of quantitative predictive models of glass durability.

Vibrational properties of organic and biological molecules nanoconfined within layered double hydroxides

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ABSTRACT

Layered double hydroxides (LDHs) are claylike materials displaying inorganic layers (positively charged) and an intercalated aqueous phase, which may contain solvated organic / biological anions: in this case, they are referred to as hybrid materials. Such materials have attracted the attention of researchers who focused on Bernal's hypothesis, according to which clay-like materials could provide a favorable environment for the synthesis of biological macromolecules from adsorbed small organic molecules.1 For instance, in the case of amino acids, specific orientations of the molecules within the interlamellar region were shown to be relevant to assess the role of LDHs as catalyzers for abiotic peptide bond formation.2 In collaboration with experimentalists, we analyzed LDHs intercalating aspartate, succinate and glutamate anions. Focusing on the evolution of the carboxyl band with increasing amounts of intercalating water, we have studied the changes in the binding modes of the anion with the surface. In particular, we have investigated the influence of the presence of the -NH2 group (not present in succinate) and the different side chains (in aspartate and glutamate). The modification in the local structure and in the water hydrogen bond network are analyzed as well.

Monodentate, bidentate bridging & chelating

Mostly bidentate chelating

Modification of aspartate-to-surface binding modes upon water uptake (water not shown) in the nanoconfined interlayer region of LDH.

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Groupement de recherche
SolvATE Solvatation : Avancées Théoriques et Expérimentales

GDR SolvATE Solvation: Advances in theory and experiments
December 9 – 10, 2021
Lille, France

Modeling the effect of ionic additives on the energetics of p-type DSSC: the case of Dye-sensitized NiO interface.

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ABSTRACT

P-type dye-sensitized solar cells (DSCs) offer the possibility to directly convert sunlight into electrical energy at a low cost. However, these devices have rather poor efficiencies (PCE~2.5%) compared to the n-type DSCs (PCE~14%) for reasons that are not yet clarified (slow hole injection, fast back recombination pathways).

At a variance with the common n-type DSCs, p-type DSCs are based on the hole injection from the HOMO of the photoexcited dye (e.g. C343) into the valence band of a semiconductor (e.g. NiO) and the driving force, which is the difference between the VB and the HOMO energy, has a key role on the overall efficiency of the devices.[1-2] As far as dye-sensitized NiO is concerned, relatively few computational works, based on density functional theory (DFT) calculations, have been reported.[1-6] A common outcome of these studies is that the interfacial energetics, dictating the driving force for hole injection from the dye to the NiO VB, turns out to be extremely sensitive to the dye anchoring mode and solvation effects, thus indicating that the structural and electronic properties of complex interface between dye, semiconductor and electrolyte play a major role in the properties of DSCs.[1-6] Experimentally, the hole injection from the HOMO, of the photoexcited dye, to the VB of the NiO, is favored when electrolyte species composed of small cations (e.g. Li^+) are present in the solution.

In this contribution, we provide a theoretical study of a C343@NiO interface using a multilevel approach that combines extensive ab-initio molecular dynamics (MD) simulations and single point DFT calculations, considering both the electrolytic-free solutions and the interface in the presence of LiF. We thus unraveled the role played by the electrolytes and by the thermal fluctuations on the energetics of the C343@NiO interface, on the interfacial structure, and the stability of the C343 on the NiO surface.

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Solvent Engineering for chemical processes engineering

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ABSTRACT

Solubility is defined as the ability of a substance to form a solution with another substance, where the solution is a single, homogeneous gas, liquid or solid phase that is a mixture where the components are homogeneously distributed through the mixture. In general, the less abundant compound is called the solute, while the most abundant one the solvent. Properties of a solution are necessarily different from the pure compounds, for instance, the elevation of the boiling temperature or the decrease of the freezing point after the addition of a solute to a solvent, are two examples of physicochemical properties that are modified when a compound is solubilized in a solvent.

The term “Solvent Engineering” emerges from the awareness that the choice of the solvent impacts the performance of a process performed in solution. In industry, pure substances are very rare, and the properties of mixtures, together with mixing and demixing phenomena are of prime importance for science and technology. It is clear as well, that the environmental footprint of a process is closely linked to the solvent used but its technical and economic achievements too. It is then evident that the optimization of the solvent is key to optimize chemical or physical processes that occur within this solvent.

In this context, Solvent Engineering can be defined as the design, building and manipulation of the solvent properties in order to optimize the chemical or physical processes performed within this solvent.

In this talk I will speak about the strategies that have been applied to perform Solvent Engineering during several years taking some examples from literature and from works developed by our group as for instance our efforts 1) to characterize the solvency performances of gas expanded biosourced solvents, and 2) to apply this concepts in enzymatic and organometallic catalyzed reactions.

Characterization of Deep Eutectic Solvent by Cold-Spray ionization mass spectrometry method

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ABSTRACT

The Cold-Spray Ionization (CSI) method is a variant of the Electrospray Ionization (ESI) method where the nebulizer gas is cooled by liquid nitrogen.1 The CSI method, considered more “soft” than the ESI method, allow characterization of Deep Eutectic Solvent (DES) as Reline: a mix of a choline chloride salt and two urea molecules. CSI mass spectra shows the presence of supramolecular assemblies’ characteristics of reline ions. These assemblies are not visible on ESI mass spectra. CSI mass spectra also implies that the assembly of one choline chloride salt with two urea molecules (the most basic form of reline) does not appear as the most stable assembly in gaseous phase.2,3 Others DES, such as the assemblies Thymol/Octanoic acid and menthol/Octanoic acid with a molar ratio (1:1), each had been characterized respectively by negative and positive CSI modes. For the first one, the mass spectra displaysthe characteristic form of a DES: an assembly of Thymol and Octanoic acid with the ratio molar (1:1). Others assemblies are visible for Thymol and Octanoic acid assemblies with two distinct molar ratios: (2:1) and (1:2). For the second one, the characteristic peak of the esterified mixture is visible. Supramolecular assemblies of this esterified mixture with one and two molecules of menthol are also present on the mass spectra. In order to understand why the characterization of DES is possible, with the CSI method and not the ESI method, a study of the internal energy distribution in ESI and CSI has been performed with the survival yield (SY) method.4,5 This method can link the fragmentation degree of reference ions, called “thermometer ions”, with their internal energy. Thermometer ions are ions that had both their dissociation energy and the kinetics of their fragmentation reactions already known. The ones used in this study are diclofenac for negative ESI and CSI methods and Benzhydrilpyridinium6 for positive ESI and CSI methods. The measurements were achieved with two different solvents (Acetonitrile and Methanol) and the modelling was done with the software “MassKinetics” 7. This permits usto quantify the residual thermal energy of ions during its passage from a solvent form into a gaseous state when the ESI source is substituted by the CSI source. This work is a step toward the understanding of the impact of the ionization solvent used during mass spectrometry DES’s analysis.

