université de BORDEAUX

EMLG - JMLG 2023 :

“ Understanding Solvation in Molecular and Ionic Fluids: Towards a Sustainable Future “

BOOK OF ABSTRACTS

Bordeaux
4 – 7 September 2023

https://emlg2023.sciencesconf.org/

Content

Preface

Dear friends, Dear colleagues,

It is our great pleasure to organize and chair the 39th edition of the EMLG-JMLG meeting (EMLG-JMLG 2023) in Bordeaux, France September 4-7, 2023.

The European Molecular Liquids Group (EMLG) has federated for more than 40 years (creation in 1981) renowned scientists specialized in theoretical and experimental physical-chemistry dedicated to the study of complex liquid media under various thermodynamic conditions. In 1996, Japanese participants established the sister organization JMLG which later became the international division of the Japan Association of Solution Chemistry (JASC). The EMLG/JMLG association is internationally recognized and is a world reference in its theme. Annual meetings have been organized since 1982 in different countries with varying focus in order to cooperate internationally and to coordinate activities in this field. Bordeaux was chosen as the venue for the 39th edition of this conference. As a world wine capital, also ranked UNESCO town, with its typical 18th century mansions and houses along the Garonne River, its friendly gastronomic restaurants and wine bars, we hope that Bordeaux will make this event an unforgettable experience.

We are pleased to bring together during 4 days over 120 researchers from all continents, experimentalists and theoreticians, to present their latest scientific results as oral contributions or as poster presentations about the physical-chemistry of molecular and ionic liquid media for applications in sustainable chemistry.

A special issue of the leading scientific journal in the field, "Journal of Molecular Liquids" will be devoted to the scientific contributions presented at this conference. The title of this special issue will be: “Understanding Solvation in Molecular and Ionic Fluids: Towards a Sustainable Future”.

As is tradition, a jury will pay particular attention to posters presented by young scientists (PhD students and young postdocs up to two years after their PhD) and will select laureates to award four poster prices.

We invite you to come together in a friendly atmosphere to share your thoughts with all the participants and in particular with young researchers to make this conference a successful meeting that will shape the future of the EMLG-JMLG community.

Dr. Thierry TASSAING, Chair, CNRS/University of Bordeaux
Prof. Jean-Christophe SOETENS, Co-Chair, University of Bordeaux

Organization of the poster sessions & poster prizes

Three poster sessions are organized following lunch on Tuesday, Wednesday and Thursday. All posters are concerned by the three poster sessions.To maximize interactions and exchanges around the posters, speakers are advised to hang their poster Monday on the labelled poster stands provided (see the list of posters to know the label of your poster PC-number).

As is tradition, a jury will pay particular attention to posters presented by young scientists (PhD students and young postdocs up to two years after their PhD) and will select laureates. This year, the organizers and several members of the EMLG have furthermore decided to award a special poster prize in memory of the late **Professor Karl Heinzinger**, who passed away at the beginning of 2023.

The special prize, the first, the second and the third prizes will go with financial awards of 400, 400, 300 and 200 euros, respectively. The chairman of EMLG, **Prof. Dr. Ralf Ludwig** and the President of the selection jury, will award these prizes during the banquet on Thursday 7 September.

Partners

The organizers warmly thank the following institutions and sponsors for their financial support and help in organizing the EMLG - JMLG 2023 conference.

université de BORDEAUX	https://www.u-bordeaux.fr/en *This project has received financial support from the French government within the framework of the* **France 2030 programme IdEx Université de Bordeaux.**
RÉGION Nouvelle-Aquitaine	https://www.nouvelle-aquitaine.fr/
NEO TERRA	https://www.neo-terra.fr/ This conference has obtained the label NEO TERRA by respecting the regional roadmap on ecological issues and energetic transition
BORDEAUX INP	https://www.bordeaux-inp.fr/en
cnrs	https://www.cnrs.fr/en
ism Institut des Sciences Moléculaires BORDEAUX	https://www.ism.u-bordeaux.fr/?lang=en
Grand Programme de Recherche PPM | Matériaux post-pétrole université de BORDEAUX	PPM - Post-Petroleum Materials
Société Chimique de France Le réseau des chimistes	https://new.societechimiquedefrance.fr/
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Société Chimique de France Aquitaine	https://new.societechimiquedefrance.fr/sections_regionales/aquitaine/
ThéMoSiA Théories - Modélisations - Simulations - Atomistiques	https://www.chimie-theorique.cnrs.fr/spip.php?rubrique1
cnrs GDR Groupement de recherche SolvATE Solvatation : Avancées Théoriques et Expérimentales	https://solvate.cnrs.fr/
cnrs GDR EMiE Groupement de recherche Edifices Moléculaires isolés et Environnés	https://www.lcar.ups-tlse.fr/emie/?page_id=37
Société Française de Physique	https://www.sfpnet.fr/

Timetable

	Monday 4/09
9:00-10:30	***Registration*** ***Welcome coffee***
10:30-10:50	***Opening***
Chair	*Laurent Servant*
10:50-11:30	**[PL-1] Sergei Kazarian**
11:30-11:50	[OC-01] Antoine Carof
11:50-12:10	[OC-02] Nacer Idrissi
12:10-12:30	[OC-03] Guillaume Galliero
12:30-12:50	[OC-04] Ioannis Skarmoutsos
12:50-13:45	***WELCOME LUNCH***
13:45-14:40	
Chair	*Dietmar Paschek*
14:40-15:05	[IL-1] Blake A. Simmons
15:05-15:25	[OC-05] Anne Strate
15:25-15:45	[OC-06] Christian Pomelli
15:45-16:05	[OC-07] Jason B. Harper
16:05-16:25	[OC-08] Lasse Hunger
16:25-16:50	***Coffee Break***
Chair	*Elixabete Rezabal*
16:50-17:10	[OC-09] Valentin Radtke
17:10-17:30	[OC-10] John M. Slattery
17:30-17:50	[OC-11] Daniel C. Morris
18:00-19:00	***EMLG Board Meeting***

	Tuesday 5/09	**Wednesday 6/09**	**Thursday 7/09**
8:30-9:00	***Registration***	***Registration***	***Registration***
Chair	*Ralf Ludwig*	*Nacer Idrissi*	*Myroslav Holovko*
9:00-9:20	**[PL-2] Barbara Kirchner**	**[PL-4] Toshiyuki Takamuku**	[OC-35] Dezső Boda
9:20-9:40			[OC-36] M. R. Mosaferi
9:40-10:00	[OC-12] Alessandro Triolo	[OC-25] Yukio Ouchi	[OC-37] Milan Předota
10:00-10:20	[OC-13] Dharamashi Rabari	[OC-26] Ivo Nezbeda	[OC-38] Anne Hockmann
10:20-10:40		[OC-27] Martina Pozar	[OC-39] Ari Paavo Seitsonen
10:40-11:05	***Coffee Break***	***Coffee Break***	***Coffee Break***
Chair	*Daniel Borgis*	*Eckhard Spohr*	*Barbara Kirchner*
11:05-11:30	[IL-2] Elixabete Rezabal	[OC-27bis] Mahula Santra	[IL-6] Virginie Mary
11:30-11:50	[OC-15] Olga Russina	[OC-28] Bernarda Lovrinčević	[OC-40] Andrey Kalinichev
11:50-12:10	[OC-16] A. van den Bruinhorst	[OC-29] Miguel Jorge	[OC-41] Jon Zubeltzu
12:10-12:30	[OC-17bis] Leonard Dick	[OC-30] F. B. Nkou	[OC-42] Maria von Einem
12:30-12:50	[OC-18] Jule K. Philipp	[OC-31] Han Jihae	[OC-43] Jiří Kolafa
12:50-13:45	***LUNCH***	***LUNCH***	***LUNCH***
13:45-14:40	***Poster Session A***	***Poster Session B***	***Poster Session C***
Chair	*Toshiyuki Takamuku*	*Philippe Bopp*	*Virginie Mary*
14:40-15:05	[IL-3] Marie PLazanet	[IL-5] Dietmar Paschek	[IL-7] Marco Paolantoni
15:05-15:25	[OC-19] Zsófia Sarkadi	[OC-32] Daniel Borgis	[OC-44] Szilvia Pothoczki
15:25-15:45	[OC-20] Myroslav Holovko	[OC-33] Martin Lísal	[OC-45] Pal Jedlovszky
15:45-16:05	[OC-21] S. Okazaki	[OC-34] William R. Smith	[OC-46] Eckhard Spohr
16:05-16:25	[OC-22] Maxime Fery	**SOCIAL EVENT**	[OC-47] Giancarlo Franzese
16:25-16:50	***Coffee Break***		***Coffee Break***
Chair	*Pal Jedlovszky*		*Marco Paolantoni*
16:50-17:10	**[PL-3] Pavel Jungwirth**		[OC-48] Barbara Rossi
17:10-17:30			[OC-49] Katsura Nishiyama
17:30-17:50	[OC-23] Kenichiro Koga		[OC-14] Tiancheng Mu
17:50-18:10	[OC-24] Imre Bako		***"Grand Public Conference"*** **Karine Vigier de Oliveira**
18:10-19:00	***EMLG General Assembly***		
19:00-20:30			
20:30			**GALA DINNER** **Poster Awards**

Conference Program

Monday, September 4

9:00 – 10:30	**Registration and welcome coffee**	
10:30 – 10:50	Opening	
10:50 – 11:30	[PL-1] Sergei Kazarian	*FTIR Spectroscopic Imaging Applied to Ionic Liquids, supercritical Fluids and Molecular Liquids*
11:30 – 11:50	[OC-01] Antoine Carof	*Ultrafast calculation of solvation in supercritical fluids*
11:50 – 12:10	[OC-02] Nacer Idrissi	*Local structure and dynamics of the Curcumin-vacuum and Curcumin-scCO2 interfaces using molecular dynamics*
12:10 – 12:30	[OC-03] Guillaume Galliero	*Supercritical fluids: from clustering effect in mixtures to gas-like and liquid like demarcation lines*
12:30 – 12:50	[OC-04] Ioannis Skarmoutsos	*Solvation structure and dynamics of pharmaceutical compounds in liquid and supercritical solvents: The cases of caffeine and favipiravir.*
12:50 – 14:40	**Welcome lunch**	
14:40 – 15:05	[IL-1] Blake A. Simmons	*Multiscale molecular simulations for the solvation of lignin in ionic liquids*
15:05 – 15:25	[OC-05] Anne Strate	*Detailed insights into the dynamics of a phosphonium-based ionic liquid – A combined experimental and molecular dynamics simulation study*
15:25 – 15:45	[OC-06] Christian Pomelli	*Recovery of metals with ionic liquids: a Eni Slurry Technology product as a case study*
15:45 – 16:05	[OC-07] Jason B. Harper	*Understanding Reaction Outcomes in Mixtures Containing Ionic Liquids. Evaluating the contribution of solvent dynamics and organisation*
16:05 – 16:25	[OC-08] Lasse Hunger	*Chain length dependence of the hydrogen-bond strength in carboxyl-functionalized ionic liquids*
16:25 – 16:50	**Coffee break**	
16:50 – 17:10	[OC-09] Valentin Radtke	*Special Ionic Liquids as “Ideal” Salt Bridges for the Development of Unified Redox and pH Scales*
17:10 – 17:30	[OC-10] John M. Slattery	*Exploring the surface and bulk structure of ionic liquid mixtures*
17:30 – 17:50	[OC-11] Daniel C. Morris	*How crucial is structure? Understanding the dynamics of ionic liquid solvent effects on an SN2 process*

Tuesday, September 5

8:30 – 9:00	**Registration**	
9:00 – 9:40	[PL-2] Barbara Kirchner	*Ion pairing and reducing uncertainties in ionic and molecular liquids*
9:40 – 10:00	[OC-12] Alessandro Triolo	*Water-based natural deep eutectic solvents*
10:00 – 10:20	[OC-13] Dharamashi Rabari	*Investigating the interactions between choline iodide-based deep eutectic solvents and CO2 using Density Functional Theory*
10:40 – 11:05	**Coffee break**	
11:05 – 11:30	[IL-2] Elixabete Rezabal	*Revealing the impact of fine-tuning force fields on microheterogeneity in Choline Chloride-Based Deep Eutectic Solvents*
11:30 – 11:50	[OC-15] Olga Russina	*Sustainable solvents for efficient cyclodextrin solubilisation*
11:50 – 12:10	[OC-16] A. van den Bruinhorst	*Deep Eutectic Solvents on a Tightrope – The Balance Between Entropy and Enthalpy*
12:10 – 12:30	[OC-17bis] Leonard Dick	*Ionic Liquids in confinement*
12:30 – 12:50	[OC-18] Jule Kristin Philipp	*Pseudo-ionic Liquid and Water-in-salt Electrolyte: Structural Diversity in Mixtures of [Li][NTf2], Triglyme and Water*
12:50 – 13:45	**Lunch**	
13:45 – 14:40	**Poster session A**	
14:40 – 15:05	[IL-3] Marie Plazanet	*How NaCl addition destabilizes ionic liquid micellar suspension until phase separation*
15:05 – 15:25	[OC-19] Zsófia Sarkadi	*Multiscale simulation of ion transport by Poisson-Nernst-Planck, Monte Carlo, Brownian dynamics, and molecular dynamics*
15:25 – 15:45	[OC-20] Myroslav Holovko	*Cation hydrolysis effects in aqueous electrolyte solution: A molecular dynamics study*
15:45 – 16:05	[OC-21] S. Okazaki	*A new dynamic Monte Carlo calculation with position-dependent diffusion coefficient and potential evaluated by all-atomistic molecular dynamics calculations and its application to the molecular transportation in the polymer electrolytes*
16:05 – 16:25	[OC-22] Maxime Fery	*Probing the molecular organization in concentrated electolytes by non-linear optics*
16:25 – 16:50	**Coffee break**	
16:50 – 17:30	[PL-3] Pavel Jungwirth	Electrons in Polar Solvents: Birch Reduction, Blue Electrolytes, and Golden Metals
17:30 – 17:50	[OC-23] Kenichiro Koga	Solute-size dependences of hydrophobic interactions in water and other effective interactions in liquids
17:50 – 18:10	[OC-24] Imre Bako	How can we interpret the X-ray structure factor of water?
18:10 – 19:00	**EMLG General assembly**	

Wednesday, September 6

8:30 – 9:00	**Registration**	
9:00 – 9:40	[PL-4] Toshiyuki Takamuku	*Properties of Ionic Liquid-Molecular Liquid Binary Mixtures as Reaction Solvents*
9:40 – 10:00	[OC-25] Yukio Ouchi	*Nonlinear Vibrational Spectroscopic Studies on Hydrophobic Buried-interfaces of Ionic Liquids/Molecular Liquids*
10:00 – 10:20	[OC-26] Ivo Nezbeda	*Thermodynamics and structure of water-alcohol mixtures at the level of simple models*
10:20 – 10:40	[OC-27] Martina Pozar	*On the role of water as chaotrope/kosmotrope: Octanol-rich aqueous n-octanol mixtures*
10:40 – 11:10	**Coffee break**	
11:10 – 11:30	[OC-27bis] Mahula Santra	*Analysis of the formation mechanism of choline chloride-based deep eutectic solvents using Density Functional Theory*
11:30 – 11:50	[OC-28] Bernarda Lovrinčević	*Charge ordering in associated liquids and its role in cluster dynamics*
11:50 – 12:10	[OC-29] Miguel Jorge	*Polarization-Consistent Force Fields to Predict Solvation and Dielectric Properties of Mixtures*
12:10 – 12:30	[OC-30] Falonne Nkou	*Selective Oxydation of Ethylene Glycol at Transition Metal Oxide Surfaces : Atomistic insight From Ab-initio Molecular Dynamics Simulation in Aqueous Solution*
12:30 – 12:50	[OC-31] Han Jihae	*Two-Dimensional Raman and Dielectric Relaxation Correlation Analysis for Lithium Salt-Propylene Carbonate Solutions*
12:50 – 13:45	**Lunch**	
13:45 – 14:40	**Poster session B**	
14:40 – 15:05	[IL-5] Dietmar Paschek	*Short- and Long-Time Dynamics of Hydrogen Bonds in Hydroxyl-Functionalized Ionic Liquids*
15:05 – 15:25	[OC-32] Daniel Borgis	*Predicting solvation properties at molecular level with classical DFT*
15:25 – 15:45	[OC-33] Martin Lísal	*Generalised energy-conserving dissipative particle dynamics: A coarse-grain framework for isoenergetic simulations of complex fluids*
15:45 – 16:05	[OC-34] William R. Smith	*Molecular Simulation of Vapour–Liquid Equilibrium by a Computationally Efficient Chemical Potential Extrapolation Algorithm*
16:05 – 19:00	**Social event : Wine tour and tasting at the “Château Pape Clément”, Pessac**	

Thursday, September 7

8:30 – 9:00	**Registration**	
9:00 – 9:20	[OC-35] Dezső Boda	*The II+IW theory: the balance of ion-ion interaction and solvation drives the behavior of ionic activities*
9:20 – 9:40	[OC-36] M. R. Mosaferi	*Fingerprint of the tilt angle of water molecules in Cu2+ aqueous solution probed by x-ray photoelectron spectroscopy*
9:40 – 10:00	[OC-37] Milan Předota	*Ionic transport in graphene-based single digit nanopores*
10:00 – 10:20	[OC-38] Anne Hockmann	*Enhancing Li+ Transference Number by the Formation of Clusters with Heterogeneous Li+ Coordination*
10:20 – 10:40	[OC-39] Ari Paavo Seitsonen	*Vibrational spectroscopies in liquid water: On temperature and coordination effects in Raman and infra-red spectroscopies*
10:40 – 11:05	**Coffee break**	
11:05 – 11:30	[IL-6] Virginie Marry	*Transport of water in clays: what can we learn from molecular dynamics?*
11:30 – 11:50	[OC-40] Andrey Kalinichev	*Clay Surfaces – Are They Hydrophilic or Hydrophobic?*
11:50 – 12:10	[OC-41] Jon Zubeltzu	*Anomalous perpendicular dielectric response of nanometer-thin water films*
12:10 – 12:30	[OC-42] Maria von Einem	*Insights into wastewater cleaning with TiO2*
12:30 – 12:50	[OC-43] Jiří Kolafa	*Surface potential of water and brines*
12:50 – 13:45	**Lunch**	
13:45 – 14:40	**Poster session C**	
14:40 – 15:05	[IL-7] Marco Paolantoni	*Hydration properties of sugars revisited*
15:05 – 15:25	[OC-44] Szilvia Pothoczki	*Hydration properties in aqueous solutions of fructose*
15:25 – 15:45	[OC-45] Pál Jedlovszky	*Understanding the Molecular Mechanism of General Anesthesia*
15:45 – 16:05	[OC-46] Eckhard Spohr	*Electrolyte Effects on Protein Stability in Solution*
16:05 – 16:25	[OC-47] Giancarlo Franzese	*Water solvation in bio-nano complex matter*
16:25 – 16:50	**Coffee break**	
16:50 – 17:10	[OC-48] Barbara Rossi	*Insights into structure and dynamics of biomolecules by multi-wavelengths UV Resonance Raman spectroscopy*
17:10 – 17:30	[OC-49] Katsura Nishiyama	*Plant absorption of metal nanoparticles cohabiting with arbuscular mycorrhizal fungi targeting for biomarker systems*
17:30 – 17:50	[OC-14] Tiancheng Mu	*Thermal Stability of Ionic Liquids and Deep Eutectic Solvents*
17:50 – 19:00	Grand Public conference Karine De Oliveira Vigier	Qu'est-ce que la chimie verte? What is green chemistry?
20:30	**Gala dinner at the "Café Maritime", Bassin à flot, Bordeaux** **Posters awards**	

List of Plenary Lectures

[PL-1]	Sergei	Kazarian	*FTIR Spectroscopic Imaging Applied to Ionic Liquids, Supercritical Fluids and Molecular Liquids*
[PL-2]	Barbara	Kirchner	*Ion pairing and reducing uncertainties in ionic and molecular liquids*
[PL-3]	Pavel	Jungwirth	*Electrons in Polar Solvents: Birch Reduction, Blue Electrolytes, and Golden Metals*
[PL-4]	Toshiyuki	Takamuku	*Properties of Ionic Liquid-Molecular Liquid Binary Mixtures as Reaction Solvents*

List of Invited Lectures

[IL-1]	Blake A.	Simmons	*Multiscale molecular simulations for the solvation of lignin in ionic liquids*
[IL-2]	Elixabete	Rezabal	*Revealing the impact of fine-tuning force fields on microheterogeneity in Choline Chloride-Based Deep Eutectic Solvents*
[IL-3]	Marie	Plazanet	*How NaCl addition destabilizes ionic liquid micellar suspension until phase separation*
~~**[IL-4]**~~	~~Oleg N.~~	~~Kalugin~~	~~*Structure, Dynamics and Solvatochromism of a D205 Dye at the Interface with TiO2 in Ionic Liquids and Acetonitrile*~~
[IL-5]	Dietmar	Paschek	*Short- and Long-Time Dynamics of Hydrogen Bonds in Hydroxyl-Functionalized Ionic Liquids*
[IL-6]	Virginie	Mary	*Transport of water in clays: what can we learn from molecular dynamics ?*
[IL-7]	Marco	Paolantoni	*Hydration properties of sugars revisited*