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GDR SolvATE Solvation: Advances in theory and experiments
December 9 – 10, 2021
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Polyphenols in Deep Eutectic Solvents. Towards modulation of their antioxidant capacity and long-term stability

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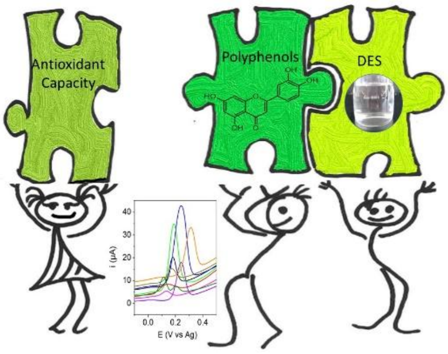
ABSTRACT

The beneficial effects of the antioxidant properties of polyphenols are nowadays known to a large public. They attract growing inetrest in the fiels of cosmetics, pharmaceutics and nutraceutics whose industries are in demand of natural, greener and safer ingredients. As a consequence, the development of sustainable extraction methods is highly desirable. In this context, DES as extraction media may improve the greeness and effectiveness of the processes. Even more important than increasing extraction yields, the preservation of the bioactivity of the extracts along with the possibility of keeping the DES itself as an active ingredient would be of great interest, leading to environmentally friendly and safe approach but also to high added-value extracts.

However, the weak link remains the quantification and identification of the polyphenols in DES extracts, routinely based on colorimetric assays. Electrochemical techniques could represent an alternative for such analyses, making it a possible a direct analysis in DES without the need of counter-extraction. In addition, it could be very useful to probe interactions between the DES and the extracted polyphenols.

We will examine the electrochemistry in a series of flavonoids in DES media based on betaine and choline chloride. The antioxydant capacity of the phenolics in the DES-based media will be discussed as a function of the DES, showing a potential synergy between DES and polyphenols.[1]



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Solvation in ionic liquids and DES using polarizable simulations

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ABSTRACT

Ionic liquids (ILs) and eutectic solvents (DES) are available in an enormous diversity, with adjustable properties, making them an excellent platform for rational solvent-design, aiming for more sustainable solvents, technological fluids (such as lubricants) and media for reactions or separations. This design can be carried out in silico, at the atomistic level that is suitable to the length and time scales needed to describe coulombic fluids, which are more ordered and more viscous than traditional solvents. A good molecular interaction model is needed to provide conformations, energetics, ordering and dynamics. While fixed-charge force fields reproduce well the structural properties, they predict too sluggish dynamics when compared to experiment. One way to improve the description of interactions is to introduce explicit polarization into the molecular force field, for example through Drude induced dipoles on the atomic sites. In order to avoid extensive reparameterization of existing force fields, the effective van der Waals potential (typically Lennard-Jones) should be be rescaled to avoid double counting of the induction effects, which are now represented explicitly.

Following this approach, we developed the CL&Pol [1] polarisable force field based on the fixed-charge CL&P model [2], and validated it on aprotic ionic liquids [3]. Its subsequent extension to protic ionic liquids, deep eutectic solvents and electrolytes required additional charge-dipole damping [4], which was introduced to prevent a so called “polarization catastrophe” caused by excessive attraction between small, densely-charged atoms and Drude dipoles. The CL&Pol force field can generate stable molecular dynamics trajectories providing us with reliable and accurate results. Extensibility is built-in, so the usage of the model goes beyond the systems discussed here, opening new perspectives, which we illustrate through gases, dyes, nanomaterials and porous liquids.

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Reactive separations using porous ionic liquids

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ABSTRACT

Among the alternative sorbents potentially capable of outperforming current separation technologies, in particular gas separations, ionic liquids are promising candidates. Their most attractive feature is the possibility of tuning their physical and chemical properties through proper pairing of anions and cations, which can include reactive groups, enabling the selective absorption of different gases, even at low partial pressures [1].

We will describe ionic liquid-based absorbents, with permanent porosity, designed to selectively absorb different gases. The absorbents are stable suspensions of metal-organic frameworks (MOFs) in salts whose ion pairs are too voluminous to enter the solid pores [2]. The increase in gas absorption, when compared with the pure ionic liquids, is proportional to the amount of porous solid in suspension. The thermodynamic analysis of the absorption data, as well as molecular dynamics simulations, show that the driving force for gas absorption by the porous ionic liquids is energetic as well as structural and thus is controlled by gas-solid affinity or by the porous liquid free volume [3].

Porous liquid absorbents can be designed to react with different gases at mild conditions of temperature and pressure. We show that porous ionic liquids prepared as stable suspensions of ZIF-8 in phosphonium acetate or levulinate salts can selectively absorb carbon dioxide with a capacity more than 100% higher than that of the pure MOF at 1 bar and 303 K [4].

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Surface state of heterogenous Ru catalysts in liquid water under gas phase environments

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ABSTRACT

Supported ruthenium is an important heterogeneous catalyst that is used in many transformations involving biomass valorization [1]. Most of these transformations are performed in liquid water under the presence of other gas phase species i.e. a pressure of hydrogen. It is, therefore, imperative to investigate the surface state of the underlying Ru catalyst under varying conditions of temperature, pressure and solvent. Using periodic-DFT aided ab-initio thermodynamics, we have studied the surface state of the Ru catalyst in both liquid or gas water with or without an external pressure of hydrogen. More than 800 configurations involving adsorption of H/O/OH/H2O species on 3 different Ru surfaces were randomly generated and were converted into thermodynamic maps in terms of temperature and pressure of H_2. The solvation effects were considered using the in-house developed Solvhybrid package which implements a hybrid QM/MM approach and makes use of fitted UFF parameters, point charges from DFT calculation and an alchemical transformation based on thermodynamic integration. Our results show that under a pressure of hydrogen the most stable phase is a monolayer of H both with and without solvation effects (Figure 1, zone 1). However, if little or no hydrogen pressure is supplied, the surface tends to oxidize by O/OH species reaching a monolayer of oxygen at temperatures above 400 K (Figure 1, zone 7). Surprisingly, the monolayers of H/O are more solvated compared to the intact or partially dissociated monolayer of H_2O [3]. The zone 2 in Figure 1 has H:O=2:1 ratio and thus represents fully dissociated water on the surface. This mixed H/O phase was found to have much stronger solvation than the sum of individual O or H monolayers making it more dominant under solvation. These results should help in our understanding of the Ru-based catalysts and help rationalize the increased reactivity of Ru catalysts in water in terms of its ability to generate O/OH moieties on the surface.

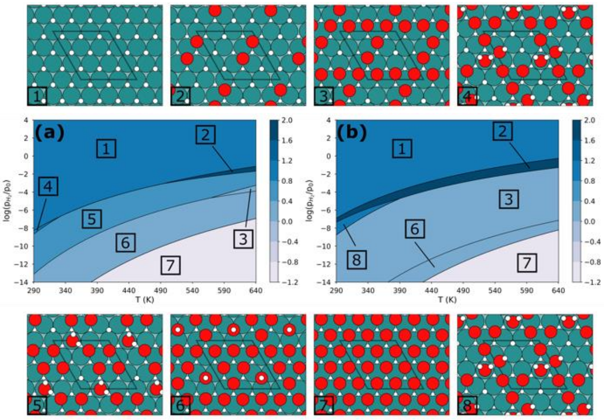

Figure 1. Thermodynamic maps of the most stable phases of Ru(0001) with water as a gas phase environment (a) and as a liquid water taking into account solvation enthalpies (b). The colormap bar shows the values of H/O ratio of the species adsorbed on the surface such that if both H and O are present the value is the ratio H/O; if no O is present the value is the coverage and if no H is present the value on the map is the negative of the coverage.Top views of the corresponding structures.

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Ion-induced long-range orientational correlations in diluted aqueous electrolytes: What do second harmonic scattering experiment measure ?

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ABSTRACT

I will discuss the ion-induced long-range orientational order between water molecules that has been recently observed in second harmonic scattering experiments at very low ionic concentrations, and illustrated with large scale molecular dynamics simulations. From the theoretical expression of second-harmonic-scattering signal, I will show that the observed enhancement of the signal with respect to pure water is a mere manifestation of the Debye screening that makes the infinite-range dipole-dipole solvent correlations in 1/r3 disappear as soon as the ionic concentration becomes finite. In q-space, this translates into a correlation function having a well- known singular behaviour around $q = 0$ that marks an abrupt transition between dielectric and metallic boundary conditions. The theory explains why the enhancement depends on the experimental geometry and occurs only for in-plane polarisation detection. On the other hand, the measured isotope effect between light and heavy water cannot be yet explained.

Thermodynamics of Mixing for Eutectic Solvents: Choline Chloride + Water/Diol

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ABSTRACT

Deep eutectic solvents (DESs) are mixtures characterised by melting point depressions that are significantly below those of ideal eutectic mixtures [1]. This extraordinary eutectic depth allows the development of task-specific liquid media from non-intuitive pure compounds, solid at ambient temperature. A subtle interplay of intermolecular interactions (e.g. hydrogen bonds and electrostatics) are responsible for the deviations from ideal eutectic behaviour. Within this framework, we studied the thermodynamics of mixing for binary mixtures containing choline chloride (ChCl)—an archetypal DES constituent [2]—using solid–liquid phase equilibria data, isothermal titration calorimetry, and polarisable molecular dynamics simulations [3]. The excess molar enthalpies were determined for the following mixtures: water + ChCl, ethylene glycol (EG) + ChCl, and 1,3-propanediol (13PD) + ChCl.

Experimentally, the partial molar excess enthalpies (H_m^E) and activity coefficients are accessible for the liquid constituents in the mixture. To probe H_m^E for ChCl, however, the salt would have to be in the liquid state. Under normal titration conditions this is not possible. Furthermore, ChCl decomposes before melting and thus the excess enthalpy cannot be derived indirectly from dissolution calorimetry and the enthalpy of fusion either. Using MD simulations, these practical limitations can be overcome *in silico* by simulating a supercooled, pure ChCl liquid as a reference state for the enthalpy of mixing. In this work we present a comparison between the experimental and simulation results for the H_m^E of the liquid constituents in the studied mixtures. Additionally, we evaluate how the thermodynamics of mixing relate to their eutectic depth. This approach provides insights into the intermolecular interactions at play, and some hints towards an explanation for the excellent solvent performance of some ChCl-based DESs.

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Aqueous interfaces: dynamics, dielectric properties, and chemical reactivity

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ABSTRACT

Aqueous interfaces are ubiquitous and central to many essential chemical, biochemical and environmental processes, ranging from atmospheric reactions on aerosols to transport in nanofluidic devices and electrochemical energy conversion. However, the properties of water at these interfaces can be dramatically different from those in the bulk. Here we will consider two paradigm aqueous interfaces, respectively the air/water interface relevant for atmospheric chemistry and the electrode/water interface relevant for electrochemistry. We will show how molecular simulations and analytic modelling can be combined to determine the molecular factors which affect the H-bond network structure, water dynamics [1], and dielectric properties[2], and we will show their consequences on chemical reactivity at these interfaces[3].

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Investigation by Dielectric Relaxation Spectroscopy and Molecular Dynamics simulations of the influence on amorphous Terfenadine dynamics of strongly Hydrogen-bonded water molecules

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ABSTRACT

Terfenadine (TFD), $C_{32}H_{41}NO_2$, is an active pharmaceutical ingredient that is poorly soluble in water in the crystalline state but, remarkably, it can absorb a few amount of water (~ 2%) in the amorphous state. By means of complementary Dynamic Relaxation Spectroscopy (DRS) and Molecular Dynamics simulations (MD), we investigate [1] the impact of such low water concentration on the dynamics of amorphous TFD, in particular on localised intramolecular mobilities the microscopic origin of which often remains unclear while they may have impacts on sub-Tg re-crystallisation.