List of Oral Contributions

[OC-01]	Antoine	Carof	*Ultrafast calculation of solvation in supercritical fluids*
[OC-02]	Nacer	Idrissi	*Local structure and dynamics of the Curcumin-vacuum and Curcumin-scCO2 interfaces using molecular dynamics*
[OC-03]	Guillaume	Galliero	*Supercritical fluids: from clustering effect in mixtures to gas-like and liquid like demarcation lines*
[OC-04]	Ioannis	Skarmoutsos	*Solvation structure and dynamics of pharmaceutical compounds in liquid and supercritical solvents: The cases of caffeine and favipiravir*
[OC-05]	Anne	Strate	*Detailed insights into the dynamics of a phosphonium-based ionic liquid – A combined experimental and molecular dynamics simulation study*
[OC-06]	Christian	Pomelli	*Recovery of metals with ionic liquids: a Eni Slurry Technology product as a case study*
[OC-07]	Jason B.	Harper	*Understanding Reaction Outcomes in Mixtures Containing Ionic Liquids. Evaluating the contribution of solvent dynamics and organisation*
[OC-08]	Lasse	Hunger	*Chain length dependence of the hydrogen-bond strength in carboxyl-functionalized ionic liquids*
[OC-09]	Valentin	Radtke	*Special Ionic Liquids as "Ideal" Salt Bridges for the Development of Unified Redox and pH Scales*

[OC-10]	John M.	Slattery	*Exploring the surface and bulk structure of ionic liquid mixtures*
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[OC-12]	Alessandro	Triolo	*Water-based natural deep eutectic solvents*
[OC-13]	Dharamashi	Rabari	*Investigating the interactions between choline iodide-based deep eutectic solvents and CO2 using Density Functional Theory*
[OC-14]	Tiancheng	Mu	*Thermal Stability of Ionic Liquids and Deep Eutectic Solvents*
[OC-15]	Olga	Russina	*Sustainable solvents for efficient cyclodextrin solubilisation*
[OC-16]	Adriaan	van den Bruinhorst	*Deep Eutectic Solvents on a Tightrope – The Balance Between Entropy and Enthalpy*
[OC-17]	Alain	Chaumont	*Investigating the Solvation Properties of Menthol-Thymol Deep Eutectic Mixtures using Molecular Dynamics Simulations*
[OC-17bis]	Leonard	Dick	*Ionic liquids in confinement*
[OC-18]	Jule Kristin	Philipp	*Pseudo-ionic Liquid and Water-in-salt Electrolyte: Structural Diversity in Mixtures of [Li][NTf2], Triglyme and Water*
[OC-19]	Zsófia	Sarkadi	*Multiscale simulation of ion transport by Poisson-Nernst-Planck, Monte Carlo, Brownian dynamics, and molecular dynamics*
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[OC-27bis]	Mahula	Santra	*Analysis of the formation mechanism of choline chloride-based deep eutectic solvents using Density Functional Theory*
[OC-28]	Bernarda	Lovrinčević	*Charge ordering in associated liquids and its role in cluster dynamics*
[OC-29]	Miguel	Jorge	*Polarization-Consistent Force Fields to Predict Solvation and Dielectric Properties of Mixtures*
[OC-30]	Falonne	Nkou	*Selective Oxydation of Ethylene Glycol at Transition Metal Oxide Surfaces : Atomistic insight From Ab-initio Molecular Dynamics Simulation in Aqueous Solution*
[OC-31]	Han	Jihae	*Two-Dimensional Raman and Dielectric Relaxation Correlation Analysis for Lithium Salt-Propylene Carbonate Solutions*
[OC-32]	Daniel	Borgis	*Predicting solvation properties at molecular level with classical DFT*

[OC-33]	Martin	Lísal	*Generalised energy-conserving dissipative particle dynamics: A coarse-grain framework for isoenergetic simulations of complex fluids*
[OC-34]	William R.	Smith	*Molecular Simulation of Vapour–Liquid Equilibrium by a Computationally Efficient Chemical Potential Extrapolation Algorithm*
[OC-35]	Dezső	Boda	*The II+IW theory: the balance of ion-ion interaction and solvation drives the behavior of ionic activities*
[OC-36]	M. R.	Mosaferi	*Fingerprint of the tilt angle of water molecules in Cu2+ aqueous solution probed by x-ray photoelectron spectroscopy*
[OC-37]	Milan	Předota	*Ionic transport in graphene-based single digit nanopores*
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[OC-43]	Jiří	Kolafa	*Surface potential of water and brines*
[OC-44]	Szilvia	Pothoczki	*Hydration properties in aqueous solutions of fructose*
[OC-45]	Pál	Jedlovszky	*Understanding the Molecular Mechanism of General Anesthesia*
[OC-46]	Eckhard	Spohr	*Electrolyte Effects on Protein Stability in Solution*
[OC-47]	Giancarlo	Franzese	*Water solvation in bio-nano complex matter*
[OC-48]	Barbara	Rossi	*Insights into structure and dynamics of biomolecules by multi-wavelengths UV Resonance Raman spectroscopy*
[OC-49]	Katsura	Nishiyama	*Plant absorption of metal nanoparticles cohabiting with arbuscular mycorrhizal fungi targeting for biomarker systems*

List of Poster Contributions

[PC-01]	László	Almásy	*Aqueous solutions of heterocyclic amines: structure and thermodynamics*
[PC-02]	Behnaz	Asadzadeh	*Phase behavior of aqueous levulinic acid in trioctylamine solution using at different temperatures*
[PC-03]	Margaux	Zollo	*Towards microfluidic separation processes using Switchable Hydrophilicity Solvents*
[PC-04]	Alexander	Castro Grijalba	*Extraction of natural compounds by green solvents: a comparative study by COSMO-RS*
[PC-05]	Helga	Tóth Ugyonka	*Adsorption of HCN on Amorphous Ice under Interstellar Conditions*
[PC-06]	Johanna	Busch	*Anisotropic Molecular Reorientation of Methanol Unravelled*

[PC-07]	Jiří	Škvára	*Supercooled water in two dimensions: Structure and thermodynamics of the Mercedes - Benz model*
[PC-08]	Karina	Shimizu	*Interfaces between Metal Organic Frameworks and Ionic Liquids Probed by Molecular Dynamics Simulations*
[PC-09]	Adilson Alves	de Freitas	*Molecular Dynamics Simulations of Lithium-ion Transport in Concentrated Sulfolane-LiBF4 Mixtures*
[PC-10]	Mónika	Valiskó	*Calcium versus potassium selectivity in a nanopore: the effect of charge inversion at localized pore charges*
[PC-11]	M.	Klíma	*Pickup properties of water clusters developed in supersonic expansion*
[PC-12]	Bruno	Issenmann	*Viscosity of supercooled water under pressure and a proposed range for its putative liquid-liquid critical pressure*
[PC-13]	Elena N.	Tsurko	*Thermodynamic Description of Aqueous Mixtures of New, Less Toxic Green Antifreezes*
[PC-14]	Lennart	Kruse	*Understanding the dynamics of ionic liquids by means of fast-field-cycling NMR relaxometry and molecular dynamics simulations*
[PC-15]	Anne	Hockmann	*Towards understanding the structure and dynamics of localized high-concentration battery electrolytes*
[PC-16]	Arnau	Jurado Romero	*Propulsion from energy bursts for nitromethane in water*
[PC-17]	Claude	Millot	*Simulation and modelling of the dynamic structure of water with the BK3 potential*
[PC-18]	Christoffer	Leif Erik	*Medium- and Short-Range Structure of LiNTf2-Water-in-Salt-Electrolytes from Molecular Dynamics Simulations*
[PC-19]	Ryo	Fukaya	*The effect of alkyl length of ionic liquids 1-alkyl-3-methylimidazolium acetate (alkyl length 2-7) on cellulose solubility*
[PC-20]	Kodai	Kikuchi	*Effect of Preparation Condition (Temperature and Hydrostatic pressure) on Physicochemical Properties of Cellulose Hydrogel Using Ionic Liquid*
[PC-21]	Jiří	Janek	*Towards universal integration scheme for molecular dynamics*
[PC-22]	Tatsuhiko	Nakase	*Study on the relationship between alkyl chain length of 1-alkyl-3-methylimidazolium bromide and hatchability of Artemia eggs*
[PC-23]	David	Kotwica	*Spectroscopic Investigations of Amino acid based Ionic Liquids for Carbon Capture*
[PC-24]	Paul	Zaby	*Liquid Dynamics in Metal-NHC Complex Formation*
[PC-25]	Leonard	Dick	*CONAN - A novel tool to create and analyze liquids in confined space*
[PC-26]	Johannes	Sutter	*Charge transport in protic ionic liquids: Effect of protonation state in 1-methylimidazolium – acetate/trifluoroacetate mixtures*
[PC-27]	Sascha	Leyendecker	*Theoretical investigation of novel ionic liquid-salt electrolytes*
[PC-28]	Volodymyr	Koverga	*An Explicit Solvation Neighbors Approach: Toward the Understanding of the Non-covalent Interactions in the Mixtures of Imidazolium-based Ionic Liquids with Molecular Solvents*
[PC-29]	Mikel	Loizate	*Solvent effects of choline and geranate-based ionic liquid on organic catalysts*
[PC-30]	Olga	Russina	*Choline chloride-water mixtures : as new generation of green solvents*
[PC-31]	Alessandro	Triolo	*Supramolecular cyclodextrin-based DES: From self-organization to molecular recognition*

[PC-32]	Han	Jihae	*Al-Speciation Analysis in Non-aqueous Solutions via 27Al NMR and Raman spectroscopy*
[PC-33]	Milan	Předota	*Prediction of heterodyne detected VSFG spectra from molecular dynamics simulations*
[PC-34]	Louisa	Mcfegan	*Surface Affinity of Tetramethylammonium Iodide in Aqueous Solutions*
[PC-35]	Antoine	Djeukeng Momo	*Structure and free energy profiles of NaCl solutions in graphene-based single digit nanopores*
[PC-36]	Salman	Shabbir	*Molecular dynamics simulation study of charge inversion phenomena in nanopores*
[PC-37]	Kazushi	Fujimoto	*Molecular Study of Solvent Effects on Polymer Materials*
[PC-38]	Ákos György	Juhász	*Characterizing electrospun 3D matrices; the effect of humidity*
[PC-39]	Myroslav	Holovko	*Liquid-Vapour Phase Behaviour of Patchy Colloids in a Patchy Porous Matrix*
[PC-40]	Francesca	Ingrosso	*Optical Properties of a Bipyridine Diol in Water: A Multilevel Computational Approach*
[PC-41]	Grégoire	Boe	*Quantitative in situ analysis of complex fluids by co-localized IR/Raman spectroscopy for the study of the chemistry of hydrothermal vents*
[PC-42]	Victor	Carré	*Assessment of the solubility of a highly fluorophillic photoredox catalyst in scCO2*
[PC-43]	Wenjuan	Wang	*Imidazolium-based polymerized ionic liquids as versatile stabilizers for ruthenium nanoparticles*

Presentation of the ”Grand public” conference

“ What is Green Chemistry ? “

by Prof. Karine De Oliveira Vigier, University of poitiers (FR)

La réunion annuelle EMLG JMLG 2023 sera ouverte à tous lors d’une conférence "Grand Public" qui sera animée par Karine De Oliveira Vigier, Professeur à l’Université de Poitiers et chercheuse au laboratoire IC2MP*. L’ensemble de ses travaux s’inscrit dans une perspective de chimie durable préservant les ressources de notre planète Elle suit par exemple des pistes prometteuses dans l’utilisation de la biomasse, la transformation des sucres en solvants, la valorisation de produits tels que le CO_2, les huiles végétales ou le glycérol pour en faire les produits tensioactifs des détergents. Ces idées sont présentées et mises en perspective dans un chapitre de l’ouvrage intitulé *Etonnante Chimie* publié chez CNRS Éditions. Karine De Oliveira Vigier a participé à plusieurs projets de vulgarisation autour de la chimie durable. Ses présentations très pédagogiques rendent une chimie complexe accessible à un public de tous âges et de tous niveaux. Un temps de discussion à l’issue de la conférence permettra à chacun d’interagir avec la conférencière et la communauté scientifique présente.

The EMLG/JMLG 2023 meeting will be open up to the general public through the "Grand Public" conference that will be led by Karine De Oliveira Vigier, Professor at the University of Poitiers and researcher at the IC2MP* laboratory. All of his work is part of a perspective of sustainable chemistry preserving the resources of our planet. For example, it follows promising avenues in the use of biomass, the transformation of sugars into solvents, the valorization of products such as CO_2, vegetable oils or glycerol to make them surfactants of detergents. These ideas are presented and put into perspective in a chapter of the book entitled *Etonnante Chimie* published by CNRS Éditions. Karine De Oliveira Vigier has participated in several popularization projects around sustainable chemistry. His highly educational presentations make a complex chemistry accessible to an audience of all ages and levels. A discussion time at the end of the conference will allow everyone to interact with the speaker and the scientific community of the meeting.

(*) IC2MP – Institut de Chimie des Milieux et Matériaux de Poitiers
UMR CNRS 7285 – Université de Poitiers.

Abstracts of Plenary Lectures: [PL-1] → [PL-4]

[PL-1]

FTIR Spectroscopic Imaging Applied to Ionic Liquids, Supercritical Fluids and Molecular Liquids

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Infrared spectroscopy is called most nearly universal chemical spectroscopy. As a structural tool, its generality, sensitivity and specificity are hard to match. The emergence of FTIR spectroscopic imaging is one of the most exciting developed analytical methods because of its chemical specificity, high-throughput capabilities and quantitative nature, we and others have demonstrated the tremendous versatility of FTIR imaging by applying it in many fields. FTIR spectroscopic imaging enables direct measurement of many samples under identical conditions to study material properties for high-throughput screening and optimisation. [1] Powerful combination of imaging, chemical specificity and quantitative information of this approach was used to obtain “chemical snapshots” from spatially-defined arrays of many different formulations and solutions, to study protein crystallisation, behaviour of different ionic liquids (IL)under controlled environment [2] and liquid flows in microfluidic devices. In situ FTIR imaging of different polymeric materials subjected to high-pressure carbon dioxide was also possible. A very recent example for the formation of the Norfloxacin-CO_2 crystal by supercritical CO_2 at pressure 25 MPa treatment of Norfloxacin form B to enhance the dissolution properties of Norfloxacin will be presented.[3] Conventional ATR-FTIR spectroscopy applied in situ was used to study CO_2 sorption by a homologous series of CnMIMBF4 (n=2, 4, 6, 8, 10) IL in situ. The interaction of CO_2 with a series of ionic liquids were studied in the pressure range from 20 to 40 atm and temperatures from 25 to 65 °C. A detailed analysis of the acquired spectra of sorbed CO_2 and the spectra of the IL with increasing alkyl chain lengths during CO_2 sorption was investigated.

It was possible to obtain “chemical snapshots” from a spatially-defined array of many different ionic liquids simultaneously. Simultaneous response (for example water sorption) of the array of samples of ionic liquids to the environmental parameters was studied.[1] This high-throughput imaging approach will be of great value in the area of IL research where the number of newly synthesized ionic liquids is growing rapidly. Great potential exists in the applications of this in situ spectroscopic method to high-throughput analysis of ionic liquids or polymers subjected to supercritical carbon dioxide. Implications of the presented novel approach range from novel sensors to simultaneous monitoring of reactions in many different ionic liquids. This high-throughput study has shown that ATR-FTIR spectroscopic imaging is a suitable approach for simultaneously studying multiple samples of ILs exposed in a controlled environment. The advantages of minimum sample preparation and the possibility to perform quantitative analysis in ATR measurement mode has been demonstrated. Fourteen different ILs, from hydrophilic (e.g. [C4mim][CH3SO3]) to hydrophobic (e.g. [C4mim][NTf2]) have been studied.

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[PL-2]

Ion pairing and reducing uncertainties in ionic and molecular liquids

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A reduced electrical or ionic conductivity measured by impedance spectroscopy compared to ion diffusivities measured by pulsed field gradient [1] is often explained by ion pairing [2]. From this experimental result many questions follow. In this presentation we focus on the following points from the computational perspective:

- How is an ion pair defined [2]? Are there a novel and “disruptive” point of views or does recent work just fall into the category of “the same old story”?
- Ion pair versus ion association: And what other effects should be considered? Charge transfer [2], or polarizability [3], or charge screening [4], or cage dynamics (weak IP) [2]?
- Why do force-field researchers scale many terms, but there is a heated discussion about charge scaling for ionic liquids and deep eutetctic solvents [5]?
- How do we control uncertainties in properties like structure, diffusion, or electrical conductivity [6]?

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[PL-3]

Electrons in Polar Solvents: Birch Reduction, Blue Electrolytes, and Golden Metals

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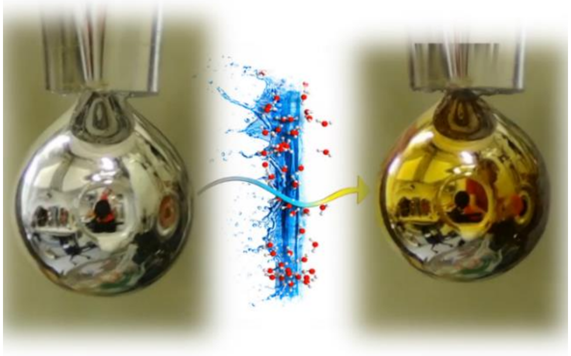
Liquid ammonia is well-known as a solvent that sustains long-lived solvated electrons formed by the dissolution of alkali metals. Solvated electrons act as powerful chemical reducing agents and, as such, find applications in numerous reduction processes both in organic chemistry and biochemistry. Probably the best-known example is the Birch reduction of benzene in the environment of liquid ammonia with the addition of an alkali metal (as a source of solvated electrons) an aliphatic alcohol. Here we discuss how we have characterized the electronic structure of alkali metal – liquid ammonia mixtures at concentrations spanning from blue electrolytes to bronze colored metallic solutions by means of photoelectron spectroscopy in liquid microjets aided by ab initio molecular dynamics simulations and quantum chemical calculations.

The above alkali metal solutions of liquid ammonia with electrolyte or metallic properties have been known for centuries now. But how about water as a solvent? It it is a textbook knowledge that dissolution of alkali metals in water leads to an explosive chemical reaction, thus only low (sub-metallic) electron concentrations have been prepared so far. Here we show that we have now found a way around the explosive chemistry by adsorbing water vapor at a pressure of about 10-4 mbar onto a train of liquid sodium-potassium alloy drops ejected from a nozzle into a vacuum chamber. This leads to a formation of a transient gold-colored layer of water doped with ~5×1021 electrons/cm3, the metallic character of which is demonstrated by a combination of optical reflection and synchrotron x-ray photoelectron spectroscopies. [2]



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[PL-4]

Properties of Ionic Liquid–Molecular Liquid Binary Mixtures as Reaction Solvents

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Room-temperature ionic liquids attract much attention due to their unique properties, such as negligible volatility, non-flammability, and high polarity, as novel solvents for various applications. However, there have been less reports on the fundamental properties of ionic liquids as reaction solvents than the use of them in reaction media for applicational research.

We have investigated physicochemical properties of imidazolium-based ionic liquids and their mixtures with molecular liquids, such as water, methanol, ethanol, acetonitrile, and dimethyl sulfoxide (DMSO) on the microscopic and mesoscopic scales [1-3]. The interactions among chemical species in ionic liquid–molecular liquid binary solutions govern their mixing states. For example, the hydrogen bonding of the imidazolium-ring H atoms with molecular liquids depending on the electron donicity of molecular liquids induces the disruption of ion pair on the microscopic scale. Self-hydrogen bonds among molecular liquids may result in inhomogeneous mixing between ionic liquid and molecular liquid, that is, molecular liquid clusters and ionic liquid clusters coexist in their mixtures on the mesoscopic scale. In ionic liquid–molecular liquid binary solvents, the interactions among cation, anion, and molecular liquid should influence chemical reactions. Nevertheless, the relations between the interactions among the chemical species and chemical reactions have not well clarified on the molecular level.

In this presentation, I would first talk about the interactions of aromatically ringed-cation with several molecular liquids investigated by IR and NMR spectroscopic techniques in 1-alkyl-3-metylimidazolium-based and 1-alkylpyridinium-based ionic liquids, whose anion is bis(trifluoromethylsulfonyl)amide ($TFSA^-$), (C_nmImTFSA and C_nPyTFSA, n gives the alkyl chain length) (Figure 1). Then, in the ionic liquid–molecular liquid binary solvents, complex formation equilibria of Ni^{2+} with molecular liquid, which were observed by UV-visible spectroscopy and titration calorimetry, will be explained [4,5]. The mechanism of the complex formation will be discussed in terms of the microscopic interactions clarified using the spectroscopies and the molecular liquid aggregation evaluated by small-angle neutron scattering (SANS).

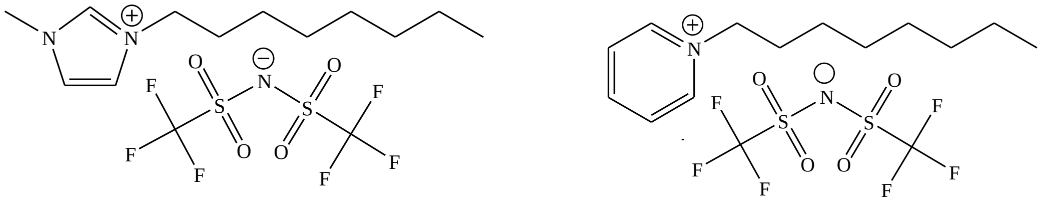

Figure 1: *Structures of ionic liquids, C_nmImTFSA (left) and C_nPyTFSA (right) with n = 8.*

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Abstracts of Invited Lectures: [IL-1] → [IL-7]

[IL-1]
Multiscale molecular simulations for the solvation of lignin in ionic liquids

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Lignin, the second most abundant biopolymer found in nature, has emerged as a potential source of sustainable fuels, chemicals, and materials. Finding suitable solvents, as well as technologies for efficient and affordable lignin dissolution and depolymerization, are major obstacles in the conversion of lignin to value-added products. Certain ionic liquids (ILs) are capable of dissolving and depolymerizing lignin but designing and developing an effective IL for lignin dissolution remains quite challenging. To address this issue, the COnductor-like Screening MOdel for Real Solvents (COSMO-RS) model was used to screen 5670 ILs by computing logarithmic activity coefficients (*ln*(*γ*)) and excess enthalpies (*HE*) of lignin, respectively. Based on the COSMO-RS computed thermodynamic properties (*ln*(*γ*) and *HE*) of lignin, anions such as acetate, methyl carbonate, octanoate, glycinate, alaninate, and lysinate in combination with cations like tetraalkylammonium, tetraalkylphosphonium, and pyridinium are predicted to be suitable solvents for lignin dissolution. The dissolution properties such as interaction energy between anion and cation, viscosity, Hansen solubility parameters, dissociation constants, and Kamlet–Taft parameters of selected ILs were evaluated to assess their propensity for lignin dissolution. Furthermore, molecular dynamics (MD) simulations were performed to understand the structural and dynamic properties of tetrabutylammonium [TBA]+-based ILs and lignin mixtures and to shed light on the mechanisms involved in lignin dissolution. MD simulation results suggested [TBA]+-based ILs have the potential to dissolve lignin because of their higher contact probability and interaction energies with lignin when compared to cholinium lysinate.1

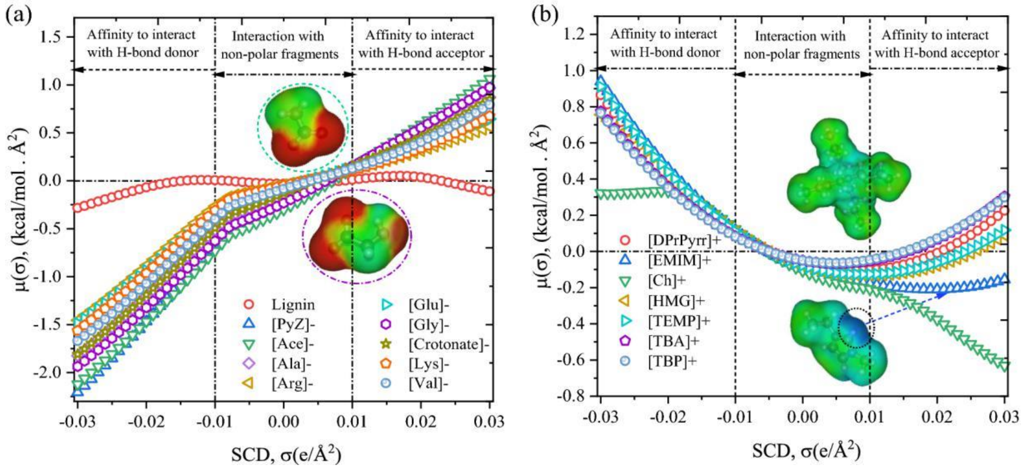

Figure 1: *COSMO-RS predicted sigma potential of lignin and IL (a) anions, and (b) cations at 363.15 K. COSMOTherm version 19.0.1 was used to calculate the sigma potentials*

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[IL-2]
Revealing the impact of fine-tuning force fields on microheterogeneity in Choline Chloride-Based Deep Eutectic Solvents

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Choline-chloride lactic acid (ChCl:LA) Deep Eutectic Solvent (DES) is an environmentally friendly and biodegradable solvent that exhibits exceptional properties for processing lignocellulosic biomass, which is crucial for the establishment of economically sustainable biorefineries. Research indicates that the material's ability for biomass processing and lignin extraction efficiency depends on the ChCl:LA ratio and water content.

It is known that DESs have a complex structure due to the H-bond network formed between its constituent molecules, which is sensitive to the HBA:HBD ratio and water content. In this study we investigated the structure of ChCl:LA for ratios of 1:1, 1:2, 1:5 and 1:10 using molecular dynamics simulations.

Although the CL&POL force field developed by Goloviznina et al [1], which is polarizable and transferable, has led to a significant improvement in the accuracy of molecular dynamics simulations of these liquids, two key modifications have been suggested for chloride containing systems [2]. First, to adjust specific Lennard-Jones parameters to accurately represent the Cl^{-}-OH^{-} interactions, and second, to incorporate Tang-Toennis damping functions to reduce the overpolarization of the chloride anion.

In this work we evaluate the performance of the original and corrected force fields as compared to DFT-based molecular dynamics for the ChCl:LA 1:1 system. Our results show that while correcting both issues improve the corresponding RDFs, only the correction of Cl^{-}-OH^{-} interactions results in an improvement of the overall performance of the force field in terms of neighborhood probabilities. These adjustments result in a moderate improvement of the local interactions within the 1:1 system, and give rise to significant differences as the model is extended to larger systems, particularly in terms of the microheterogeneity of the system. These disparities become more pronounced as the LA content increases.

These findings have enormous implications for understanding the chemical behaviour of ChCl:LA as its composition changes, and highlight the need for a careful assessment of the theoretical methods to capture their fundamental physicochemical properties.

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[IL-3]

How NaCl addition destabilizes ionic liquid micellar suspension until phase separation

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Understanding the fundamental mechanisms of self-organization and phase separation in molecular solutions is of utmost importance from the extraction perspective. Aqueous biphasic systems have recently attracted a lot of attention because of their lowest toxicity (i.e. large water cotent) with respect to classical solvents. The ionic liquid tributyltetradecylphosphonium chloride ($P_{4,4,4,14}Cl$), mixed in a salt or acid aqueous solution, is a biphasic system. In pure water, it forms micelles with a very low CMC, below 1 wt% [1]. However, even large amounts of $P_{4,4,4,14}Cl$ in water do not induce phase separation while the ternary system $P_{4,4,4,14}Cl/NaCl/H_2O$ is a biphasic system. It moreover displays a LCST (Lower Critical Separation Temperature) behavior, being monophasic at low T and experiencing phase separation when T is increased [2]. This phenomenon has been ascribed to the T-increased adsorption onto the micellar surface of these additional chloride ions, thus lowering repulsive interactions between micelles, finally allowing coalescence and thus phase separation [3].

In this work, we disentangle the effect of charge and temperature on the phase separation, similarly induced by both parameters. We explore the impact of NaCl addition onto the phase separation, at fixed T, in order to address the origin of the phase separation by the increase of charged species in the solution. Specific chloride electrode allows the determination of chloride counterion adsorption for different samples in the phase diagram, all of them being single-phase. The comparison with a regulation charge theory shows how specific chloride adsorption controls the stability of the micellar solution.

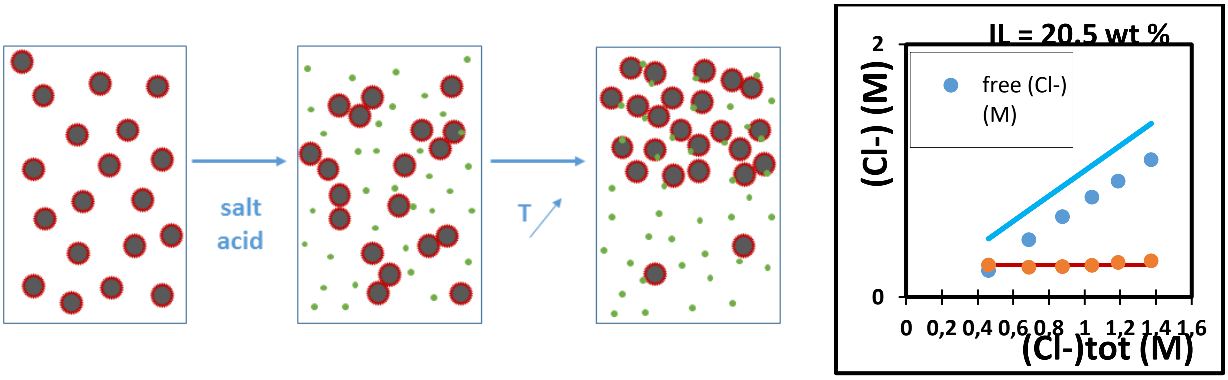

Figure 1*: Left: schematic drawing of the of structural organization induced by salt and temperature.Right: Free and adsorbed Cl^- as a function of total chloride concentration.*

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[IL-4]

Structure, Dynamics and Solvatochromism of a D205 Dye at the Interface with TiO_2 in Ionic Liquids and Acetonitrile

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In this work, first we studied the effect of the electrolyte environments by using 1-butyl-3-methylimidazolium-based ILs with hexafluorophosphate ($BmimPF_6$) and trifluoromethanesulfonate (BmimTFO) anions, and ACN, on the microscopic structure and dynamics of the D205 dye, bonded covalently to the TiO_2-anatase surface (fig. 1) by using classical molecular dynamics (MD) simulations [1].

Moreover, a combined MD simulation and density functional theory (DFT) calculations were used to investigate the effect of the acetonitrile (ACN) solution on the absorption, the electronic injection and the charge transfer in a D205 indoline dye at the interface of a TiO_2 nanoparticle. For this purpose, DFT calculations were carried out to estimate the equilibrium geometry of a small $Ti_{30}O_{62}H_4$-anatase nanoparticle and to derive interaction parameters for bidentate binding of a D205 dye to the nanoparticle surface. Various configurations of the D205 dye anchored to $Ti_{30}O_{62}H_4$ were generated from the MD simulations and were used as input for the time-dependent DFT (TD-DFT) calculations [2].

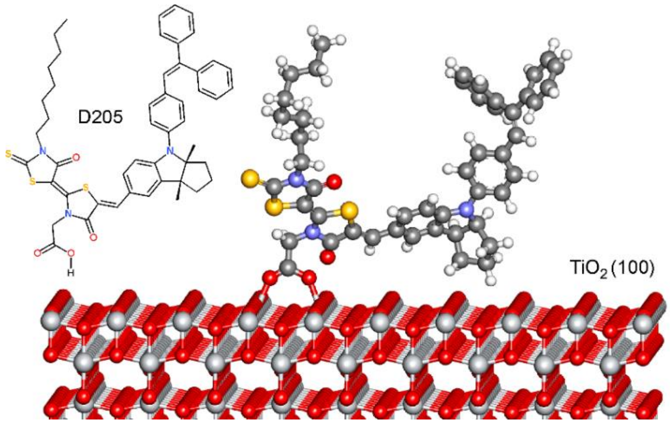

Figure 1: Chemical structure of a free D205 dye and the illustration of the D205 dye, anchored covalently to TiO_2 (100) slab by the carboxylic group, as shown with *ball-and-stick* representation.

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[IL-5]

Short- and Long-Time Dynamics of Hydrogen Bonds in Hydroxyl-Functionalized Ionic Liquids

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Hydroxyl-functionalised ionic liquids (ILs) represent a new interesting class of ILs where hydrogen bonds (HBs) play an important role: here ``typical'' HBs between cations and anions (ca) are competing with ``atypical'' HBs connecting pairs of cations (cc). We study the equilibrium and kinetics of (cc) and (ca) HBs in those ILs by means of molecular dynamics (MD) simulations. Mostly (cc) HBs are found to be stronger than their (ca) counterparts, depending on the alkyl chain length. HB lifetimes and kinetics are analysed by means of HB population and reactive flux correlation functions. Essentially *four* different HB lifetimes have to be considered, spanning about three orders of magnitude, each valid in its own right, and each associated with different aspects of HB breaking and HB re-formation. The long-time limiting behaviour of the HB population correlation function is controlled by diffusion of the ions and can be well described by analytical expressions. The short-time HB behaviour is tied to the localised dynamics of the hydroxyl group exploring its local solvation environment. A minimalist kinetic two-domain model is introduced, which is able to describe realistically the time evolution of the HB population correlation function for both, (ca) and (cc) HBs over 5 orders of magnitude. By employing the reactive flux method, we also determine the kinetics of HB breaking, unaffected by diffusion processes. We determine both, the ultra-fast upper boundary, as well as the average rate of HB breaking, allowing recrossing-events during the transient relaxation time period. For sufficiently long alkyl chains, all those computed HB lifetimes indicate a higher kinetic stability of (cc) HBs over (ca) HBs, for short chains it's vice-versa.

[IL-6]

Transport of water in clays: what can we learn from molecular dynamics?

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Fluid transport in clays plays a role in many environmental and energy-related processes, from oil and gas recovery to carbon sequestration and geological storage of radioactive waste. One of the difficulties in understanding and predicting transport properties is linked to the multiporous nature of these materials. At the pore scale, molecular simulations enable us to describe the behavior of mobile species at the interface as a function of their type and charge, as well as the structural characteristics of the clay sheets. The force fields used to calculate interactions can be tested/validated in the light of experiments that can be used at these scales, like QENS experiments. Then, molecular dynamics can be used to test de validity or calibrate analytical theories used to model the transport at higher scales.
I will show how the dialogue between simulations and experiments allows us to make progress in describing water transport in these materials, and how properties obtained at the molecular scale can then be used to model transport at the sample scale.

[IL-7]

Hydration properties of sugars revisited

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Hydration properties of sugars have been subjected to a huge number of investigations due to the relevance of this class of compounds in many fields including, life and medical sciences, biology, pharmaceutics, and food technology. Despite being a classical topic in solvation science, understanding how and to what extent sugars affect the hydrogen bonding network of water remains rather elusive, as testified by the fact that very contradictory pictures can be found in the recent literature. Often different spectroscopic approaches led to different views concerning both H-bonding structure and dynamics of water, such that a molecular-level understanding of the sugars' hydration features is still incomplete.

In the last decade, in Perugia, the Extended frequency range Depolarized Light Scattering (EDLS) techniques has been developed to gain insights on the fast dynamics of water in aqueous solutions of different systems, including peptides, proteins and sugars [1-3]. EDLS has proven suitable to disentangle solute from solvent dynamics and, within the latter, hydration from bulk water contributions [1-3].

Here, novel information has been obtained concerning the hydrogen bonding structure of glucose and trehalose aqueous solutions, by using different vibrational techniques such as Raman, Mid-IR and Near-IR spectroscopies. Other than being classical hydrophilic model systems, glucose and trehalose are also relevant in the context of biopreservation, often connected to water-mediated effects [4,5]. Solute-correlated (SC) spectra have been determined [6], to evidence the contribution of hydration water to the spectral profiles, demonstrating that the employ of complementary approaches is mandatory to clarify some of the inconsistencies present in literature.

The results of this comparative analysis will be discussed, and a coherent view will be proposed on the effect of glucose and trehalose on both hydrogen bonding structure and dynamics of water.

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Abstracts of Oral Contributions: [OC-01] → [OC-49]

[OC-01]
ULTRAFAST CALCULATION OF SOLVATION IN SUPERCRITICAL FLUIDS

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Increasing concerns for the environmental impact of industrial activities pushes the chemists to devise more ecological processes. One major goal is the development of a new range of solvents, “greener” but as efficient as the widely used organic solvents. Supercritical fluids (e.g., water, CO2, and their mixtures) represent an interesting alternative.[1] They have no toxicity for humans and environment, are not flammable and can be easily fine-tuned to precisely control their solvation power. They are already used in various industrial processes: extraction of natural product, impregnation of polymer matrices, water depollution or nanoparticle synthesis.[2] A larger deployment of such ecological solvents would however need an accurate prediction tool of the solvation properties.

Different approaches exist to estimate the solvation properties in supercritical fluids. Industrial chemists rely on parametric models, where the solubility is given with a good accuracy in function or pressure, temperature, solvent density. But many parameters must be fitted for each solute and each new solvent (e.g., each concentration of the mixture).[3] The molecular simulations (MD or DFT) are more flexible than the parametric models. They permit to calculate accurately the solvation free energy and the others solvation properties: structure, enthalpy, molar volume. But despite huge progresses, MDs remain too costly to envision it as a prediction tool for large scale investigations (many solutes, different solvents and solvent mixtures and various thermodynamical conditions). [4]

We will present a powerful alternative strategy based on integral equations and classical density functional theory. Such approaches provide the same solvation properties as MDs, but for a cost 1000 cheaper from a computational point of view.[5] Their accuracy depends on the level of approximation of the excess free energy (classical) functional. In this work, we determine the excess free energy for supercritical CO2, both at the simplest (quadratic) to the exact level. We will discuss the accuracy and the efficiency of our approach in determining structural and thermodynamics properties. We will underline how such strategy can lead to an accurate, flexible, and ultrafast prediction tool for solvation properties in supercritical fluids.

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[OC-02]

Local structure and dynamics of the Curcumin-vacuum and Curcumin-scCO$_2$ interfaces using molecular dynamics

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There is a growing amount of literature evidence [1] that suggest that, during a melt-recrystallization process, the changes in the conformation of pharmaceutical ingredients (PI) at the interface of the supercritical solvents (scCO2 in particular) determine to a large extent the transformation between their corresponding polymorphic forms. However, how the thermodynamic conditions can affect the distribution of the PI conformation that promote a specific polymorphic form are not yet understood.

The present study focuses on providing a theoretical explanation (using molecular dynamics) of the effects of the melt-vacuum and melt-scCO2 on the drug-like compounds. As such, curcumin has been chosen as the object of the study. Curcumin, derived from Curcuma longa L. (turmeric), has recently garnered a lot of attention [2] for its potential anti-oxidant, anti-inflammatory and anti-carcinogenic properties. One of the main disadvantages of curcumin is its low solubility in water. However, alternative polymorphic forms of curcumin have been shown to possess much higher solubility in polar media. As such, under the right conditions, scCO2 may be used to selectively obtain those alternative polymorphs.

In this work, molecular dynamics simulations of melting and recrystallization of crystals of three polymorphic forms of curcumin have been performed using a selection of common transferable force fields (CGenFF, GAFF, OPLS, GROMOS). We discuss the differences between proposed models, as well as the influence of the interfaces (vacuum and scCO2) on the interfacial curcumin molecules (see Figure 1). Distribution of possible curcumin conformations, as well as nearest-neighbour distributions, DBSCAN cluster sizes and compositions and Voronoi volumes have been analysed.

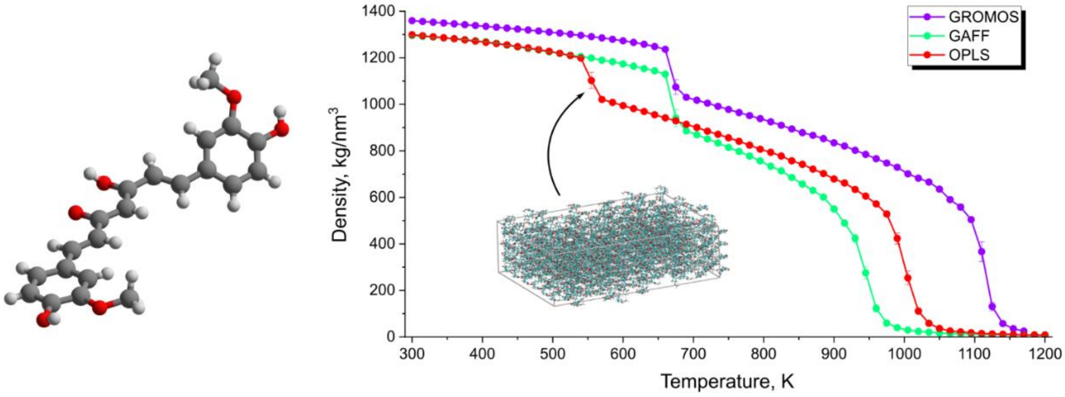

Figure 1. Curcumin (left) and the dependence of the density of curcumin on temperature (right).

Acknowledgements: The authors would like to thank the Mésocentre de Lille (University of Lille HPC) and ISC RAS for providing computational resources needed to perform molecular dynamical simulations.

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[OC-03]

Supercritical fluids: from clustering effect in mixtures to gas-like and liquid like demarcation lines

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Some processes related to energy and environmental topics involve asymmetric supercritical fluid systems. These systems are formed by the addition of light elements which are typically in a gaseous state at standard conditions and heavy components in small amounts. The resulting mixture is brought to a monophasic state above the critical point of the light element, which is considered as the solvent. In such supercritical conditions, the solute can be extremely well solvated, resulting in a clustering effect. This is the case when a gas, such as CO_2, is injected to improve oil production of or to store the injected gas in situ [1], during the hydro-conversion of vegetable oils for biofuel production [2] or when using supercritical fluids to extract specific components from a solid or a liquid carrier [3]. Designing such processes requires the consideration of thermophysical properties (phase equilibria, PVT properties, viscosity, etc.). However, few measurements of such properties have been conducted on these systems. Furthermore, modeling these systems remains problematic due to the asymmetry between the species of interest and the thermodynamic conditions that are close to the critical point. This can lead to strong non-ideal effects, particularly at infinite dilution, as shown in Figure 1.