By DRS, we evidence that these residual water molecules give rise to a new secondary relaxation mode in the glassy state. It originates through the motion of water molecules Hydrogen-bonded to TFD molecules and this dynamic is coupled to the intramolecular motions of the flexible central part of TFD molecules. MD computations and analyses of the hydrogen bonding interaction (HB) allows to understand and rationalise these results. They establish that these water molecules can be divided in two categories:

- a majority of weakly or moderately HB water molecules to TFD which are easily removed from the system by usual drying process,
- a minority of much more highly HB water molecules strongly interacting with the OH hydroxyl group and the nitrogen atom located in the central part of the TFD molecules, creating some kind of bridges between TFD molecules. These strongly HB water molecules localise themselves in small pockets in empty space existing between the TFD molecules due to the poor packing of the glassy state and are much more difficult to remove without a specific treatment.

This project has received funding from the Interreg 2 Seas program 2014-2020 co-funded by the European Regional Development Fund (FEDER) under subsidy contract 2S01-059_IMODE.

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Heterogeneous Microscopic Dynamics of Intruded Water in a Superhydrophobic Nanoconfinement : Neutron Scattering and Molecular Modeling

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ABSTRACT

Static and dynamical properties of water strongly depend on its environment, specially in case of nano-confinement. If hydrophilic confinement has been widely explored, the situation is different for hydrophobic matrices where water has to be intruded under high pressure.

The Zeolitic Imidazolate Framework 8 (ZIF-8) material is made of highly hydrophobic nanopores and its low intrusion pressure (250 bars) makes it an ideal material for the study of water dynamics in such environment. Its structure, composed of transition metal ions ($Zn2+$) linked by functionalized imidazolate organic groups, consists of ~12 Å diameter spherical pores connected by narrow gates. To date and to the best of our knowledge, no direct experimental characterization of the water dynamics in such environment were available. Thus, we performed QENS experiments under pressure up to 380 bars (Figure 1) to measure the diffusion coefficients of the water molecules trapped in the ZIF-8 nanopores and identified two different water populations [1]. Our measurements, in qualitative agreement with molecular dynamics simulations from the literature [2] were completed with more numerical investigations to get further insight on the dynamics thanks to complementary GCMC/MD studies. We highlighted the existence of dynamical heterogeneities in agreement with the two underlying water populations extracted from experimental analysis. The close examination of the numerical simulations enabled to identify different rotational and translational dynamics linked to water located at strongly adsorbing sites (ZIF-8 ligand), at the cage surface or in the cavity center, as well as exchange between the different sites on slower timescales.

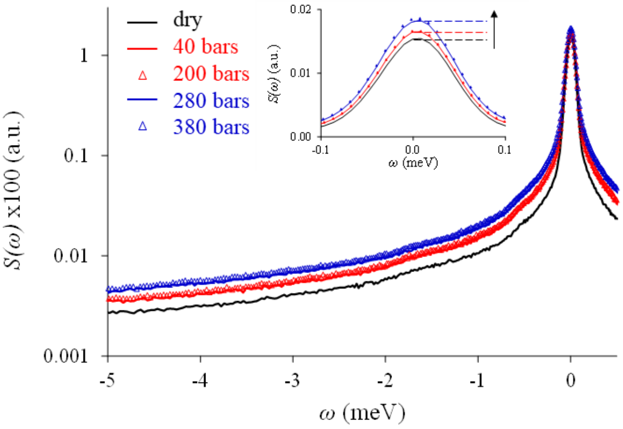

Figure 1: Sum S(w) over q of the quasi-elastic spectra S(q,w) obtained for dry ZIF-8 (black), low-pressure (<250 bars) water in contact with ZIF-8 (red) and high-pressure (>250 bars) water intruded in ZIF-8 (blue)

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Creating three-dimensional biopolymer matrices for biomedical purposes

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ABSTRACT

The history of the electrospinning technique started couple of centuries ago. The technique has evolved continuously and found several applications. As science has progressed, the physical phenomena involved in the formation of fibers have been more and more precisely defined, thus creating equipment to meet different needs. Nowadays, not only microfibers but also nanofibers can be created using this method, making it possible to create materials suitable for biomedical applications. Nanotechnology reached to the point to be able to create artificial matrices which have fiber diameters like in the living organism. The method of electrospinning is a widely investigated and used technique for creating nano and microfibers which has a wide range of medical and pharmaceutical applications. For cell culturing and tissue engineering it is a greatly investigated method because it resembles the extracellular matrix. Changing the electrospinning parameters, we can affect the properties to fine tune it for our needs. To create a high porosity fibrous mesh for culturing different cells in a suitable 3D way, we need to step forward from conventional electrospinning.

My aim was to create 3D fiber structures from Poly(succinimide) with the help of electrospinning. Therefore, the effect of different inorganic salts were investigated. The scaffolds were analyzed with the help of Scanning Electron Microscopy and Raman spectroscopy. To understand the effect of salt on the resulting meshes characterization of the ion-ion and ion-solvent interactions were carried out using vibration spectroscopy and density functional theory calculation. These interactions correlate to what we experienced with the electrospinning process. In the future, our results could contribute to creating designed structures which main and most important area of usage could be biomedical applications.

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ACKNOWLEDGMENT

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Solvants eutectiques profonds pour le traitement topique de maladies infectieuses : toxicité et perspectives.

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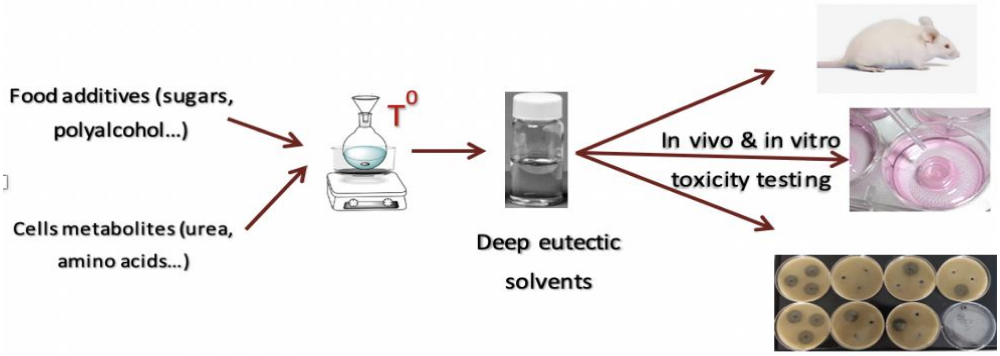
ABSTRACT

Selon des travaux récents, les solvants eutectiques profonds (DES) sont devenus des alternatives aux solvants traditionnels pour la formulation de molécules actives en raison de leur capacité à améliorer la solubilité et la perméabilité de molécules actives ou bien pour leurs activités antimicrobiennes. De plus, les DES sont considérés comme non toxiques, biocompatibles et respectueux de l'environnement, car ils peuvent être préparés simplement par agitation douce et chauffage de mélanges d'additifs alimentaires et de métabolites cellulaires [1]. Cependant, dans les études antérieures, la toxicité du DES n'a été principalement étudiée que sur des cellules en culture, ce qui peut entraîner la perte de l'intégrité structurelle du DES et donc conduire à un profil de toxicité erroné.