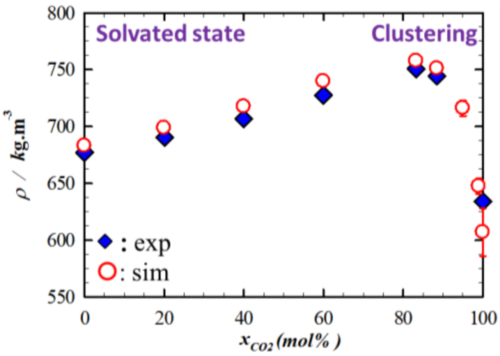

Figure 1: *Density and clustering behaviour as a function of* x_{CO2} *at 313.15 K and 10.1 MPa in a CO2-nC7 mixture [4].*

The aim of the present work is to combine experiments, equation of states, and molecular simulations to characterize asymmetric supercritical mixtures and ultimately improve the modeling of these complex systems. There is a particular emphasis on exploring the possible link between lines demarcating gas-like and liquid-like behaviors (such as Widom, Frenkel, and entropy) in pure supercritical fluids [5, 6] and the clustering effect that occurs in a supercritical solvent when a small amount of solute is added (at infinite dilution) [4].

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[OC-04]

Solvation structure and dynamics of pharmaceutical compounds in liquid and supercritical solvents: The cases of caffeine and favipiravir

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The solvation structure and dynamics of caffeine and favipiravir in liquid and supercritical solvents have been extensively studied by employing a systematic molecular modelling approach. Effective interaction potential models have been employed for favipiravir and caffeine, using the intramolecular geometry and charge distribution from quantum chemical calculations and adopting well-established Lennard-Jones parameters. The solvation structure and related dynamics were further investigated by means of classical molecular dynamics simulations. Particular emphasis has been given to the effect of solute-solvent hydrogen bonding interactions on the local structure and dynamics, especially in the cases of liquid aqueous solutions [1] and supercritical CO_2-alcohol mixed solvents [2]. In the latter case, the role of the addition of the alcohol cosolvent in increasing the relatively low solubility of polar compounds in pure supercritical CO_2 has been particularly demonstrated.

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[OC-05]
Detailed insights into the dynamics of a phosphonium-based ionic liquid – A combined experimental and molecular dynamics simulation study

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Ionic liquids based on ammonium or phosphonium cations are widely used in basic science and application-oriented research. [1] While the dynamics of ammonium-based ionic liquids is well investigated in literature, a detailed description of phosphonium-based ionic liquids is lacking, especially in terms of monoprotic representatives. In this work, we focus on a detailed description of triethylphosphonium bis(trifluoromethylsulfonyl)imide $[P_{222H}][NTf_2]$, that is characterized by one single weak hydrogen bond between cation and anion. Therefore, we use a powerful combination of experimental methods like fast field cycling (FFC) NMR relaxometry and PFG NMR together with molecular dynamics (MD) simulation in order to gain dynamical insights on a molecular level.

Firstly, spin-lattice relaxation rates R_1 for ^1H and ^{19}F have been recorded for different temperatures. In contrast to conventional NMR techniques the spectrometer frequency in FFC NMR relaxometry can be swept between 10 kHz and 40 MHz, yielding NMR dispersion profiles which allow for the simultaneous observation of several molecular processes at different timescales in one single experiment. In order to dissect the spin lattice relaxation rates into their intra- and intermolecular contributions, relaxation models are required. While translational diffusion coefficients D_{trans} can be extracted using the force free hard sphere model, the determination of rotational correlation times τ_{rot} strongly depends on the molecular structure of the ions. The rotational dynamics of the $[P_{222H}]^+$ cation can be described using the well-known BLOEMBURGEN-PURCELL-POUND approach. In contrast to that, we could show that the relaxation model for the $[NTf_2]^-$ anion has to be more complex including additional internal rotation of the CF_3 groups. [2]

Secondly, MD simulations based on a polarizable forcefield are used to complement our FFC NMR experiments: We compute both, the intra- and intermolecular frequency-dependent contributions to the dipolar NMR relaxation rates for the ^1H and ^{19}F nuclei directly from MD-data. We find them in good agreement with our FFC-NMR experimental data. The same is true for the measured and computed rotational correlation times and self-diffusion coefficients. Moreover, our MD simulations not only provide detailed insight into the dynamical processes, but also can mechanistically verify the applied relaxation models as well as emphasize the importance of e.g. considering internal rotations.

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[OC-06]

Recovery of metals with ionic liquids: a Eni Slurry Technology product as a case study

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Some low value hydrocarbon stream from refinery processes are reservoirs of precious metals, which have been almost overlooked up to date. For instance, it has been shown that Molybdenum and Vanadium are present in relevant quantities (~10.000 ppm) in a carbonaceous heavy and danse product obtained from the purge stream of the proprietary EST (Eni Slurry Technology) plant, an hydroconversion process whose catalyst is constituted mainly of MoS_2. The present study aims at exploring the capability of a panel of ionic liquids in extracting these metals, in conjunction with non-ionic additives, from such complex matrix.

A set of selected ILs characterized by a fixed cation (1-butyl-3-methylimidazolium) and a variety of anions (acetate, dicyanamide, salicylate and thiosalicylate) was tested.

The experimental results show that the acetate IL is highly selective for the extraction of Vanadium, while non-ionic additives do not significantly alter the extraction outcome.

To rationalize these results, a computational study of the stability of anion-metal complexes was performed. The intrinsic complexity of the matrix does not allow to infer the metal speciation. Therefore, a complete screening of the possible complexes, compatible with the chemistry of Vanadium and Molybdenum, with different oxidation and spin states needed to be performed.

The stability of complexes with different structures and charges by Vanadium and Molybdenum with different anions and their interaction with the solvent can justify, at a qualitative level, the experimental selectivity data.

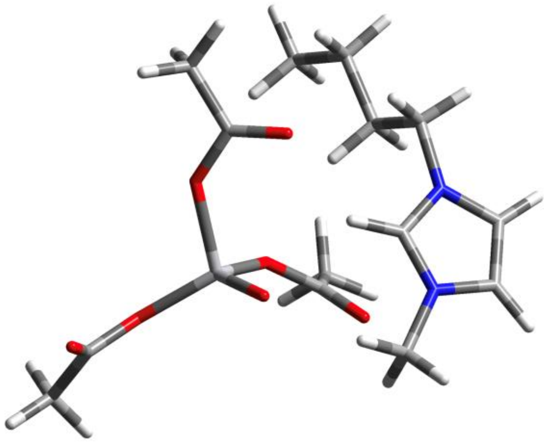

***Figure 1:** Structure of the ionic pair of the [$VOAc_3$]$^-$ complex with 1-Butyl-3-methylimidazolium.*

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[OC-07]

Understanding Reaction Outcomes in Mixtures Containing Ionic Liquids. Evaluating the contribution of solvent dynamics and organisation

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While ionic liquids have been suggested as replacements for organic solvents in preparative chemistry,[1] their application has been limited by the fact that reaction outcomes (such as reaction rate and product selectivity) are frequently different in ionic liquids compared to traditional molecular solvents.[2] Importantly, these solvent effects varied with the nature of the ionic liquid and the amount of ionic liquid in the reaction mixture, and were generally not well-understood, let alone predictable.

A significant amount of work has now been carried out to try to understand these solvent effects, with microscopic interactions in solution being able to explain the manner in which solvent effects vary with amount and nature of the ionic liquid.[3] Such understanding has allowed solvent design to control reaction outcomes,[4] machine learning approaches to solvent choice[5] and quantification of reactivity parameters in these mixtures.[6]. In all cases, the argument relies on understanding solute-solvent interactions.

We have now[7] shown that, in addition solute-solvent effects, the effects of organisation of the components of ionic liquids in solution need to be taken into account; this is demonstrated by examining the well-studied reaction between pyridine **1** and benzyl bromide **2** (Figure 1(a)). Through considering the solvent effects of mixtures containing either one of the homologous series **3** or one of biscationic series **4** (Figure 1(b)), it was clear the rate constants for the reaction were affected by structuring in solution. We have subsequently investigated the diffusion of components in these reactions,[8] which highlighted the structural changes that occur in the monocationic homologues **1** *cf*. those in the biscationic analogues **2** (Figure 1(c)).

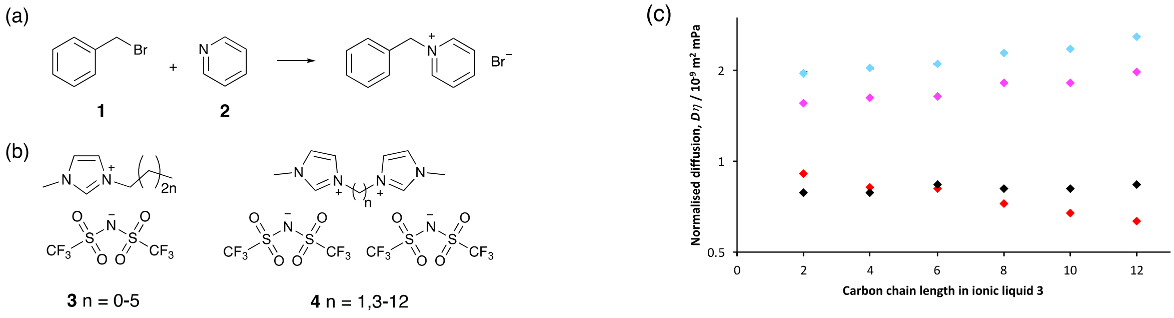

*Figure 1: (a) “The reaction between pyridine **1** and benzyl bromide **2**. (b) The homologous series of ionic liquids **3** and **4** considered here. (c) A plot of the normalised diffusion (Dη) for acetonitrile (cyan), pyridine **1** (pink), the cation of the ionic liquid (red) and the anion of the ionic liquid (black) with changing alkyl cation in the ionic liquid (χ_3=0.1) at 25 °C.*

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[OC-08]

Chain length dependence of the hydrogen-bond strength in carboxyl-functionalized ionic liquids

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We report the formation of hydrogen-bonded structural motifs in the carboxyl-functionalized ionic liquid (IL) 1-(carboxymethyl)pyridinium bis(trifluoromethylsulfonyl)imide [HOOC-CH$_2$-Py][NTf$_2$] by means of temperature-dependent infrared spectroscopy. The analysis of the CO and OH stretching bands reveals the formation of the anticipated singly hydrogen bonded (H-bonded) cation-anion-dimers and surprisingly even doubly hydrogen bonded cationic dimers. The latter dimers resemble the archetypical H-bond motifs known for formic acid in the gas phase. [1]

The X-ray structure shows solely the formation of the characteristic doubly hydrogen bonded cationic dimers (c=c). Increasing temperature breaks at least one H-bond in this (c=c) binding motif, which gradually opens and is replaced by a linear species (c-c-a) (Fig. 1). Here, additionally to one remaining single cationic hydrogen bond an extra H-bond between cation and anion is formed. [2] By deconvoluting the IR spectra simultaneously with temperature we derived the transitional enthalpy for the IL ($\Delta H° = -8.0$ kJ mol^{-1}) and phenylacetic acid ($\Delta H° = -17.4$ kJ mol^{-1}), the molecular mimic, respectively. Obviously, the repulsive COULOMB interaction between two like-charged ions weakens the strength of the H-bonds in comparison to the molecular species. [3]

We extended our investigations to a series of ILs [HOOC-(CH$_2$)$_n$-Py][NTf$_2$] ($1 \leq n \leq 9$) where the carboxyl group gradually distances from the cation. Up to an alkyl chain length of $n = 5$, the IR spectra clearly show, that the COULOMB repulsion due to increasing number of methylene group spacers decreases and the H-bond strength increases at the same time. The hydrogen bond strength remains stable for longer alkyl chains ($6 \leq n \leq 9$).

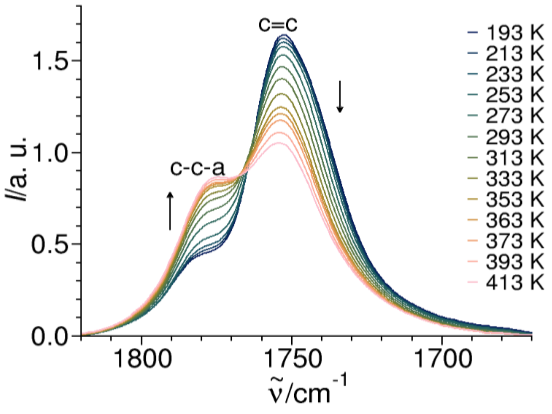

Figure 1: *Temperature-dependent IR spectra of the C=O stretching region for the IL [HOOC-CH$_2$-Py][NTf$_2$]. Contributions from the cyclic dimer (c=c) decrease and contributions from the linear dimer (c-c-a) increase with increasing temperature. The arrows indicate the changes in intensity with increasing temperature.*

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[OC-09]

Special Ionic Liquids as “Ideal” Salt Bridges for the Development of Unified Redox and pH Scales

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Gibbs transfer energies of single ions from one solvent S_1 to another S_2 are the key quantities to establish unifying pH and redox scales that allow the straightforward comparison of pH- and *E*-values over solvent boundaries, as is done by the $pH_{abs}^{H_2O}$ and the $E_{abs}^{H_2O}$ as well as their combination, the Protoelectric Potential Map PPM.[1] However, these are elusive quantities, obtained with assumptions not verifiable by thermodynamic means so far.[2] We outline a method based on basic potentiometric measurements of electrochemical cells such as cell I using a special ionic liquid salt-bridge (ILSB) to improve this situation.[3]

$$\mathrm{Ag}|\mathrm{Ag}^+\,(\mathrm{solv},\,S_2)\,\underset{Ej2}{|}\,\mathrm{ILSB}\,\underset{Ej1}{|}\,\mathrm{Ag}^+\,(\mathrm{solv},\,S_1)|\mathrm{Ag} \qquad \text{cell I}$$

The IL used is amyltriethylammonium bis(trifluoromethanesulfonyl)imide $[N_{2225}][NTf_2]$, with its cation and anion have the same diffusion coefficients in the neat IL and in very good approximation also in the solvents investigated. This characteristic is essential for the development of an ideal salt bridge preventing large parts of the emerging liquid junction potential (LJP) at both ends of the bridge. Further, we reasonably expect the remaining parts of the LJPs, caused by the Gibbs transfer energies of the IL-ions between the investigated solvents, are negligibly small.
We present experimental results for the Ag^+-[4] and Cl^--ions between the solvents water (H_2O), acetonitrile (AN), propylene carbonate (PC) dimethylformamide (DMF), ethanol (EtOH) and methanol (MeOH). By means of a statistical analysis of the measured data, we can state that the LJPs (*E*j1 and *E*j2) at the solvent S|IL-boundaries are ruled within 6 mV by the IL-constituing ions exclusively. This results in a consistent datat set that can be used to be connected to any redox system, thereby establishing the $E_{abs}^{H_2O}$ scale, which of entries can be compared directly and independendly of the solvent (see Figure 1).

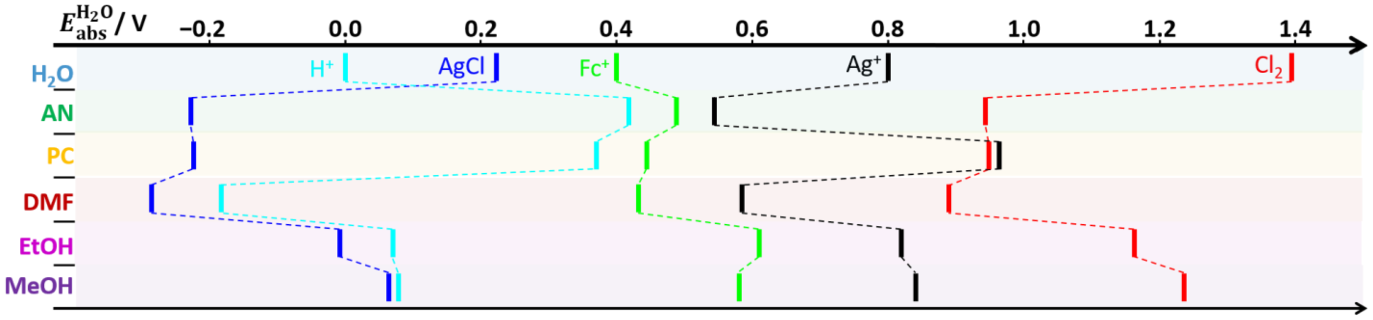

Figure 1: The $E_{abs}^{H_2O}$ values of the redox systems Ag^+/Ag, Fc^+/Fc (Fc = ferrocene), H^+/H_2, AgCl/Ag, Cl^- and Cl_2/Cl^- in the solvents indicated. All values can be compared to each other without any further processing.

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[OC-10]

Exploring the surface and bulk structure of ionic liquid mixtures

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Ionic liquids (ILs) are salts with low melting temperatures, often below room temperature. In recent years they have been shown to be useful in a range of applications, but their use as alternative solvents for synthesis and catalysis has been a key area of interest.[1] ILs have been shown to self-organise across a range of length scales in both the bulk liquid and at the gas-liquid interface.[2] The ability to understand and control this organisation will allow us to tune the solvent micro-environment around solutes, the mass transport of gasses into/out of the liquid and other properties that will enable ILs to achieve their potential as designer solvents.

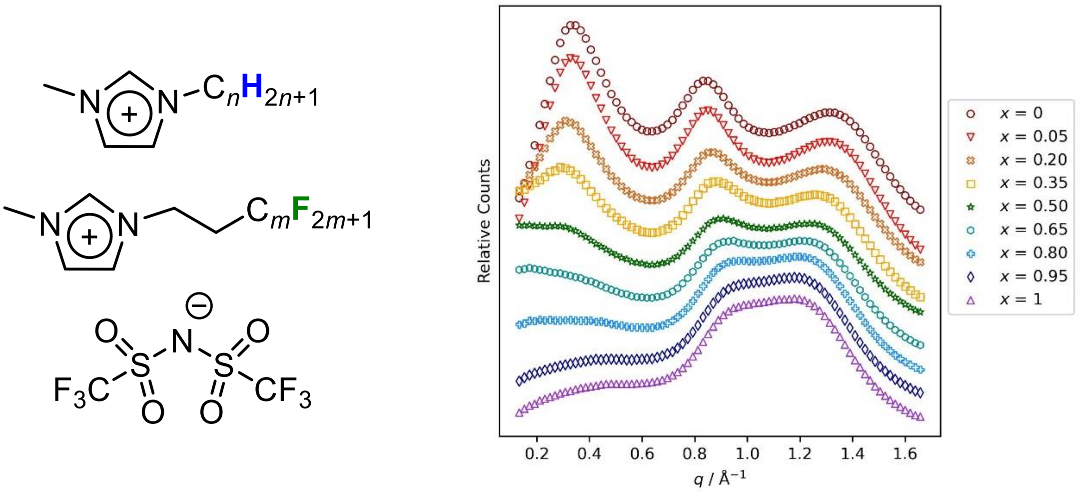

***Figure 1:** Some IL ions of interest (left) and an example of small-angle X-ray scattering from IL mixtures (right)*

IL mixtures are of particular interest, as they offer the potential to access a wide range of liquid structure and properties by mixing a small number of pure ILs. Thus, the synthetic effort required to prepare a range of materials with desired properties is reduced. This talk will give an overview of our contributions, as part of a wider collaborative network, to the synthesis, characterisation and understanding of self-organised ILs.[4] A particular focus will be on recent work on IL mixtures containing fluorinated and aliphatic components, which allow a great deal of flexibility over the structure and properties of the liquids.

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[OC-11]

How crucial is structure? Understanding the dynamics of ionic liquid solvent effects on an S_N2 process

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Ionic liquids have been investigated as potential replacements for molecular solvents due to their particular properties and customisability.[1] Despite their merits, common application of ionic liquids remains inaccessible due to their often-unpredictable effects on reaction outcome.[2] Recent work has investigated a simple bimolecular nucleophilic substitution (S_N2) process carried out in mixtures of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_{2n+2}C_1im][NTf_2]$, n = 0-5, Fig. 1a) and acetonitrile.[3] Bulk solution dynamics measured as the ^1H spin-spin relaxation time, T_2, may be correlated with the rate coefficient associated with this process, k_2. Both T_2 and k_2 are entropically influenced and show similar dependence on bulk dynamics of the solution.[3]

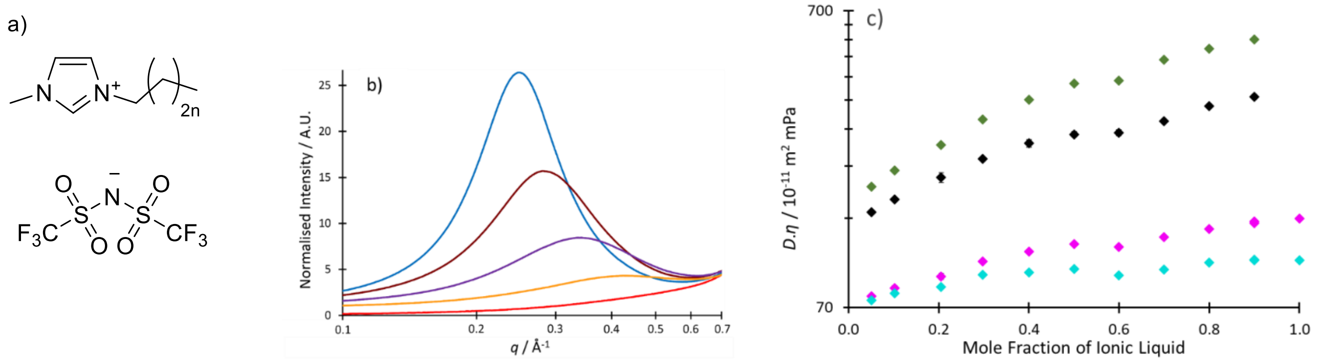

***Figure 1:** a) The $[C_{2n+2}C_1im][NTf_2]$ homologous series of ionic liquids. b) Small-Angle X-ray Scattering patterns of ionic liquids $[C_{2n+2}C_1im][NTf_2]$, n = 1(|), 2(|), 3(|), 4(|), 5(|). c) Viscosity normalised diffusion coefficients associated with the cation (◆), anion (◆), pyridine (◆) or acetonitrile (◆) as a function of mole fraction of $[C_4C_1im][NTf_2]$.*

Although this provides surface level insight into how ionic liquids affect this reaction type, quantitative measurement of nanoscale solvent-structuring[4] and diffusive behaviours[5] of individual chemical species (or distinct portions of a chemical species) in solution can provide a more in-depth look at the microscopic interactions occurring. By combining a suite of physical measurement techniques including Small-Angle X-ray Scattering (SAXS, Fig. 1b), Small-Angle Neutron Scattering (SANS), Pulsed-Field Gradient (PFG) diffusion Nuclear Magnetic Resonance (NMR) spectroscopy (Fig. 1c), ^1H NMR relaxometry and Quasi-Elastic Neutron Scattering (QENS), we can start to construct a more complete and detailed picture of the partial differences in solution interactions that arise specifically from varying the length of alkyl side-chain in this homologous series of ionic liquids.