Par conséquent, notre objectif est d'étudier la toxicité de DES sur des tissus humains et animaux ainsi que sur certains agents pathologiques, en nous concentrant sur des conditions simulant une utilisation réelle comme véhicule pour les voies topiques (cutanée, vaginale ou buccale), qui ont rarement été prises en compte dans les études précédentes. Des compositions de DES, comprenant soit un ammonium quaternaire (QA), une molécule zwitterionique (ZM) ou un acide carboxylique (CA) combiné à un donneur de liaison hydrogène [1, 2] ont été sélectionnées sur la base de la littérature et d'études préliminaires puis étudiées par des approches *in vitro* et *in vivo*.



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USING LOW-FIELD NMR RELAXOMETRY TO REVEAL SLOW DYNAMICS AND STRUCTURE IN POLYGALACTURONATE HYDROGELS

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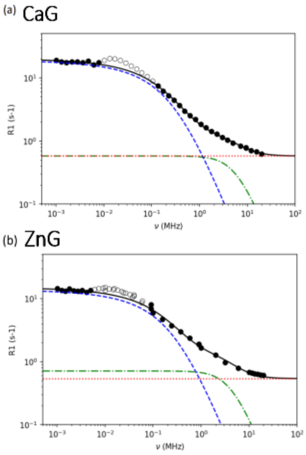
ABSTRACT

Gels are essential materials in physics and chemistry, and they have primary importance in medicine, pharmaceutical and food sciences, to name but a few. In this work, we performed an in-depth NMR analysis of the water dynamics in the fiber structuring two heterogeneous polygalacturonic acid (polyGalA) hydrogels formed by Ca and Zn ions.

On one side, the NMRD profiles recorded in-situ by fast field cycling relaxometry (from 1 kHz to 20 MHz, Figure 1) allowed us to measure the rotational and translational mobilities of water in the polymer forming fibers. A translational diffusion coefficient close to 8x10-13 m2/s for both gels was measured, in agreement with typically measured diffusion coefficients in polymers [1]. Moreover, these experimental results were in fair agreement with molecular dynamics calculations.

On the other side, the analysis of the relaxation curves at high frequency (20 MHz) reveals the mesh size distribution in the hydrogels, which was compared to those obtained from SANS [2] and rheological measurements (Figure 2).



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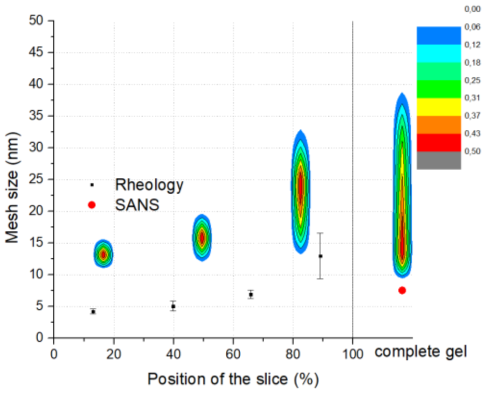

2)

Figure: 1: Proton NMRD profile of calcium (a) and zinc (b) polyGalA gels. The solid lines are fitted profiles. The individual calculated components: translation (blue), rotation (green), free water (red) 2: Distribution of the mesh size according to NMR relaxometry (heat maps) compared to those obtained from rheological (black square) and Small Angle Neutron Scattering (red dot) measurements.

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WHEN RESIDUAL WATER INFLUENCES THE COCRYSTALLIZATION OUTPUT: THE CARBAMAZEPINE AND TARTARIC ACID CASE

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ABSTRACT

The design of poorly water-soluble pharmaceutical molecules using cocrystallization has drawn increasing interest as these new materials can be used in order to improve their dissolution rate, aqueous solubility, bioavailability and/or hygroscopicity. Different synthesis techniques can be used in order to obtain cocrystals such as crystallization from solution, neat and liquid-assisted grinding (LAG), among many others.

In this work, the impact of residual water in the final cocrystallization product has been investigated by using two different synthesis techniques, solution evaporation and liquid assisted grinding. For this purpose, previously published systems were studied: carbamazepine with L-tartaric acid and carbamazepine with DLtartaric acid1,2. From these systems, two different cocrystals were obtained and characterized by using their thermal and structural behaviour. On one hand, the crystalline structure resolution of one of the cocrystals shows the obtention of an ordered system with an exact molar ratio3,4. On the other hand, a known cocrystal, described as a coformer channel-filled structure with an unknown molar ratio, was thoroughly investigated to determine the molar ratio. During this study, the influence (or lack of) of residual water on these systems was shown to be dependent on the obtained cocrystal as well as the chosen synthesis method and to have a great impact on the cocrystallization output.

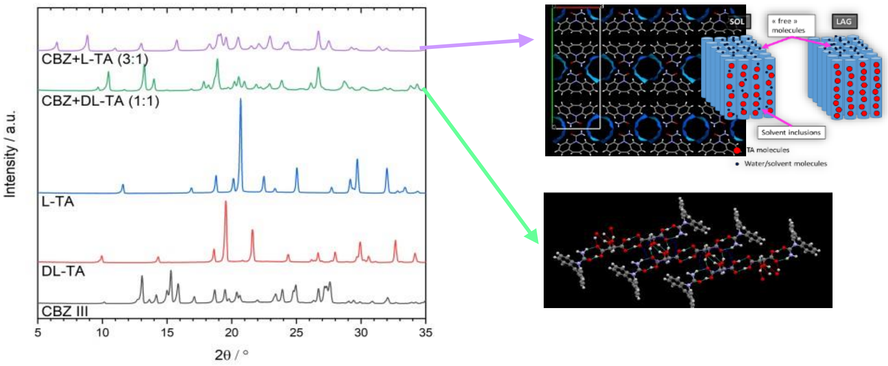

Figure 1 – Comparison of the cocrystals vs. the parent compounds diffractograms and their structural illustrations taken from the Cambridge Structural Database (Refcode MOXWIG2 for CBZ:DL-TA (1:x) and MOXWIG014 for CBZ:DL-TA (1:1)).