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[OC-12]
Water-based natural deep eutectic solvents

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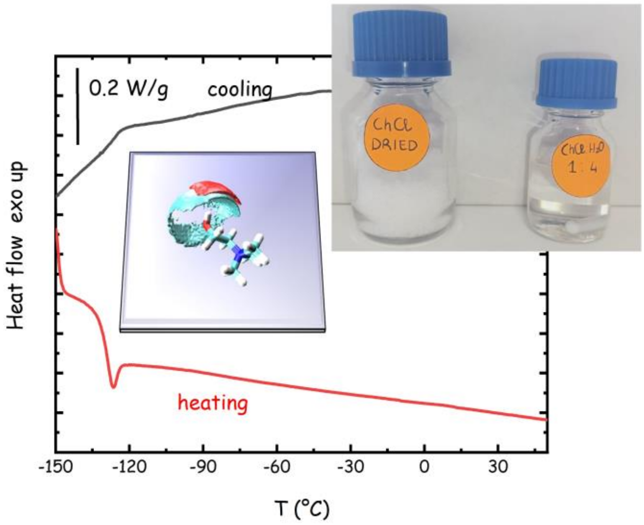
Deep eutectic solvents (DES) are an attracting class of compounds, composed of a mixture of hydrogen bonding (HB) donor and acceptor species that develop an extended HB network, which leads to a drop in the melting point of the resultant mixture with respect to its ideal behavior. While several different types of DES have been so far highlighted, including those of natural origin (hence the term NADES), in all these systems, water has always been considered either a noxious contaminant or a wished additive to an already existing DES (e.g. to drop its viscosity). Recently it emerged that the HB donor capability of water can lead to its use as a legitimate major component of new, water-based NADES. Such a finding paves the way to a new wave of green, sustainable and highly tunable class of solvent media, with so far unexplored properties.



In this scenario, we recently explored several features of different water based NADES and here we aim at presenting findings from such studies.[1], [2]

We will show that water based NADES can be both hydrophilic (that is reasonable)[1], but also hydrophobic[2]: in this case, further water addition would lead to phase separation.
Joint experimental (including X-ray scattering) and computational characterizations of different water-based NADES led to a deep knowledge of the behavior of such systems at atomistic level. Therein the role of HB as a major driving force for establishing the liquid state is established, but also dispersive interactions are found to be active and their role is assessed.
Moreover, we show a few examples of the peculiar solvation behavior of such media towards different compounds, such as hydrophilic polymers and amphiphilic molecules.

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[OC-13]

Investigating the interactions between choline iodide-based deep eutectic solvents and CO₂ using Density Functional Theory

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With the increasing interest in CO_2 utilization using deep eutectic solvents (DES),a systematic approach to identify molecular level interactions between CO_2 and DES is highly significant to understand the capacity of a DES for CO_2 capture[1]. This work focuses on the structural formation on choline iodide(CHI)-based DES and their interactions with CO_2.CHI is selected as hydrogen bond acceptors with urea(U),ethylene glycol(EG) and glycerol(G) as the hydrogen bond donors.The DES have been denoted as DES1, DES2 and DES3 respectively for molar ratios 1CHI:2U,1CHI:1EG and 1CHI:1G.The molecular interactions have been performed via density functional theory method using B3LYP/LanL2DZ basis set in Gaussian 6.0.16 version.Counterpoise correction method was employed to evaluate basis set superposition errors (BSSE) for pairwise interactions in DES formation as well as molecular interaction between DES and CO_2 at B3LYP-D3/LanL2MB level.The electrostatic potential (ESP) derived charges were calculated employing the CHELPG scheme.The type and intensity of interactions between DES and CO_2 molecules as well as to quantify short-range interactions, QTAIM theory and RDG analysis have been used.

The interaction energy of DES1, DES2 and DES3 were -27.45 and -18.72 and -31.99 kcal/mol respectively. The partial charges on the iodide atoms of DES1,DES2 and DES3 are -1.013,-1.012 and -0.979 respectively,indicating the strongest interaction between CHI and urea. Among the three DES, the interaction energy observed between DES3 and CO_2 was -26.69 kcal/mol,higher than DES1 and DES2(-1.97 kcal/mol and -0.95 kcal/mol respectively). The higher CHELPG at the -OH group indicates this as the possible CO_2-DES interaction site.These results are consistent with the QTAIM and RDG analysis. The nature of the molecular interactions have also been verified 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. The HOMO-LUMO orbitals of the optimized DES3 - CO_2 molecular system is shown in Fig. 1.

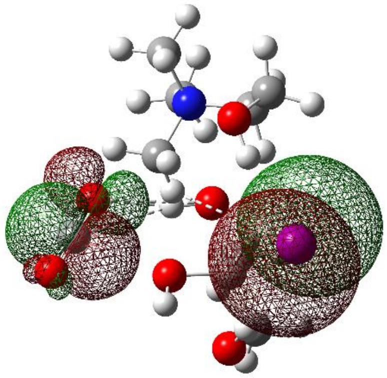

Figure 1: *HOMO-LUMO orbitals during interactions between DES3 & CO_2*

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[OC-14]

Thermal Stability of Ionic Liquids and Deep Eutectic Solvents

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Ionic liquids (ILs)1,2 and deep eutectic solvents (DESs)3 are two important types of green solvents. They have drawn numerous attentions for their unique properties. We have given systematic investigations of the design, properties, intermolecular interactions, and applications of ILs and DESs1-15.

Herein, I would like to introduce my work on applying thermal analysis techniques to investigate ILs and DESs. At first, the strategy to obtain evaporation enthalpy and decomposition activation energy of ILs and the decomposition and volatilization ratios at different temperatures of ILs was proposed.4 Then, the long-term stability of 66 representative ILs were investigated.2 After that, the investigation of the decomposition mechanism of ILs was carried out.6,7 Besides, the distillable ILs were formed and investigated.8 Moreover, the thermal decomposition of DESs9, the volatility of DESs10,11, and vapor pressure and the enthalpy of evaporation of DESs12 were investigated. Furthermore, the confinement thermodynamics of DESs13 and the formation enthalpy of DESs14 were studied. Recently, HR-TGA was proposed for investigation of thermal stability of DESs15.

I am also very welcome queries on our work and cooperation. Anyone interested in our work can look through my group website at http://chemgroups.ruc.edu.cn/mugroup/.

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[OC-15]

Sustainable solvents for efficient cyclodextrin solubilisation

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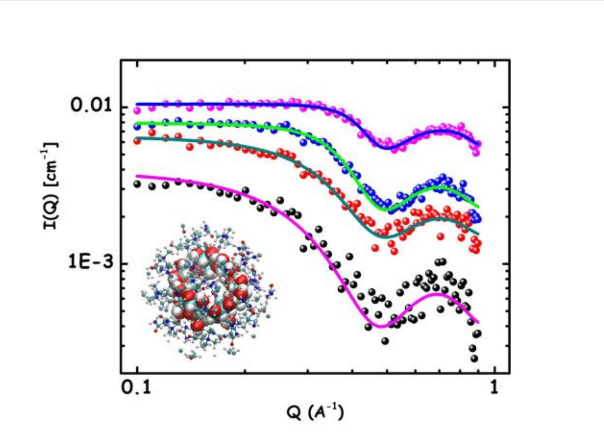
Supramolecular chemistry is a steadily growing research field, due to the smart opportunities that it opens in dealing with a variety of societal issues. Cyclodextrins are major actors in this respect and because of their geometry and chemical nature they act as ideal host species for inclusion complexes for food and aromas technology, synthesis, catalysis, etc. Very often, however, their range of applications is severely limited by the poor solubility in water. Accordingly the exploitation of green, or at least environmentally compatible, and sustainable solvent media that succeed in efficiently dissolving CDs could pave the way to a substantial change in paradigm for CD exploitation.

In this scenario the role played by neoteric, environmentally responsible media such as ionic liquids (ILs) and, more recently, Deep Eutectic Solvents (DES, mixtures of solid compounds that form liquids due to a large depression of the melting point) is very promising.



These media have low melting points (often much below room T) and are characterized by appealing features including negligible vapor pressure, high thermal stability and enhanced compatibility with a variety of different compounds. ILs and DES have been showed to behave as smart solvents for CDs, showing a large CD solubility in these media.[1], [2]

In this presentation, we will report on our recent exploration of microscopic organization of different CDs dissolved in ionic liquids (ILs) and deep eutectic solvents (DES) at ambient conditions, aiming at providing a detailed microscopic description of CD dissolution in these media, both in order to rationalize and potentially further extend CD solubility.

Experimentally X-ray Scattering techniques are ideal to probe the state of dissolved CDs. We explored several binary systems by SAXS aiming at understanding potential CDs aggregation that might limit performances and observed that in several cases CDs remain un-aggregated in these media even at high concentrations (e.g. as high as 150 mg/mL of βCD in Reline, a typical DES (for comparison, solubility of βCD in water is 18 mg/mL)).

Molecular Dynamics simulations were fundamental to access microscopic details on the solvation mechanism that different IL/DES moieties engage with CD's hydrophilic and hydrophobic portions.

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[OC-16]

Deep Eutectic Solvents on a Tightrope – The Balance Between Entropy and Enthalpy

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Solid components can be mixed to form liquid eutectic mixtures with strong melting point depressions—the so-called deep eutectic solvents (DESs). Through DES formation, solid compounds are unlocked in the search for new designable task-specific solvents. The stronger the melting point depression, the ampler the DES's liquid window, i.e. the temperatures and compositions at which a homogeneous liquid is formed. But why do some mixtures form deep eutectics and others not? And how can these melting point depressions be predicted and described thermodynamically? These fundamental questions are addressed in this work.

For choline chloride (ChCl) based DESs, the state-of-the-art molecular picture underpinning the large melting point depressions was referred to as an 'alphabet soup'.[1] This term signifies a wide variety of hydrogen bonds between the ions and molecular compounds that have a similar bonding energy, but have a different conformation. The resulting liquid is highly disordered and an entropic contribution to the thermodynamics of mixing has been hinted upon.[2] Here we present the first experimental quantification of this delicate balance between the partial molar enthalpy and entropy of mixing (Figure 1). We studied two ChCl-based eutectic mixtures: water + ChCl and ethylene glycol + ChCl. The macroscopic experimental results are complemented with an updated molecular picture and an energy decomposition over the whole composition range, obtained from advanced polarizable molecular dynamics simulations.

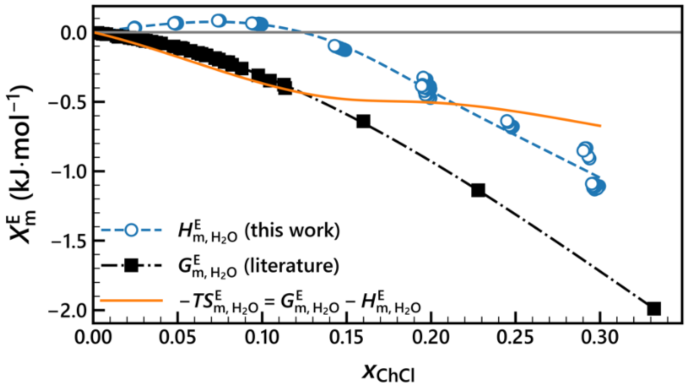

Figure 1: *Partial molar excess Gibbs energy (G^E_{m,H_2O}), enthalpy (H^E_{m,H_2O}), and entropy (S^E_{m,H_2O}) for H₂O in a H₂O + ChCl mixture as a function of the ChCl mole fraction (x_{ChCl}). H^E_{m,H_2O} was obtained with isothermal titration calorimetry.*

For water, we found that the partial molar excess entropy and enthalpy contribute to the melting point depression to the same extent (Figure 1). For ethylene glycol the unfavourable enthalpic contributions were overcome by significant excess entropy. The variety of intermolecular interactions is thus reflected in the excess entropy of mixing and it is a determining factor in DES formation. Current predictive thermodynamic models primarily account for the enthalpy of mixing. This oversimplication of the rich molecular environment DESs have to offer could lead to serious underpredictions of the liquid window for novel DESs.

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[OC-17]

Investigating the Solvation Properties of Menthol-Thymol Deep Eutectic Mixtures using Molecular Dynamics Simulations.

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Using classical molecular dynamics, we have investigated the solvation of benzene-1,2-diol (*catechol*), benzene-1,3-diol (*resorcinol*), benzene-1,4-diol (*hydroquinone*) as well as 1,4-benzoquinone, the doubly reduced form of hydroquinone, in a series of menthol - thymol mixtures in which the molar fraction of thymol (x_{THY}) has been varied from x_{THY} = 0, corresponding to pure menthol, to x_{THY} = 1, corresponding to pure thymol, by successive steps of Δx_{THY} of 0.1. Analysis of the solvation of the different solutes in these various mixtures reveals that when the x_{THY} in the mixture is increased the average number of H-*Bond* interactions between the solute and the solvent, in which the solvent acts as H-*Bond* donor (H-*B*d) and the solute as H-*Bond* acceptor (H-*B*a), increases on the one hand, while on the other hand, the average number of H-*Bond* interactions, in which the solute plays the role of H-*B*d and the solvent that of H-*B*a, decreases. This is consistent with the fact that thymol is a better H-*B*d but a worser H-*B*a than menthol due to the presence of resonance effects in the former. Furthermore, while the total average number of H-*Bonds* between the various benzenediols solutes and the solvent is found to decrease with an increase of x_{THY} in the mixture, in the case of 1,4-benzoquinone, which is only able to act as H-*Ba*, the total average number of H-*Bonds formed* is seen to increase. This points to the fact that "acidic" or H-*B*d molecules, such as the various benzenediols considered herein, are better solvated in mixtures with a high proportion of menthol, while "basic" or H-*B*a molecules, such as for example the 1,4-benzoquinone, are better solvated in thymol rich mixtures. This is further underlined by the evaluation of the variation of solvation energy as a function of increasing x_{THY} in the mixture, which is found to decrease for the various benzenediols but increase in the case of benzoquinone, again pointing to the fact that while the former are better solvated in a menthol enriched mixture, the latter is better solvated in a thymol enhanced solution. Hence the results reported herein present interesting insights on how the composition of these deep eutectic mixtures maybe tweaked in order to optimize their solvation properties for a specific solute.

[OC-18]

Pseudo-ionic Liquid and Water-in-salt Electrolyte: Structural Diversity in Mixtures of [Li][NTf$_2$], Triglyme and Water

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In the search for improved energy storage devices, lithium batteries still offer great opportunities due to their high energy density. However, many current electrolyte-systems often show undesirable properties like a high inflammability [1]. Therefore, possible alternatives to conventional electrolytes are searched for. Combinations of lithium salts and glymes, which are known to form so called pseudo-ionic liquids for certain mixing ratios [2], could be one possibility.

To investigate their structure and dynamics in detail, several mixtures of [Li][NTf$_2$] and triglyme (H-(CH$_2$-O-CH$_2$)$_4$-H) were analysed by means of molecular dynamics simulations at temperatures between 300 K and 480 K. To study the possibly beneficial effect of small amounts of water, MD simulations were also carried out for equimolar mixtures of the binary system with added water molecules.

We could show that the structural motifs in the lithium coordination sphere depend almost exclusively on the mixing ratio of triglyme and ion pairs (and water) but do not show a significant temperature dependency. By adding triglyme to [Li][NTf$_2$], the lithium salt changes from contact ion pairs to solvent-separated ion pairs. For an equimolar mixture, every cation is, on average, enclosed by one triglyme molecule, forming a complex with its four oxygen atoms. By this, the cations are spatially separated from their counterions and mixture acts as a pseudo-ionic liquid. If the ratio of triglyme is further increased, the one-fold triglyme-coordinated state of the cations changes to a two-fold coordination state where two triglyme molecules embrace the lithium ion, often in a double-helical-like manner.

If small amounts of water are added to the equimolar mixture of [Li][NTf$_2$] and triglyme, the water molecules tend to intercalate between the cation and one of the “outer”, less well bound oxygen atoms of the coordinating triglyme molecule. The water molecules typically form a coordinative bond with the cation as well as hydrogen bonds with the detached triglyme oxygen atom and an anion. Hence, the water molecules are mostly shielded from surrounding water and are prone to behave chemically different than water molecules in their bulk-phase. Here, a comparison can be made to so called water-in-salt electrolytes [3].

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[OC-19]

Multiscale simulation of ion transport by Poisson-Nernst-Planck, Monte Carlo, Brownian dynamics, and molecular dynamics

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We apply models of varying resolution to study ion transport in bulk electrolytes and through nanopores. In the classical treatment, the most detailed description is given by the atomic resolution naturally treated by the molecular dynamics (MD) simulation method. This resolution favors a detailed description of reality. If we are interested in the behavior of the system as a device, namely, the relationship between the controllable input and the measurable output properties of the system, a continuum method, such as the Poisson-Nernst-Planck (PNP) theory, may be sufficient. In this mean-field theory, the interaction of an ion with the rest of the system is based on an average response of the rest of the system. PNP includes treating the solvent as a dielectric background characterized by a dielectric constant.

While MD provides a lot of (maybe, too much) information about the system, PNP provides only a broad picture about the overall behavior while ignoring important molecular details. While MD is generally time consuming, PNP offers a fast solution (in seconds/minutes, Fig. 1) with the burden that important many-body correlations (e.g., finite size of ions) are neglected. It is hard to get rid of the feeling that the really useful models and methods are somewhere in between. In Brownian dynamics (BD) simulations, for example, the Langevin equation is solved for the particles with the solvent being implicit. While we simulate the movement of ions explicitly in BD, there is a hybrid solution, where we compute the transport of ions with the Nernst-Plank (NP) transport equation while applying the methodology of equilibrium statistical mechanics to non-equilibrium functions such as the non-constant chemical potential and concentration profiles. We can resolve the contradiction by dividing the system into small volume elements that are considered as open grand canonical ensembles in local equilibrium. The relationship between the chemical potential and concentration profiles can be determined with various methods, most importantly with the Local Equilibrium Monte Carlo (LEMC) method.

We survey all these methods and try to bring them to a common ground by linking them with the diffusion coefficient profile that may be either an input or an output property depending on the resolution of the model.

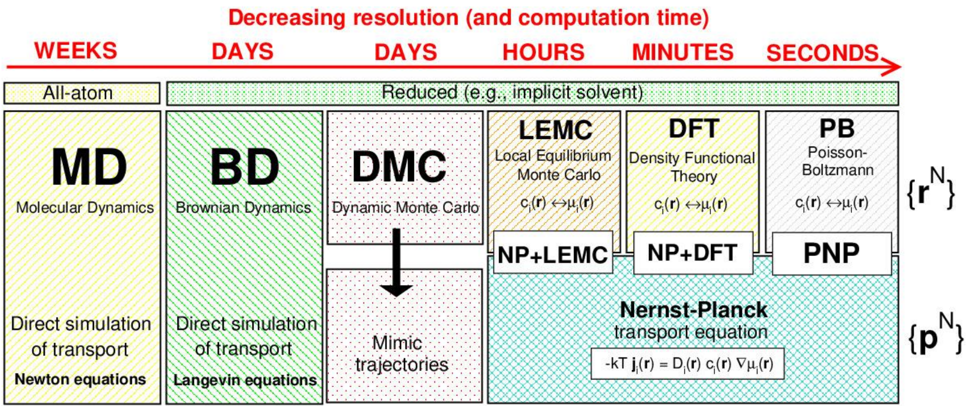

Figure 1: Different methods for models of different resolutions with different computation times [1].

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[OC-20]

Cation hydrolysis effects in aqueous electrolyte solution: A molecular dynamics study

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This contribution is devoted to memory of Karl Heinzinger. His group was probably the first to investigate influence of cation charge on the geometry of water molecules in hydration shell. Inspired by this research we also conducted a series of studies in the field of solvation and cation hydrolysis. In particular, we performed a molecular dynamics simulation of the influence of ion charge on hydrolated-hydrolyzed structure and dynamic properties of highly charged cations. In order to clarify this effect we introduced a simple model cation M^{Z+}, called primitive cation, in aqueous solution represented by a flexible nonconstrained model for water. In the case of monovalent cation M^+, the model reduces to an aqueous solution of Na^+ ion. Our simulations demonstrated the whole spectrum of hydrated-hydrolyzed forms of the primitive cation including aquo, hydroxo-aquo, hydroxo, oxo-hydroxo and oxo forms. A transition between these forms is governed by a value of cation charge Z. The model has been improved to account for the effects of charge redistribution between hydrolysis products, which essentially modified and stabilized the hydrated-hydrolyzed structure of the cation. Self-diffusion coefficients and spectral densities of hindered translation motions of primitive cation and oxygens of the first hydration shell demonstrate a strong correlation with the hydrated-hydrolyzed structure of cations. Along the modeling of primitive cation solution, we also simulated aqueous solutions of cations Al^{3+} and $(UO_2)^{2+}$. The aluminium ions demonstrate a strict octahedral arrangement of neighbors in the hydration shell with a tendency to hydrolysis, while for the case of uranyl solution a bipyramidal pentacoordinated arrangement of uranil ion found. Usually the process does not stop at the stage of emergence of hydrate-hydrolyzed cation structure and at the finite ionic concentrations polynuclear ions can appear as a result of condensation reaction. In order to understand the mechanism of polynuclear ion formation we studied uranyl aqueous solution at finite ionic concentration and at different pH levels by molecular dynamics simulations.

[OC-21]

A new dynamic Monte Carlo calculation with position-dependent diffusion coefficient and potential evaluated by all-atomistic molecular dynamics calculations and its application to the molecular transportation in the polymer electrolytes

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A set of new Monte Carlo (MC) transition probabilities was proposed that could produce molecular trajectories statistically satisfying the diffusion equation with a position-dependent diffusion coefficient and potential energy [1]. The calculated time evolution of the probability distribution and the mean first passage time from the MC trajectories were compared with the numerical solution of the diffusion equation. They showed excellent agreement with each other. The method can also be applied to many-particle systems where the diffusing particles interact with each other.

The method has been applied to the investigation of transportation of hydrogen molecules in the polymer electrolyte membranes in fuel cells [2]. The three-dimensional position-dependent free energies [3] and the diffusion coefficients [4] of the hydrogen molecules evaluated in advance by all-atomistic molecular dynamics calculations were used for the dynamic MC calculations. Milliseconds-long MC trajectories were available, giving the global diffusion coefficients over structural heterogeneities of the polymer electrolytes produced by the microscopic phase separation between water phases and polymer phases. Permeability coefficients of hydrogen molecules estimated by the global diffusion coefficients and free energies based on the solubility diffusion model were in good agreement with the experiments.

The method is powerful when we investigate long-distance and long-time global transportation of molecules in very large heterogeneous systems.

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[OC-22]

Probing the molecular organization in concentrated electolytes by non-linear optics

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Liquid molecular organization is involved in many physical, chemical, or medical relevant processes. For example, this organization is of utmost importance to understand hydration and more generally solvation, ions dissolution and precipitation, protein folding and activity, all result from the interaction of ions with solvent molecules. Having a better knowledge of this molecular organization will necessary lead to a better understanding of the properties of these electrolytes. However, such structure and interaction between solvent and ions are not fully understood today especially at high concentration where conductivity or viscosity measurements deviate from theory.

In this context, the structure and the dynamics of liquids have been studied with experimental methods based on neutrons, X-rays or UV-to-IR optical spectroscopy as well as theoretical methods like molecular dynamics. More recently, nonlinear optical methods [1,2,3] and Hyper Raman spectroscopy [4] have been proposed with great success. The existence of long-range orientational correlations over nanometer distances have been experimentally demonstrated in water as well as the role of ions in disrupting this network [2].

In this study, we have used Second Harmonic Scattering (SHS) as a tool to probe the bulk structure of electrolytes. Indeed, this non-linear optical process whereby two photons at a fundamental frequency are converted into one photon at the harmonic frequency, is intrinsically sensitive to the liquid structure and permits to obtain valuable information on the structure of the liquids on scales ranging from the very short distance (solvation shells) [5] to the long distance (orientation correlations) [2].

We will present our SHS measurements made on NaBr and NaCl electrolyte solutions at several concentrations and notably near the solubility limit. By using polarisation resolved SHS, we show a transition in the signal retrieved at very high concentration, highlighting a change in the electrolyte structure. We will discuss this optical information in regards with conductimetry results.

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[OC-23]

Solute-size dependences of hydrophobic interactions in water and other effective interactions in liquids

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One of the fundamental questions in theory of liquids is how hydrophobic interactions in aqueous solutions and, in general, effective interactions in solvents vary with the size of solute particles. Our computer simulation study [1] indicates that the osmotic second virial coefficient B, a measure of the strength of the effective solute-solute pair interactions in a solvent, varies approximately as the sixth power of the solute diameter with a negative proportionality constant for typical hydrophobic solute particles in water. The negative sign of B means that the effective pair interaction is overall attractive. In the study the solute-solvent interaction is modeled by the Lennard-Jones (LJ) potential with the energy parameter ε being that for the methane-water interaction. We also remarked that the sixth power law dependence of B is not inconsistent with the thermodynamic identity [2]:

$$B = B'' - (v - kT\chi)^2/2kT\chi,$$

where v is the partial molecular volume of the solute, χ the compressibility of the pure solvent, k Boltzmann's constant, and T the absolute temperature. B'' is the space integral of the solute-solute direct pair correlation function multiplied by (–1/2). The sixth power law is entirely due to the contribution to B from the solvent induced interaction, for the second virial coefficient of a gas in which particles interact with the LJ potential with ε fixed varies as the cubic power of the particle diameter. Now we report how B and the first peak height of the solute-solute $g(r)$ change with the solute size for a variety of solute-solvent interactions in water and in simple liquids. It is found that the solute-size dependences of B and the first peak height are both very sensitive to the solute-solvent interaction energy. In the case of LJ mixtures, the first peak height decreases and B (> 0) increases as the solute size increases if $\varepsilon_{UV} \geq \varepsilon_{VV}$ (the subscripts UV and VV denote solute-solvent and solvent-solvent); but the opposite trends are observed if $\varepsilon_{UV} = \frac{1}{2}\varepsilon_{VV}$. The solute size dependence of the hydrophobic interaction corresponds at least qualitatively to the latter case in the LJ mixtures.

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[OC-24]

How can we interpret the X-ray structure factor of water?

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Water is the most ubiquitous liquid for our existence as a reaction partner for lot of chemical and enzymatic reactions. It also acts as a solvent in many processes, covering a wide temperature and pressure range, in biology, chemistry and geology. No surprise then that water is the most heavily studied system. Despite that, a precise understanding of some essential properties of water, like the origin of its many unusual properties, has not been reached to this date. One of the most widely accepted explanation for the anomalous properties of liquid water is based on a 'liquid-liquid critical point' hypothesis. According to this conjecture, at supercooled temperatures and elevated pressures the structure of water can be decomposed into two different phases (high density liquid (HDL), and low density liquid (LDL)). These phases can be characterised by various order parameters (LSI, tetrathedricity, local translational order..). In this contribution, we present a new type of decomposition of the measurable X-ray diffraction pattern of liquid water, based on the concept of interstitial water. We determine, using statistical methods, the positions of interstitial water around a central water molecule (Fig 1a) and calculate the structure factor for (Fig 1b). In addition, as a sideline, we discuss problems arising from using atomic form factors while treating measured X-ray intensities.

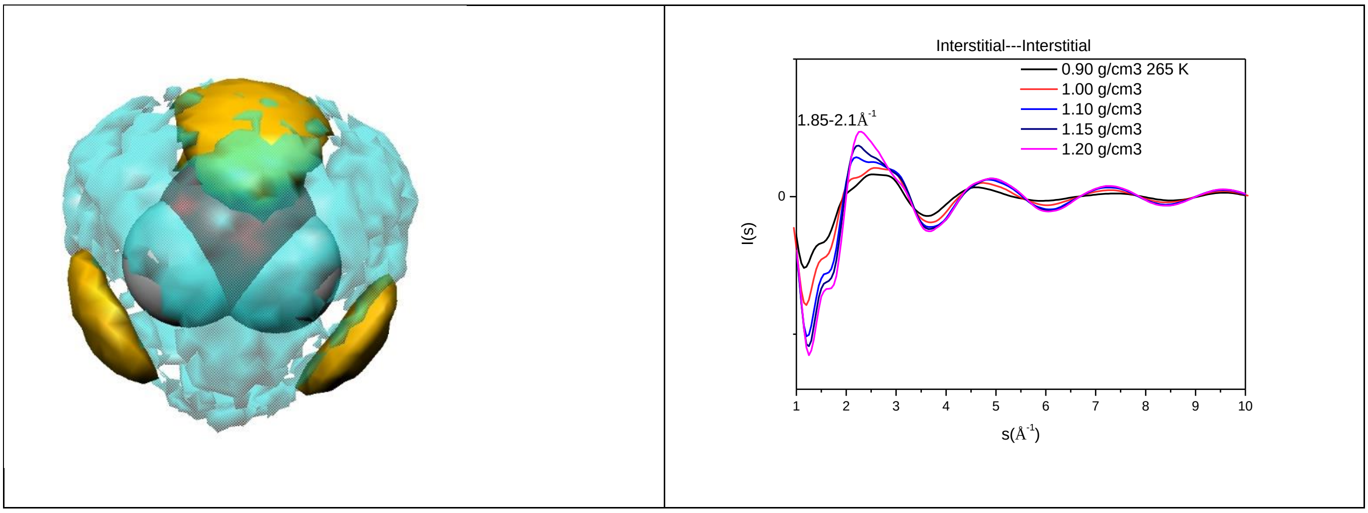

***Figure 1 a:** Localisation of interstitial and H-bonded water molecules around a central one. b: X-ray diffraction structure factor calculated for interstitial water molecules.*

[OC-25]

Nonlinear Vibrational Spectroscopic Studies on Hydrophobic Buried-interfaces of Ionic Liquids/Molecular Liquids

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As potential and novel alternatives to conventional electrochemical and/or organic solvents, room temperature ionic liquids (RTILs) have been utilized in electrochemical reactions and devices, extraction, enzymatic reactions, functional materials, and bio-mass applications. Compared to the large growth in their R&D, molecular level understanding of the interface structures of RTILs are still insufficient, although such information should be critical to improve and enhance their performances. So far, main techniques effective for structural studies of such buried-interfaces are quite limited and only a few are applicable to the liquid systems.

Infrared-visible sum-frequency generation (IV-SFG) vibrational spectroscopy has been demonstrated as a powerful tool for investigating surfaces and the interfaces of various media. So far, structural and environmental information of RTILs obtained by IV-SFG has been limited to mostly those of free-surfaces or substrate/RTIL interfaces. In this study, IV-SFG spectroscopy has been successfully applied to sketch the structure of the liquid/liquid buried-interfaces of RTILs ([$C_n$mim] [TFSA] n=4~12,) with hydrophobic organic solvents such as CCl_4. SF signals from the interface in C-H, S-O, and C-F stretching regions are clearly observed depending upon the nature of the solvents. For example, inhomogeneous interaction of the terminal CH_3 group of the [$C_n$mim]$^+$ cation with the CCl_4 molecules can result in the broadening of SF signals of the CH_3 asymmetric stretch mode. Our SFG results strongly suggest that CCl_4 molecules permeate into the outermost alkyl chain layer of the [$C_n$mim][TFSA] side, resulting in more ordered configuration of the alkyl chains with the orientational change of the [TFSA]$^-$ anion below the alkyl chain layer (Figure 1). The alkyl chain length dependence of the SF signals derived from the [$C_n$mim]$^+$ cation and the [TFSA]$^-$ anion appear to be very similar to those from the air/[$C_n$mim][TFSA] interface. This result indicates that bi-layering structure consisting of the first layer and submerged second layer in a "head to head" molecular arrangement [1] at the [$C_n$mim][TFSA] surface remains even after RTILs' contacting with the CCl_4 molecules. Structural details and configuration analyses of the interfaces are fully discussed in the presentation.

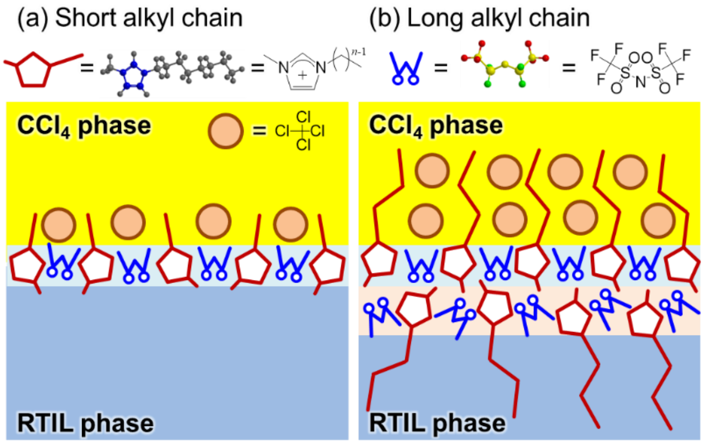

Figure 1 *Schematic structural models of the alkyl chain length dependence of the CCl_4/[$C_n$mim][TFSA] interfaces with (a) short alkyl chain and (b) long alkyl chain.*

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[OC-26]

Thermodynamics and structure of water-alcohol mixtures at the level of simple models

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Water-alcohol mixtures exhibit several unusual/anomalous properties whose proper molecular interpretation is still missing. Among them it is the minimum of the partial molar volume and azeotropy. As regards the former, common non-polarizable force fields do not seem to be able to reproduce this phenomenon, and concerning the latter, its molecular origin has not been identified yet. In this contribution we consider two aqueous solutions, namely with methanol and propanol, one exhibiting azeotropy and the other not. We examine a molecular approach starting with a realistic (pair-wise additive) force field and applying then a perturbation approach. It results in a non-additive hard body reference fluid which captures the minimum in the partial molar volume. As regards azeotropy, molecular simulations with an explicit interface reveal an unusual distribution of molecules of both species in the interface region which may provide an explanation of this phenomenon. Further more, simulation of a ternary mixture with a third component, a simple model of ionic liquids, is also examined as a potential azeotropy breaker.

[OC-27]

On the role of water as chaotrope/kosmotrope: Octanol-rich aqueous n-octanol mixtures

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Aqueous n-octanol (n = 1, 2, 3, 4) mixtures from the octanol rich side are studied by x-ray scattering and computer simulation, with focus on structural changes, particularly in what concerns the hydration of the

hydroxyl-group aggregated chain-like structures, under the influence of various branching of the alkyl tails. Previous studies have indicated that hydroxyl-group chain-cluster formation is hindered in proportion to the

branching number [1]. Here, water mole-fractions up to x = 0.2 are examined, i.e. conditions to avoid demixing. It is found that water molecules within the hydroxyl-chain domains, participate to the chain formations in different manner for the 1-octanol and the branched octanols. The hydration of the octanol hydroxyl chains is confirmed by shifting of the scattering pre-peak to low momentum transfer both from measured and simulated x-ray scattering intensities, which corresponds to an increased size of the clusters. Experimental x-ray scattering amplitudes are seen to increase with increasing content of water for 1-octanol, while this trend is reversed in all branched octanols, with the amplitude decrease is seen to increase with the branching number n. This is interpreted as water breaking large hydroxyl chains in 1-octanol, hence increasing the density of aggregates, while enhancing formation of hydroxyl aggregates in branched alcohols by inserting into the chains. Hence, water acts as a structure maker or breaker in inverse proportion to the hindering of chain structures from the topology of the alkyl tails.

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[OC-27bis]

Analysis of the formation mechanism of choline chloride-based deep eutectic solvents using Density Functional Theory

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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) [1]. 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 chloride based DES, performed with the density functional theory methods using B3LYP/6-311+G (d, p) basis set (Gaussian 6.0.16 version). Urea, ethylene glycol and glycerol were selected as HBD with choline chloride as HBA.

Varying the position of HBD at a fixed position of choline chloride, the most stable structure was found for each HBA: HBD system. With this, another HBD molecule was attached at various positions to study the DES structure. Same procedure was followed for the other DES. Their bond energies and bond lengths are reported. The nature of DES formation was 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. Figure 1 shows the HOMO-LUMO orbital of DES structure comprising ChCl: urea in the molar ratio of 1:2 with mínimum energy -33741.68724576 eV. Properties like chemical potential (μ), global hardness (η), softness (S), electrophilicity index (ω), electronegativity (X) and properties of thermochemistry (enthalpy and Gibb's free energy) of the DES formation are also reported. The electrostatic potential derived charges were calculated via CHELPG scheme The type and intensity of interactions between HBA and HBD in DES molecule have been studied using Bader's Quantum Theory of Atoms-in-Molecules (QTAIM) theory. To quantify short-range interactions, Reduced Density Gradient Analysis (RDG) have been performed.

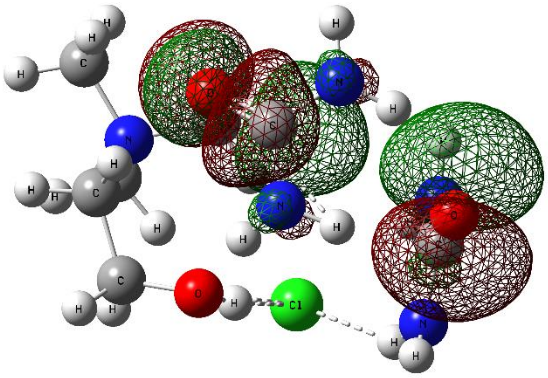

Figure 1: HOMO-LUMO orbitals in DES comprising ChCl: urea in the molar ratio 1:2

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[OC-28]

Charge ordering in associated liquids and its role in cluster dynamics

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Liquids are generally considered as disordered systems, but liquids consisting of polar molecules are locally more ordered than those of non-polar molecules. The main incentive behind this is the charge ordering, which is based on the Coulomb interaction between charged sites. Water is of particular importance among polar liquids, since it has the ability to hydrogen bond and form local tetrahedral order. In alcohols, on the other hand, chain clusters were found both from experiments and simulations. In most of the MD simulations, molecules are treated in a classical way, so hydrogen bonding, being an essentially quantum-mechanical effect, needs to be reinterpreted.

For this reason, we propose considering it as a charge ordering effect and analyze the dynamical correlation functions in this light. Our interpretation allows us to confirm the jump rotation [1] in water and to understand the dynamical origin behind the scattering pre-peak in alcohols [2].

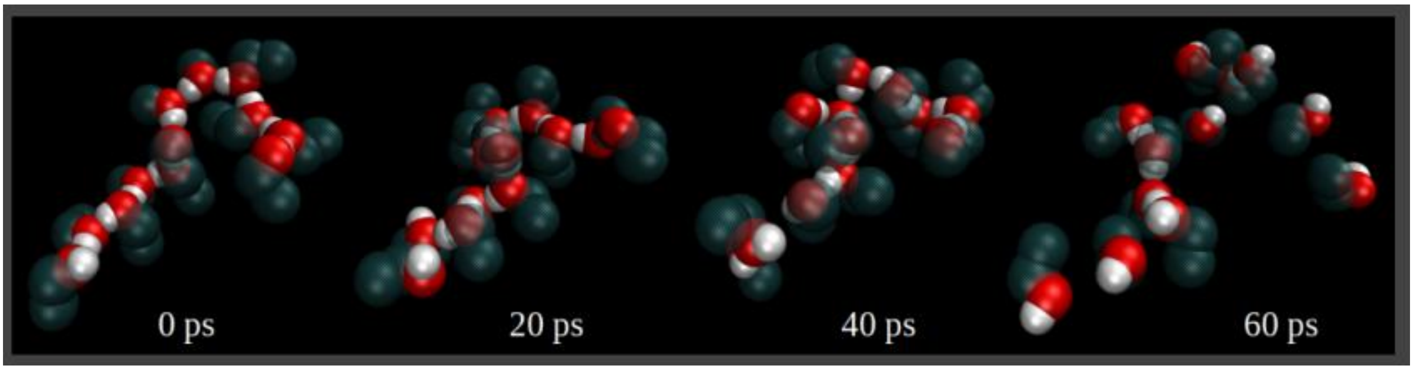

Figure 1: *Evolution in time of the cluster dynamics for ethanol OPLS-UA model in MD simulation.*

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[OC-29]

Polarization-Consistent Force Fields to Predict Solvation and Dielectric Properties of Mixtures

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Classical non-polarizable models, normally based on simple Lennard-Jones (LJ) sites and point charges, are extensively used to model thermodynamic properties of pure fluids, solutions and mixtures. An important shortcoming of this class of models is the lack of explicit polarization effects - i.e. a description of how the electron density responds to changes in the molecular environment. Instead, polarization is implicitly included, in a mean-field sense, into the parameters of the model, usually by fitting to pure liquid properties (e.g. density). Problems arise when trying to describe thermodynamic properties that involve a change of phase (e.g. enthalpy of vaporization), solutions/mixtures (e.g. solvation free energies), or that directly depend on the electronic response of the medium (e.g. dielectric constant). In this work, we demonstrate a new approach based on applying *post facto* corrections to properties computed by non-polarizable models in order to account for the effects of polarization. This idea allows us to systematically improve prediction accuracy while maintaining computational efficiency. Our main aim is to obtain a force field that is able to predict properties of both pure liquids and solutions/mixtures with a high degree of accuracy.