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Molecular Modeling for Pyrrolidine: Using Computational Chemistry Techniques Associated with Experimental study

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ABSTRACT

The reactions of 2-methoxy-3-X-5-nitrothiophenes **1a–e** with pyrrolidine **2** were studied kinetically by UV-Visible spectroscopy in mixture solvent CH_3CN-CH_3OH at 20 °C. Then, the nucleophilicity parameters N and s for pyrrolidine on different mixture compositions have been determined using the Mayr's relationship:

$$\log k\ (20\ °C) = s_N (E + N)$$

On the other hand, the nucleophilicity index 1/ω for pyrrolidine in solvent mixture acetonitrile and methanol were calculated by combining DFT coupled with classical MD simulations. The theoretical values agree with the experimental ones, and the experimental dependence of the nucleophilicity parameters of pyrrolidine on mixture solvent methanol-acetonitrile was confirmed and supported by the molecular dynamic simulation.

The net dependence of the nucleophilicity parameter of pyrrolidine on solvent was mainly explained by a gradual methanol desolvation when the amount of acetonitrile is increased.

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Methane hydrate formation in the confined space of porous materials for gas storage

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ABSTRACT

Natural gas (CH_4) has become a promising fuel due to its higher efficiency and lower CO_2 emissions compared to coal and gasoline. However, CH_4 has a very low energetic density which makes difficult its storage and transportation (either liquefied natural gas at-165°C and 1 atm or compressed natural gas at 25°C and 250 atm). Adsorbed natural gas (ANG) is another method for CH_4 storage that takes place at milder conditions of pressure and temperature. Nevertheless, the storage capacity of ANG is too low, the most likely chargeable quantity of ANG is 150 v/v.

An alternative to CH_4 physisorption are CH4 hydrates or clathrates. CH_4 hydrates are crystalline solid compounds which are naturally formed at high pressures and low temperatures. These compounds have woken up a great interest as new high energetic fuels since 1 m^3 of CH_4 hydrate contains up to 180 m^3 of CH_4 gas at STP[1].

The purpose of this talk is to give a short insight on CH_4 hydrate formation in the confined space of nanomaterials. The formation of hydrates in porous materials (activated carbons mainly) is largely increased compared to bulk water and the final CH_4 uptake is nearly 4 times higher than conventional adsorption[2]. Furthermore, the induction time of hydrates (kinetics formation) is substantially decreased (within hours), suggesting that the high surface area of the nanomaterials enhances the gas-liquid interphase. Chemical surface and pore size have also a big impact on the growth of these structures, being hydrophobic materials with a 20 nm mesopore size the most successful ones for the CH_4 hydrate promotion[3].

As a result, by taking advantage of porous materials as host systems to grow artificial CH_4 hydrates, the storage and transportation of natural gas could be implemented in a more efficient way.

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Some recent advances on technological applications of gas hydrates

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ABSTRACT

Clathrate hydrates are ice-like inclusion compounds that form under conditions of low temperature and high pressure. In hydrates, water molecules enclose small guests such as methane, carbon dioxide, and hydrogen, among others, into a hydrogen-bonded crystal network of Eulerian polyhedra [1]. Hydrates represent a problem in flow assurance, since their formation causes plugs in oil and gas pipelines. To prevent this, some kinds of chemical additives are used: thermodynamic inhibitors such as methanol and glycols, low dosage hydrate inhibitors (LDHIs), and biological inhibitors (anti-freeze proteins). Recent studies for the development of novel cationic surfactants as low-dosage hydrate inhibitors were conducted by Di Profio *et al.* by using an in-silico chemoinformatic design to predict kinetic properties and the hydrate inhibition ability of different organic molecules [2]. A careful evaluation of the chemometric analyses, and the numerical descriptors of tested surfactants, allowed to define some possible features of a good inhibitor, as far as the amount of absorbed gas is concerned.

Besides, gas hydrates have received considerable attention as a means for gas storage and transportation (natural gas and hydrogen) [3,4], water desalination and biogas upgrading. As to the latter, the upgrading of model biogas mixtures by gas hydrates has recently been considered as a safe alternative to high-pressure or liquefied gas storage, and as an economic, chemical-free process for the separation of gas mixtures. We evaluated several factors affecting the driving force to hydrate formation, such as the degree of overpressurization and the presence of chemical promoters [5]. Tested promoters were several anionic and zwitterionic surfactants which are demonstrated to affect the hydrate-forming ability of water. Results show that the separation ability of clathrate hydrates as determined by the separation factor S is highest when no promoters are added to the water phase.

Another interesting application of hydrate technology is CH_4 - CO_2 exchange in natural gas hydrate fields for CO_2 sequestration with concurrent natural gas recovery [6]. Through the development of a new method, it was possible to carry out the exchange simulation into a reactor under constant pressure while checking the ratio of the constantly injected gases. Furthermore, experiments were carried out considering different experimental conditions such as the presence of sand or the type of water used.

The final topic relates to hydrogen storage into clathrate hydrates, and some considerations on the energy efficiency of hydrogen hydrates as compared to other hydrogen storage media will be presented [7].