We have applied our new Polarization-Consistent Approach (PolCA) [1] to develop new atomistic models for alkanes, alcohols and ketones, and are currently extending it to other classes of molecules. In comparison with state-of-the-art non-polarizable models, PolCA not only yields better predictions of pure liquid properties (e.g. density, self-diffusion, enthalpy of vaporization), but also leads to much more accurate predictions of solvation free energies in heterogeneous systems, for example, when polar molecules are solvated in non-polar solvents like alkanes (Figure 1). This significantly improves the transferability of the model with practically negligible computational overhead. We also demonstrate that our approach is able to dramatically improve predictions of the dielectric constant, both for pure fluids and for mixtures [2,3]. These improvements arise from a theoretically grounded consideration of the realistic effects of polarization in the liquid state, which relies on an accurate estimation of the molecular dipole moment in the liquid state. In this context, we also describe the recently developed Self-Consistent Electrostatic Embedding method that is able to predict realistic liquid phase dipole moments with a reasonable computational cost [4,5]. Overall, the PolCA framework and associated toolkit paves the way for a paradigm change in force field development.

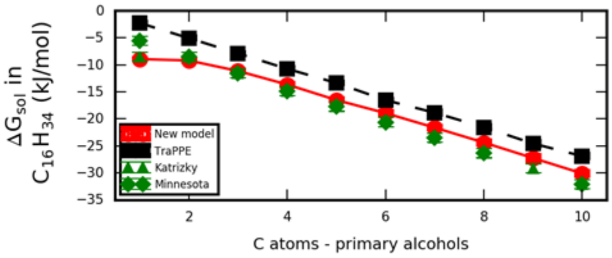

Figure 1: The PolCA model shows improved predictions for the solvation of alcohols in alkane solvents.

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[OC-30]

Selective Oxydation of Ethylene Glycol at Transition Metal Oxide Surfaces : Atomistic insight From Ab-initio Molecular Dynamics Simulation in Aqueous Solution

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The oxidation of 2-propanol to acetone at the Co_3O_4 (001)/H_2O interface has been studied recently, using ab-initio molecular dynamic to understand the role of temperature, surface structure and electrochemical environment [1]. In the same vein, we now study the case of a more complex molecule, namely ethylene glycol, on the same metal oxide surface to understand its oxidation processes. We study the system under dry and humid conditions on the B-terminated surface of Co_3O_4 at room temperature. Under dry conditions, a chemical reaction occurs, when the glycol coverage is increased, and only a deprotonated ethyldioxy compound is formed as the oxidation product after a simulation time of 10 ps. We then considered the case of a low glycol coverage in presence of up to 3 water molecules and, as expected, more chemical reactions occur (proton exchange and transfer) and concluded that water molecules play a key role in the oxidation of the diol.

Knowing this, we extended these preliminaries studies to a system in liquid water under oxidative conditions (proton deficit and relatively high temperature) for a simulation time of 20 ps. These results will be presented in the contribution.

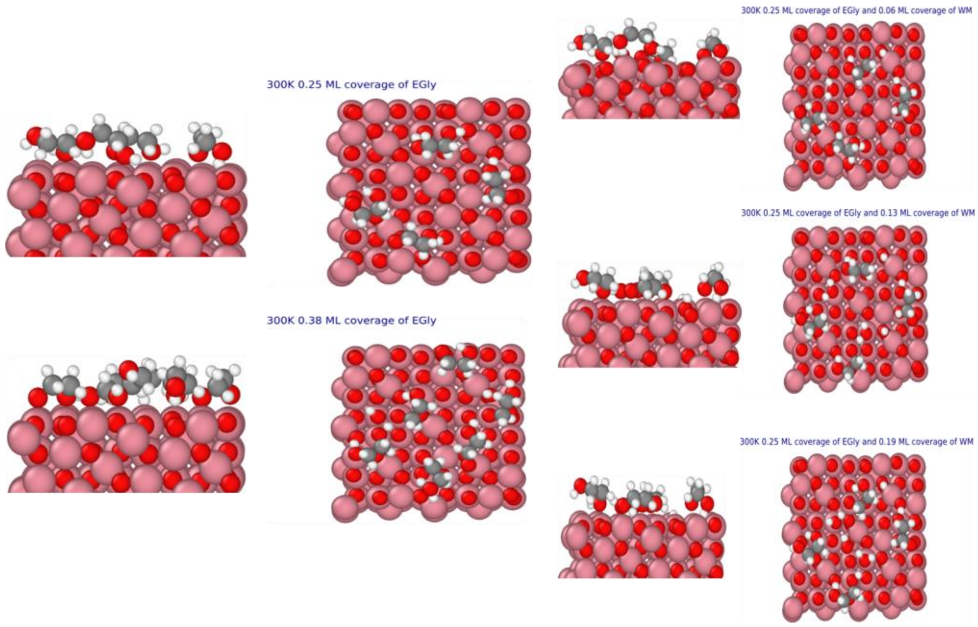

Figure 1: *Snapshots of MD simulations of ethylene glycol under dry conditions (left) and humid conditions (right) with 1, 2 and 3 water molecules.*

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[OC-31]

Two-Dimensional Raman and Dielectric Relaxation Correlation Analysis for Lithium Salt-Propylene Carbonate Solutions

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Electrolytes with high ionic conductivity play a critical role to achieve higher energy density for next generation lithium-ion batteries (LIBs). On the other hand, super-concentrated lithium salt solution has attracted attention as a next-generation LIB electrolyte because it has a specific lithium-ion conduction mechanism with high Li^+ transference number and conductivity. However, the lithium-ion conduction mechanism in super-concentrated lithium salt solutions has not been clearly elucidated, and the relationship with the lithium-ion local structure in the solution is also unknown. In this study, we investigated the anion effects on the lithium-ion conduction mechanism and the lithium-ion local structure in PC (propylene carbonate) based solutions containing lithium salts with various anions; PF_6, ClO_4, BF_4. Dipole reorientation dynamics were investigated by the dielectric relaxation spectroscopy (DRS) with molecular dynamics (MD) simulation, and Raman spectroscopy. The speciation was also elucidated with the Raman spectra.

We performed a two-dimensional correlation analysis (2D-RDCA) of the Raman spectra with the imaginary part of the dielectric relaxation. This is the correlation coefficient obtained with the linear least squares (regression analysis) analysis between the Raman and dielectric loss intensities at the respective given frequency as a lithium salt concentration dependence. According to the 2D-RDDCA and Raman speciation analysis of the $LiBF_4$ - PC solutions, which have specific lithium-ion conduction, shown in Figure 1, the relaxation that appears at the lowest frequency at the higher lithium salt composition can be attributed to contact ion pair (CIP) or aggregates (AGG). We estimated the dipolar relaxation for chemical species such as PC molecule, CIP and AGG for $LiBF_4$ system by MD simulation. According to MD simulation, the relaxation ascribed to CIP and AGG appears at high concentration of $LiBF_4$ salt and has contribution to the low frequency below 1 GHz.

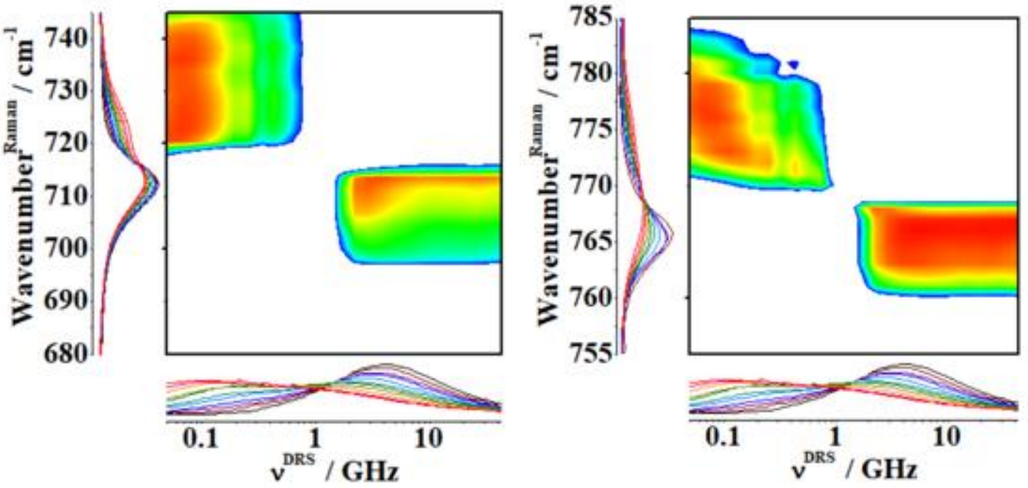

Figure 1: 2D-RDCA for the $LiBF_4$ – PC solutions. The finger print region of Raman bands for PC and BF_4^- are shown in left and right panel, respectively.

[OC-32]

Predicting solvation properties at molecular level with classical DFT

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The principles of molecular density functional theory (MDFT), a molecular extension of classical DFT, are recalled and the capability of the theory to predict efficiently, albeit accurately, the hydration free-energies and microscopic solvent structure of molecular solutes is discussed for a variety of systems: hydrophobic solutes and pairs, ions, and the FreeSolv dataset including more than 600 drug- like molecules, and spanning the whole hydrophobic to hydrophilic scale. The successes and the caveats of the approach are carefully pinpointed. The latest version of the theory includes so-called bridge functional contributions going beyond the lowest, second-order expansion in density, that is equivalent to the hypernetted chain (HNC) approximation in integral equations. The overall functional is parameter-free in the sense that the only inputs are bulk water properties, independent of the solutes considered. Compared to molecular simulations with the same force field and the same fixed solute geometries, the theory describes accurately the solvation free-energy and structure of both hydrophobic and hydrophilic solutes with a speed-up of 3 orders of magnitude in computer time. Overall, the methods yields a precision of order half a kT for the hydration free energies of the whole FreeSolv dataset. Although not yet in its final version, the method appears now mature enough to be used in large-scale electrochemical or biological applications, and in mixed electronic DFT/molecular DFT calculations that provides an intermediate, fully molecular description of the solvent lying between continuum PCM approaches and QM/MM simulations. Applications to other solvents than water will be discussed too.

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[OC-33]

Generalised energy-conserving dissipative particle dynamics: A coarse-grain framework for isoenergetic simulations of complex fluids

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From a general perspective, coarse-grain (CG) methods that utilise CG particles are a suitable alternative when the size of a physical system and time-scales of the processes are too large to be addressed through atomistic simulations. As such, the CG particles should be regarded as mesoscopic objects containing a number of unresolved degrees of freedom (DoF) that interact with the environment through the exchange of momentum, energy, and composition. Due to these internal DoF, a thermodynamic description of each CG particle is meaningful. In addition, irreversible processes occur due to the coupling of the resolved DoF (particle momentum, position, internal energy, temperature, and composition) and these internal DoF. The dynamics of the variables describing the state of the mesoparticles give rise to the hydrodynamic fields at long times and long wavelengths compared to the mesoparticle dimensions.

This contribution presents the generalised energy-conserving dissipative particle dynamics (GenDPDE), a CG framework for isoenergetic simulations of many-body models, which are an appealing class of density- and temperature-dependent CG models. These models have several key attributes that allow them to overcome common CG model deficiencies, including scaling consistency and transferability [1, 2]. The GenDPDE framework treats the mesoparticles as *property carriers* using an *internal fluctuating particle thermodynamics*. Therefore in the GenDPDE framework, the force between mesoparticles becomes a function of the local particle density and the particle temperature.

The flexibility of the GenDPDE framework further allows to include the mass exchange between mesoparticles [3, 4] and chemical intra-particle reactivity [5], addressing reaction-diffusion multiphase systems. The inter-particle mass transfer is described via the theory of mesoscale irreversible processes based on linear relationships between the fluxes and thermodynamic forces, where their fluctuations are described by Langevin-like equations. The reactivity is implemented via a CG reactor construct where extent-of-reaction variables assigned to each CG particle monitor the temporal evolution of the prescribed reaction mechanisms and kinetics.

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[OC-34]

Molecular Simulation of Vapour–Liquid Equilibrium by a Computationally Efficient Chemical Potential Extrapolation Algorithm

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We describe a new computationally efficient algorithm for the calculation of vapor–liquid equilibria (VLE) for a fluid modelled by a classical force field. It can be implemented by means of any Monte Carlo (MC) or Molecular Dynamics (MD) simulation software capable of calculating densities in the NPT ensemble and residual chemical potentials in the NVT ensemble. The algorithm avoids the computational difficulties encountered in the cases of low vapor pressures and of complex flexible molecules in general, difficulties which are suffered by approaches that employ inter–phase particle transfers (for example, [1]-[4]), and it also avoids the computational problems inherent in algorithms that incorporate the vapor-liquid interface within the simulation. The algorithm is presented and validated for pure fluids, and is readily extended to mixtures.

No initial estimate of the vapour pressure P^* is required, and the algorithm implements a thermodynamically based fixed–point iteration method for calculating P^* and the coexisting phase densities and chemical potentials at a given T. A byproduct of the algorithm is the calculation of approximations to second (and in some cases third) virial coefficients without additional computational effort.

We first show validation of the algorithm in the case of an analytical equation of state (EOS), using the NIST REFPROP software as an example data source. In such cases, convergence occurs within a handful of iterations. We then show molecular simulation applications to the Lennard–Jones fluid, the SPC/E water model, and an all–atom force-field model for n-dodecane. The algorithm is rapidly convergent down to very low (less than 1 Pascal) vapor pressures. Although no difficulties are encountered at near–critical temperatures in the case of an analytical EOS, it fails similarly to other VLE molecular simulation algorithms at such conditions.

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[OC-35]

The II+IW theory: the balance of ion-ion interaction and solvation drives the behavior of ionic activities

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The II+IW theory [1] is based on the implicit solvent model of electrolytes where the ions swim in a dielectric continuum characterized by a dielectric constant that depends on concentration, ε(c), as it was already suggested by Hückel in 1925 [2]. Since the reference point is the infinitely diluted electrolyte, this leads to two terms in the excess chemical potential, one corresponding to ion-ion (II) interaction, the other to ion-water (IW) interaction. The II term can be computed with various methods from the Debye-Hückel theory [3], the Mean Spherical Approximation [4], to Grand Canonical Monte Carlo simulations used by us [5]. The latter two are based on the "Primitive Model" of electrolytes where the ions are modeled by charged hard spheres. The IW term can be computed from the Born theory of solvation [6]. The non-monotonic concentration dependence of the activity coefficient is reproduced in this model as the balance of the large negative II term and the large positive IW term (Fig. 1) rather than the balance of the hard sphere term and the electrostatic term as in studies using constant ε and the concept of the solvated ionic radius. Since the 2010 publication [1] of our theory, the core idea (concentration dependent ε) has been enjoying a renaissance resulting in a landslide of papers (see the recent review of Kontogeorgis [7]). In this talk the II+IW theory and its implications are presented together with results for temperature dependence of the activity coefficient [8], individual ionic activities [9], and multivalent electrolytes [10].

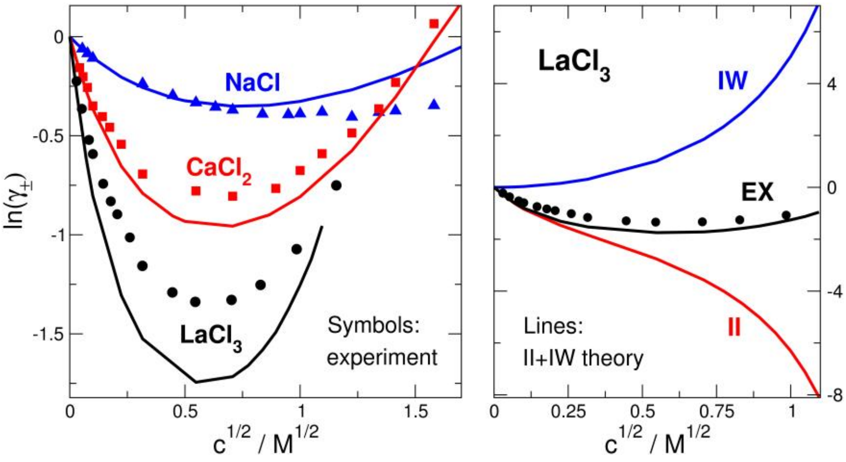

Figure 1: Activity coefficients of various electrolytes as functions of concentration and terms of the II+IW theory [10].

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[OC-36]

Fingerprint of the tilt angle of water molecules in Cu2+ aqueous solution probed by x-ray photoelectron spectroscopy

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The electronic structure and geometrical organization of the $[Cu(aq)]^{2+}$ cation after the dissolution of CuCl2 salt in liquid water have been investigated using x-ray photoemission at the Cu-L edge (Cu2p) combined with state-of-the-art ab-initio molecular dynamics and a quantum molecular approach developed to simulate Cu2p x-ray photoelectron spectra. This model is developed over the Post Hartree-Fock method. The description includes electronic relaxation/correlation and spin−orbit coupling effects and is implemented within nonorthogonal sets of Molecular orbitals (MO) for the initial and final states [1].

The presence of a satellite in the core-level spectrum is interpreted as the signature of a distribution of tilt angles centered at ≈ 40 degrees, defined by the water molecules in the first shell and the central copper di-cation. The calculations reveal how repositioning the Cu3d levels in the core-ionized final state induces the formation of new bonding and anti-bonding orbitals. The shake-up mechanisms toward HOMO are responsible for the presence of the satellites in the spectra, so that in $[Cu(aq)]^{2+}$, intra water → water and metal → water is in charge for them.

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[OC-37]

Ionic transport in graphene-based single digit nanopores

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Understanding the microscopic behavior of aqueous electrolyte solutions in graphene-based nanochannels with heights comparable to a few molecular diameters is important in nanofluidics applications such as water purification, fuel cells, and molecular sensing. Under such extreme nanoscale confinement (< 2 nm), the physical and chemical properties of water and ions differ drastically from those in the bulk phase. In this work, we study the structural and dynamic behavior of several prototypical aqueous solutions of electrolytes (LiCl, NaCl, and KCl) confined in both neutral and positively-, and negatively-charged graphene nanochannels [1].

The dynamic properties of water and ions in aqueous solutions include (i) diffusivity of water and ions determined in absence of external electric field or pressure gradient, (ii) mobilities of water and ions determined in the presence of external fields and the corresponding fluxes through the nanopore. We focus on graphene-based planar nanopores [1,2] and study the role of graphene surface charge, the separation of the graphene planes defining the height of the nanopore, as well as the length of the nanopore. The effect of the magnitude of the external fields (electric field, pressure drop) is also investigated. Pore entrance/exit barriers determined by potential of mean force method. Links with experiments on carbon materials are made [4].

These pieces of information are combined in our work towards efficient nanodevices applied to aqueous solutions, namely desalination devices based on capacitive deionisation (CDI) [2,3]. We utilize Gromacs and LAMMPS molecular dynamics simulations coupled with our post-processing codes to provide not only overall, but also position-dependent properties in the nanochannels.

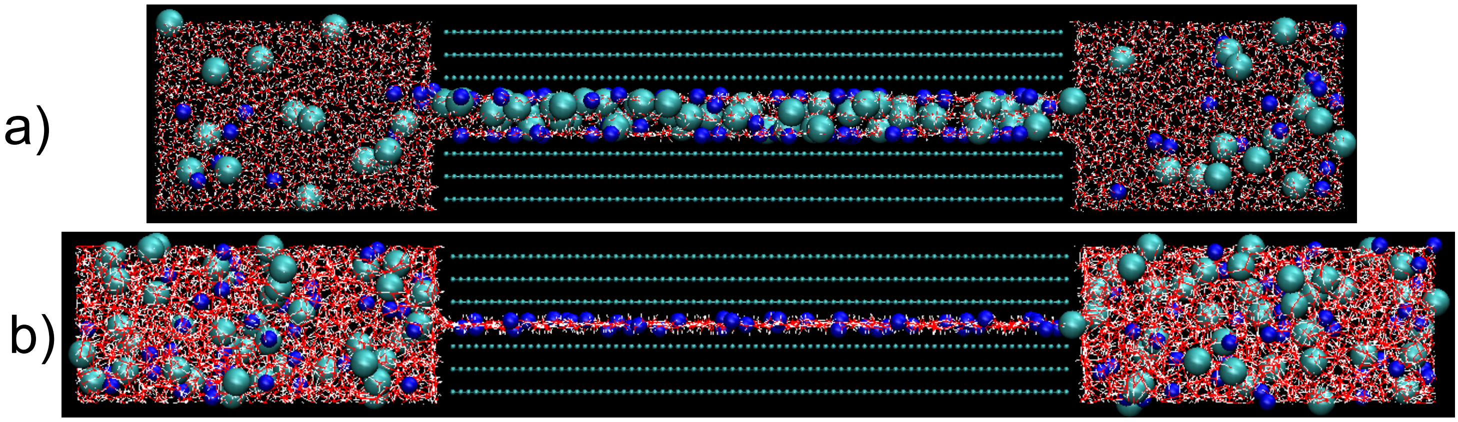

Figure 1: *Examples of graphene nanochannels in contact with bulk reservoir set-up with an aqueous NaCl solution. (a) Neutral graphene nanochannel of the height H = 12 Å with a three-layer water structure, and (b) negatively-charged graphene nanochannel of H = 7 Å with a one-layer water structure.*

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[OC-38]

Enhancing Li+ Transference Number by the Formation of Clusters with Heterogeneous Li+ Coordination

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In terms of developing energy storage systems with energy density higher than the state-of-the-art lithium ion batteries, lithium sulfur batteries stand for a promising alternative. Nonetheless, they suffer from safety issues and capacity fading due to lithium dendrite growth and polysulfide dissolution. To overcome these drawbacks, Suo et al. developed an electrolyte with a conducting salt/solvent ratio > 1 (by volume and/or by weight), known as solvent-in-salt (SiS) electrolyte. This SiS electrolyte suppresses the lithium dendrite growth and polysulfide dissolution, thus leading to a high coulombic efficiency and prolonged cycle life of the resulting battery chemistry. Moreover, the same group reported a high Li^+ transport number of 0.7.[1,2] However, to explain the fast Li^+ transport and advance the overall battery performance, the underlying structure, composition, and dynamics of the SiS electrolyte formulation has to be thoroughly analyzed and understood.