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CO_2 hydrates as an alternative solution to water desalination and greenhouse gas mitigation

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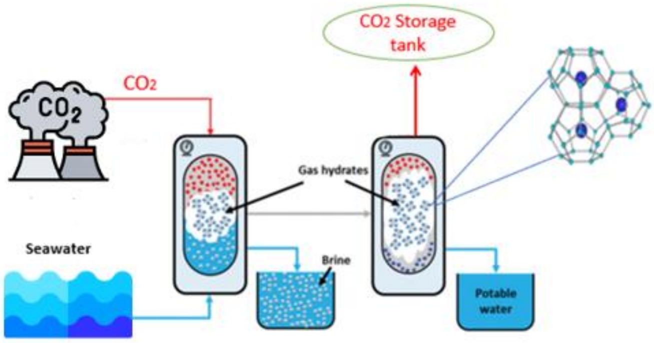
ABSTRACT

Currently, releasing high levels of CO_2 into the atmosphere – as in flue-gas emissions – is not sustainable and must be reduced due to the significant impact on global warming. Indeed, the Intergovernmental Panel on Climate Change (IPCC, 2018) predicts an increase in temperature of around 1.5 degrees Celsius between 2030 and 2052 if present CO_2 emissions continue. In the meantime, water scarcity is a major problem all around the world which could be alleviated by seawater desalination[1]. Gas hydrate technology is one of the promising approaches to mitigate both ongoing challenges when performing simultaneous CO_2 capture and water desalination[2]. The process is depicted in a modified scheme below[3].

A unique in-situ Raman-coupled high-pressure cell was used to demonstrate the effect of salt (NaCl) concentration on water recovery with CO_2 hydrates. Raman spectroscopy was applied for the first time to determine water recovery utilizing water-stretching vibrations and corresponding calibration curves. At low temperature and high pressure, CO_2 clathrates were synthesized in the presence of 15 and 3.5 wt.% salt solutions.

Upon CO_2 hydrate formation, it is shown that the salt concentration in saline water around hydrates rises due to the contribution of pure water molecules to the clathrate structure. Inversely, the salinity decreases by increasing temperature due to the progressive dissociation of CO_2 clathrates as well as the release of the water molecules in the salt solution. The influence of the initial salt concentration is further investigated by in-situ Raman spectroscopy to determine the relevant parameters that can improve the water recovery process.



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Gas hydrates: characterization and properties probed by micro-Raman

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ABSTRACT

Gas (clathrate) hydrates are inclusion compounds constituted of a hydrogen bonded network of water molecules that are periodically arranged to form cages. The cages of different size and shape can accommodate gas molecules which will interact with the water molecules through van der Waals forces. Gas hydrates represent in many aspects high technological potential compounds which are therefore currently extensively studied in methane production from natural gas hydrates, gas separation and purification, gas transportation, sea–water desalination, pipeline safety and phase change, energy (hydrogen) storage, etc. [1,2]

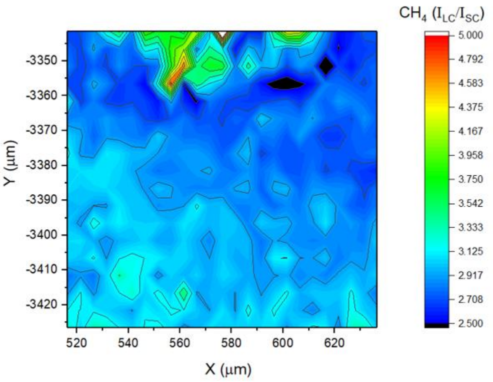

Fig.1 Raman image of the spatial variability of methane cage occupancy ratio in natural gas hydrates from Black Sea [5]

In the present study, we will review recent advances on how Raman spectroscopy can be applied (1) to gain insights into quantitative performance parameters like selectivity, or recovery fraction in processes like gas separation for CO_2 capture [3], (2) to derive kinetic parameters in the simulation of gas exchange CO_2-CH_4 by clathrates [4], (3) to establish the spatial variability at molecular scale of natural gas hydrates composition by Raman imaging techniques (Fig1). [5]

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Optical microscopy observations of gas hydrate growth processes

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ABSTRACT

An account will be given of recent advances in the understanding of hydrate growth processes obtained from optical microscopy and microRaman spectroscopy mapping. These processes are observed in thin glass capillaries serving as optical cells under well-controlled temperature and pressure conditions. The experimental setup and procedure are very versatile and have allowed to gain insights into the hydrate growth mechanisms caused by the presence of either a hydrophobic porous substrate (Figure 1, ref. 1), or a surfactant promoter (Figure 2, ref. 2). In the latter situation, the microRaman mapping reveals the high porosity and pore sizes of the porous hydrate structure.

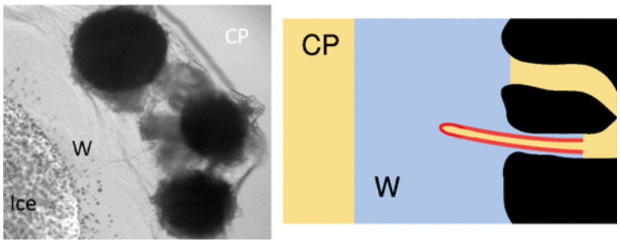

Figure 1. Gas hydrate fibers growing at 0.5°C from an activated carbon bead (with diameter 0.8 mm) at the interface between melt water (W) and cyclopentane (CP) and proposed growth mechanism.

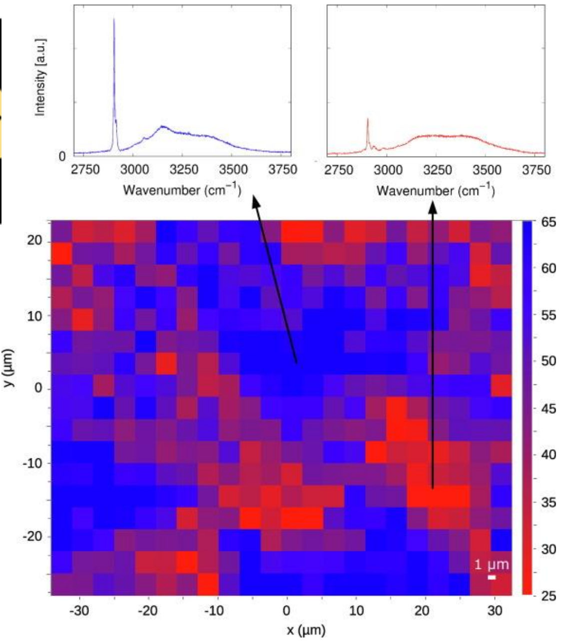

Figure 2 (right): Raman spectroscopy mapping of the porous methane hydrate formed at 0°C & 40 bar from a 500 ppmw sodium dodecyl sulfate solution. The map has been constructed by considering the methane-to-water Raman band ratio. The areas rich in methane hydrate and shown in blue and those with a large quantity of liquid water are shown in red.

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Low melting mixtures based on cyclodextrins for the solubilization of non-steroidal anti-inflammatory drugs

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ABSTRACT

The most exigent phase in the process of drug development and formulation nowadays, is the enhancement of drug solubility since the majority of the newly discovered bioactive compounds are poorly soluble [1]. Many attempts have been reported in the literature for improving the aqueous solubility of various drugs through various solubilization approaches [2], among them we cite, the use of cyclodextrins (CD) and cosolvents [3,4]. The latter approach is a simple and effective method commonly used in the pharmaceutical industry [5], where non-toxic cosolvents are used to enhance the solubility of poorly water-soluble compounds. In this context, deep eutectic solvents (DESs) characterized by high solubilizing ability and low toxicity are gaining a growing attention and seem to emerge as promising alternatives to conventional solvents. DESs belong to the greater family of low melting mixtures (LMMs). Recently, a novel class of LMMs has been introduced, they are LMMs based on CDs and liquid at room temperature. CDs are cage molecules able to encapsulate various guests in their hydrophobic cavity and known for their use as functional pharmaceutical excipients to enhance drug solubility [6,7,8]. In this study, we were interested in comparing the solubilizing potential of two classes of LMMs, that are DESs and LMMs based on CD, to highlight the benefit of combining the solubilization properties of a solvent and a drug carrier. Our results showed a significant increase in solubility for the different non-steroidal anti-inflammatory drugs (NSAIDs) studied, with factors ranging from 1243 to 5012. The solubility was either equally enhanced in both solvents, or more enhanced with the LMM based on CD. So, we went beyond solubility assessment and investigated the formation of inclusion complexes in the LMM based on CD. This hypothesis was validated by NMR studies. The effect of water addition on the solubilizing potential of the solvents was also determined and the stability of the formulations was followed up to a year.

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Excited State Dynamics of Indoline Dye D149 in BmimBF$_4$-Acetonitrile Mixtures: An Ultrafast Transient Absorption study

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ABSTRACT

We have studied the excited state dynamics of a dye D149 in the whole composition range of the mixture of an imidazolium ionic liquid (BmimBF$_4$) and polar aprotic solvent acetonitrile (ACN) by using Steady-state and femtosecond transient absorption (TA) spectroscopy. The Stokes shift values of the dye show a nonlinear correlation with the polarity parameter of the mixture. The irradiation of the dye using ultrafast laser pulse at 460 nm helped us to access the first excited state. The global analysis of ultrafast TA spectra revealed that there are four different time constants related to different excited-state processes of the dye. Among them, the two faster time scales are associated with the intermolecular vibrational relaxation and solvation dynamics processes, as discussed in previous literatures. [1,2] Both these faster timescales vary with the polarity and viscosity of the mixture. The longest timescale is attributed to the relaxation of the excited state of the dye. [1,2] Increase in viscosity and decrease in polarity of the mixtures result in an overall increase of this timescale, while the minimum at a lower mole fraction of ionic liquid indicates suggest the change in the behavior of the local environment of the dye. Our global analysis has also found a timescale that is substantially smaller than the decay timescale of dye excited state, whose assignment remains debatable. Indeed, El-Zohry et al. [3] had described it as a decay timescale of the twisted population of the dye while Fakis et al. and Lohse et al. assigned it to vibration relaxation of the dye excited state. [1,2] The analysis of both the decay-associated spectra (DAS) and TA spectra has allowed us to assign this timescale to the decay of the excited state of short-lived species in pure acetonitrile. However, this timescale has the solvation characteristics in pure BmimBF$_4$ and also in different BmimBF$_4$-ACN mixtures

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A Thermodynamic of mixing of ILs/water As Seen from Monte Carlo Simulations and Thermodynamic Integration Using Different Models

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ABSTRACT

In recent years, force fields of ionic liquids have been proposed with values of the van-der-Waals parameters that were adapted from AMBER, CHARMM or OPLS-AA, and the fractional charges carried by atoms were obtained from ab initio calculations. In studies of RTIL/water mixtures, these parameters are combined with those of water models such as SPC, SPC/E or TIP4P. However, these models do not necessarily reproduce the miscibility of the two components. The miscibility of two components is generally controlled by the free energy of mixing. The sign of free energy determines what mixture or components correspond to a more thermodynamically stable system. Consequently, the reproduction of experimental free energy of mixing is prerequisite for accurately describing the microscopic structure of the ionic liquid mixture.

In this contribution, the Helmholtz free energy, energy, and entropy of mixing of [BMIM][BF_4] using the potential model proposed by Tsun et al. [1] and SPC/E water potential model [2] are calculated in the entire composition range by means of Monte Carlo computer simulations and thermodynamic integration, using. MCCCS Towhee package [3].

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Molecular dynamic simulation of D205 in Bmim$^+$- based Ionic liquids in ground end excited states

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The dye D205 (Fig. 1) can be used in dye-sensitized solar cells (DSSC) due to high molar light absorption coefficient, electrochemical, photochemical and thermal stability for a long time, ability to absorb photons in all visible range, good solubility in molecular solvents and the presence of anchor-COOH group, which easily binds to the TiO_2-anatase nanoparticles at an electrode[1].

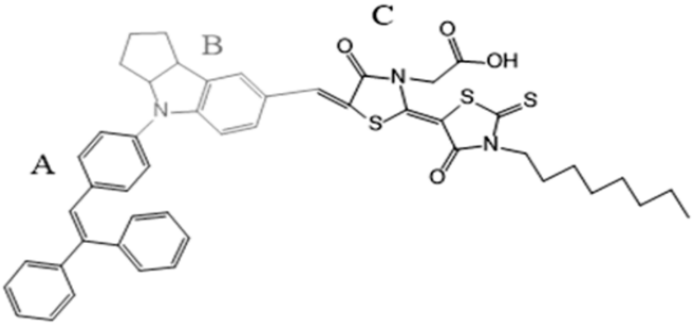

Figure 1. D205 dye

Here we present the results of the investigation of molecular dynamic simulation using Gromacs (MD) of D205 dye in a mixture with ionic liquid $BmimBF_4$. The aim is to characterize the microscopic local structure around the donor, acceptor and the bridge of the dye. For this purpose, we developed a force field characterizing the intra and inter molecular interaction of the D205. We also determined the charge distribution in the ground and excited states. Statistical distributions such as radial distribution functions, the nearest neighbor approach were used to characterize the local structure.

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