In this study, the conducting salt concentration in an electrolyte consisting of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), 1,2-dimethoxyethane (DME), and 1,3-dioxolane (DOL) was systematically increased up to the solvent-in-salt regime. By employing electrophoretic NMR (eNMR), the electrophoretic mobilities of all present species were obtained. From this, the Li^+ transference number was calculated, which yielded a comparably high value than the Li^+ transport number measured under anion blocking conditions reported by Suo et al.[1]

In order to explain this fast Li^+ transport in the highly concentrated regime, NMR and Raman spectroscopy analysis was conducted and complemented by molecular dynamics (MD) simulations. By monitoring the changes in the chemical shift of the NMR signals as well as the changes in the Raman bands of the anion and solvent molecules, a basic stochiometric model of the Li^+ coordination shell was introduced and confirmed by the MD simulation analysis. Using this model and additional results obtained by MD simulations and eNMR, a deepened understanding about the structure and dynamics in this SiS electrolyte formulation was gained, thus providing possible explanation for the high transference number of Li^+ in the SiS regime.

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[OC-39]

Vibrational spectroscopies in liquid water: On temperature and coordination effects in Raman and infra-red spectroscopies

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Water is an ubiquitous liquid that has several exotic and anomalous properties. Despite its apparent simple chemical formula, its capability of forming a dynamic network of hydrogen bonds leads to a rich variety of physics. Here we study the vibrations of water using molecular dynamics simulations, mainly concentrating on the Raman and infra-red spectroscopic signatures. We investigate the consequences of the temperature on the vibrational frequencies, and we enter the details of the hydrogen bonding coordination by using restrained simulations in order to gain quantitative insight on the dependence of the frequencies on the neighbouring molecules. Further we consider the differences due to the different methods of solving the electronic structure to evaluate the forces on the ions, and report results on the angular correlations, isotopic mixtures HOD in H_2O/D_2O and and the dielectric constants in water. We also explore the collective vibrational excitation modes in the liquid.

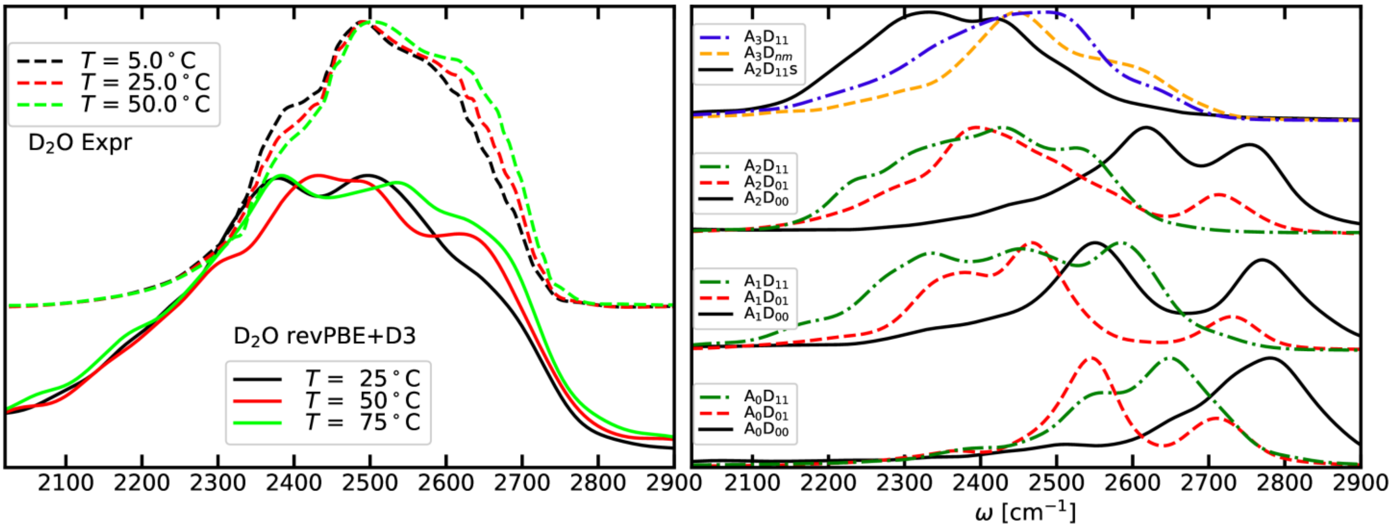

Figure 1: *Left: The infra-red spectrum in D_2O from experiments and our simulations at different temperatures; right: The simulated infra-red spectrum at the central water molecule when the hydrogen bonding network around it is constrained to a specific configuration*

[OC-40]
Clay Surfaces – Are They Hydrophilic or Hydrophobic?

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Clays are layered silicates whose crystal structure usually consists of three sub-layers: one layer of octahedrally coordinated hydroxides of M^{2+} or M^{3+} metals, sandwiched on both sides between two layers of SiO_4 tetrahedra. These tetrahedra are organized into six-membered rings and form a siloxane surface. The huge variety of compositions and properties of such clay structures is due to the wide range of so-called isomorphic substitutions possible both in their octahedral and tetrahedral sublayers, which lead to the development of a permanent negative charge of the crystal lattice compensated by additional cations in the interlayer space and on the surfaces of such materials. Many of them can be easily hydrated and can swell in the presence of water, which is one of the most important properties of clays for a wide variety of technological applications. As most clay materials readily sorb water in fairly large quantities, they are usually considered hydrophilic (Figure 1). The exceptions are crystal structures, in which isomorphic substitutions are completely absent (e.g. talc, pyrophyllite), and whose electrostatically neutral surfaces exhibit distinctly hydrophobic properties.

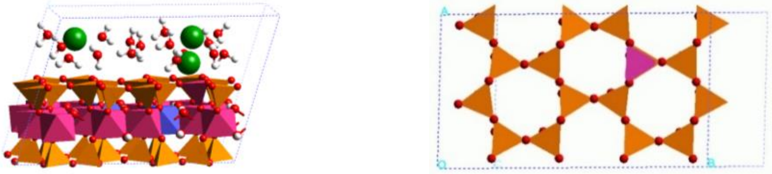

Figure 1: Model of a swelling clay (montmorillonite) with Na^+ ions and H_2O molecules on its surface. A top view of the siloxane surface is shown on the right. The isomorphic substitutions in each layer are highlighted in a different color. Yellow – Si, pink – Al, blue – Mg, red – O. green – Na, white – H.

However, this simplified picture is currently undergoing a serious revision in light of new experimental and simulation results [1-5]. In particular, a quantitative analysis of the structure, dynamics, and topology of the H-bonding network formed in the aqueous interlayers and on the surfaces of typical clays demonstrates quite convincingly that the same siloxane surfaces can exhibit both hydrophilic and hydrophobic properties, depending on the thermodynamic state of the system and the composition of the aqueous phase [2-5]. The presence of isomorphic substitutions and the structural charge play important, but only secondary roles [5] in the entire molecular scale picture of the observed phenomena.

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[OC-41]

Anomalous perpendicular dielectric response of nanometer-thin water films

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The significant role of water in a wide range of systems across various scientific fields is quite evident. Specifically, comprehending its behavior at interfaces with other substrates holds utmost importance in molecular biology, geology, or nanotechnology. At nanometer scales, the structural and dynamic behavior of water is anticipated to undergo drastic changes in comparison to bulk water [1]. Recently, there has been a particular focus on studying the dielectric response of water confined at the nanoscale. This property is critical because it directly impacts the molecular interactions of water and its surroundings.

The perpendicular dielectric response of a one nm-thin water film was experimentally found to be surprisingly low [2], with a relative dielectric constant of 2.1. There had been predictions of such an effect from simulations [3], and further simulations after the experiments corroborated them [4]. The problem is, however, far from understood, since the simulations describe a mostly (or even uniquely) orientational response of the water molecules, while the experimental response seems to be mostly electronic (1.8 is the bulk value of the high-frequency relative dielectric constant). Using molecular dynamics simulations of such a water film over long trajectories obtained from a TIP4P/2005 model, the dielectric response for the model is compared with the one obtained using density-functional theory calculations sampling the same trajectory, both using explicit dipole versus applied field calculations. With the same technique, the high-frequency response is also calculated for the film. The results are quite revealing and offer a better understanding of this anomalous behaviour.

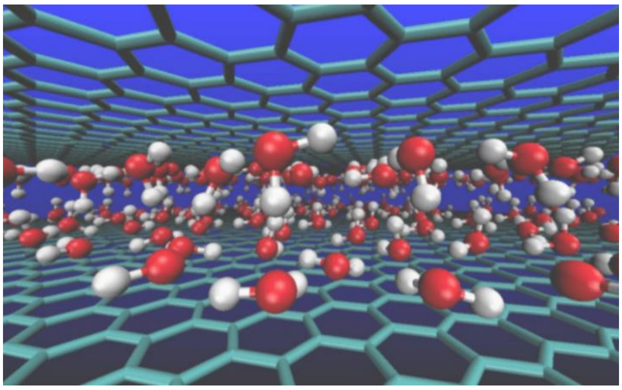

***Figure 1:** 2 dimensionally confined water between 0.8 nm interwall distance planar walls.*

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[OC-42]
Insights into wastewater cleaning with TiO2

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It is easy to notice visible wastes like plastic packaging that we pollute our waters with. But there are also invisible wastes that are harder to detect and, in addition, harder to remove. These invisible wastes consist of chemicals from various offspring: e.g. industry, agriculture, pharmaceutics and everyday life products [1,2].

We have to develop methods to clean polluted water if we want to stay in balance with our environment. From experiments it is known that TiO_2 as a photocatalytic material possesses a great potential to serve as a pollutant degradation agent [3]. But there are still open questions when trying to understand this process at the atomic level: Which pollutants interact with TiO_2? Why is the process more effective under definite environmental conditions? What is the role of water in this process?

In this study we are investigating these questions with a multi method approach of molecular dynamics simulations. The calculations are conducted on amorphous [4] and crystalline [5] TiO_2 surfaces in aqueous solution with varying pH conditions and molecular competitions. We study the adsorption barriers, aggregation driving forces, splitting pathways of selected wastewater pollutants and the role of water in the adsorption process by methods ranging from enhanced sampling to ab initio calculations [6,7].

All these different simulations initiate a better insight into the complex process of pollutant degradation on TiO_2 and are helping us to understand the potential of this material as a wastewater cleaning solution.

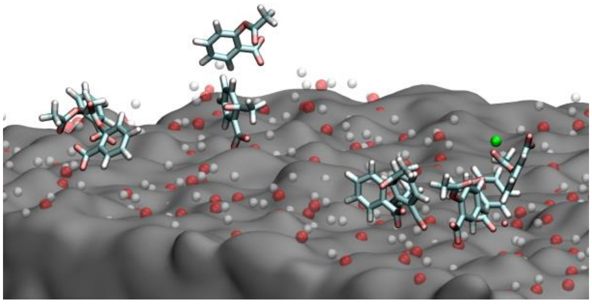

Figure 1: *Snapshot of acetylsalicylic acid adsorbing on amorphous TiO_2 (pH 5.0).*

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[OC-43]
Surface potential of water and brines

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The surface potential or “work function” equals the energy needed to reversibly remove a “probe” unbound negative elementary charge from the bulk to a vacuum. Experiments with liquid jets irradiated by soft X-rays give +0.6 V [1] whereas *ab initio* molecular dynamics predicts higher values [2,3]. We tackle this problem by classical molecular dynamics with various atomistic models in the slab geometry. The Poisson equation is solved for the charge profile. The validity of the method is tested using a Gaussian probe charge. In agreement with literature [3], we find that all classical point-charge models (including polarizable ones) exhibit a negative potential. The only model able to give a positive potential is the polarizable model with Gaussian Drude charges [4]. As a compromise approach, we convolute an *ab initio*-based charge density of a molecule over a classical trajectory.

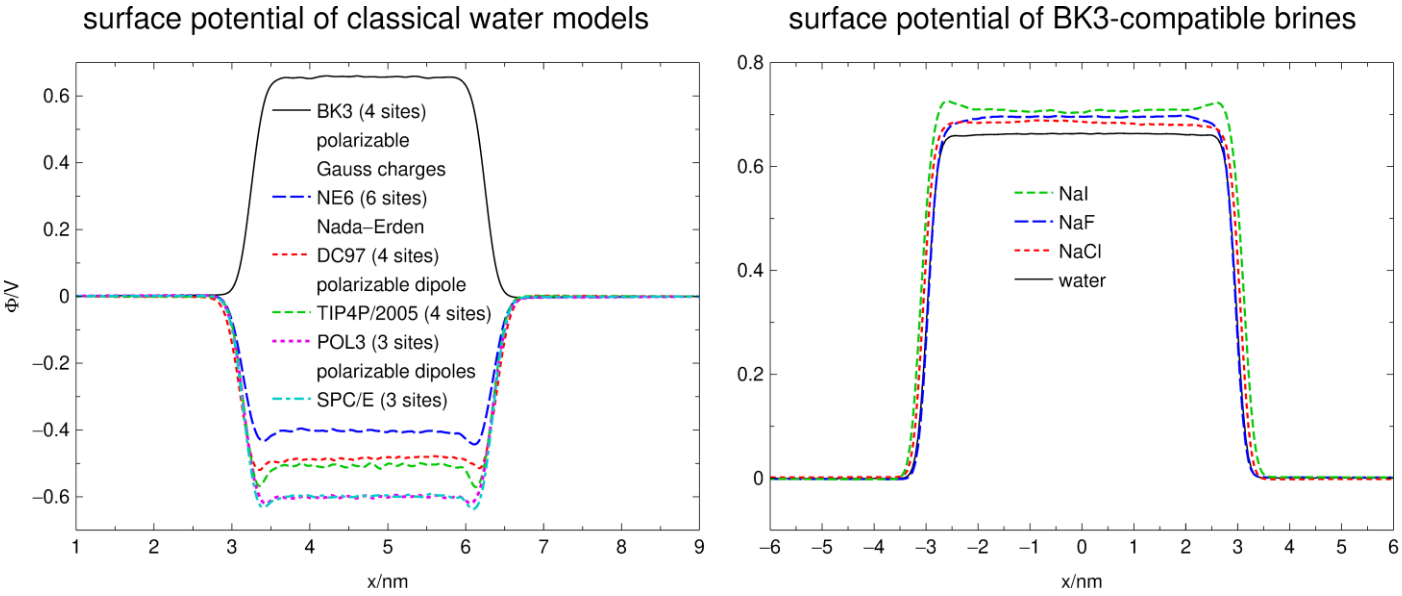

Figure 1: *Left: calculated potentials of water slab using various atomistic models, right: potentials of brines (1.33* mol/kg*) calculated using BK3 water and compatible ion models [4].*

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[OC-44]

Hydration properties in aqueous solutions of fructose

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Fructose is one of the most important monosaccharides because it is one of the three dietary monosaccharides that are absorbed directly into the blood. It primarily occurs naturally in many fruits and also in other plant foods such as honey, sugar beets, sugar cane and vegetables. What makes it particularly interesting, even among other sugars, is that it is the sweetest naturally occurring carbohydrate, sweeter than sucrose (table sugar). [1]

In the aqueous solution of fructose, four tautomers (α-D-fructofuranose, β-D-fructofuranose, α-D-fructopyranose and β-D-fructopyranose) are present. [2] The orientation of hydroxymethyl and hydroxyl groups and their interaction with water largely determine the physicochemical properties of the solution. Furthermore, the hydrophobic interaction also has to be taken into account. We aim to investigate the solvation shell (both the hydrophobic and the hydrophilic contribution) at the atomic level using both classical and ab initio molecular dynamics (MD) simulations.

Ab initio molecular dynamics simulation enables the determination and the comparison of the hydrogen bonding (HB) properties for the individual tautomers, such as the number of donor and acceptor type HB-s, and the lengths and strengths of hydrogen bonds between fructose and water molecules. Related electronic properties such as the dipole moments of water molecules can also be calculated.

On the other hand, MD simulation was applied at various concentrations containing the equilibrium ratio of tautomers to reveal fructose-fructose and water-water interactions. Total scattering structure factors can be calculated from the resulting large particle configurations, which forms a bridge between simulation and experimental diffraction results. [3]

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[OC-45]

Understanding the Molecular Mechanism of General Anesthesia

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General anesthesia can be caused by various, chemically very different molecules, while several other molecules, many of which are structurally rather similar to them, do not exhibit anesthetic effect, at all. To understand the origin of this difference, and shed some light on the molecular mechanism of general anesthesia, we report here molecular dynamics simulations of the neat dipalmitoylphosphatidylcholine (DPPC) membrane as well as DPPC membranes containing the anesthetics diethyl ether and chloroform, and the structurally similar non-anesthetics *n*-pentane and carbon tetrachloride, respectively. To also account for the pressure reversal of anesthesia, these simulations are performed both at 1 bar and at 600 bar. Our results indicate that all solutes considered prefer to stay both in the middle of the membrane and close to the boundary of the hydrocarbon domain, at the vicinity of the crowded region of the polar headgroups. However, this latter preference is considerably stronger for the (weakly polar) anesthetics than for the (apolar) non-anesthetics. Anesthetics staying in this outer preferred position increase the lateral separation between the lipid molecules, giving rise to a decrease of the lateral density. The lower lateral density leads to an increased mobility of the DPPC molecules, a decreased order of their tails, an increase of the free volume around this outer preferred position, and a decrease of the lateral pressure at the hydrocarbon side of the apolar/polar interface, a change that might well be in a causal relation with the occurrence of the anesthetic effect. All these changes are clearly reverted by the increase of the pressure. Furthermore, non-anesthetics occur in this outer preferred position in a considerably smaller concentration, and hence either induce such changes in a much weaker form, or do not induce them, at all.

[OC-46]
Electrolyte Effects on Protein Stability in Solution

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Recently, we studied the mechanism of the onset of phase separation of globular proteins in aqueous solutions via molecular dynamics simulations [1]. For two different lysozyme proteins, hen egg-white and T4 WT*, and the human eye lens protein γ-D crystallin, we monitored the phase stability by time-dependent density fluctuations and found that, despite the occurrence of aggregation, all proteins remained in their compact form. By an extensive analysis of intermolecular residue-residue interactions we concluded that the amino acids arginine and lysine are most important during the initial stages of aggregation.

In this contribution, we extend these early studies to larger systems containing 64 proteins, different base electrolytes (e.g., NaCl, NaBr, LiCl) and longer simulation times (around 500 nanoseconds). We analyze the protein aggregation by means of anisotropic radial distribution functions, and by monitoring the dehydration of specific residue-residue pairs during the early stages of complex formation.

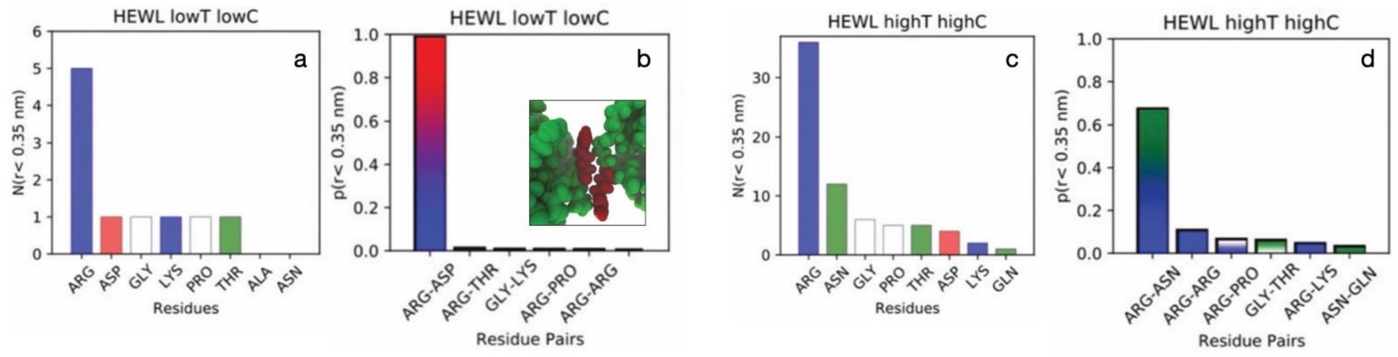

***Figure 1:** Probability of transient 'first-contact' amino acids and amino acid pairs for hen egg white lysozyme (HEWL) at low and high temperature in pure water. The inset in b shows a typical configuration of two antiparallel arginine residues. Figure adapted from Ref. [1])*

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[OC-47]
Water solvation in bio-nano complex matter

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Water-solvation effects on biological and nanoscopic solutes are of utmost importance in applications but their mechanisms are not fully understood yet. For example, when an aqueous mixture embeds a graphene nanopore (sponge), the concentrations of the mixture components in solution depend on the fine details of the interaction of each component with the pore and on the pore size [1]. Furthermore, hydration water modulates the folding, condensation, aggregation, and adsorption onto nanomaterials of proteins in solutions (Fig.1) [2]. We will discuss these results within a multiscale approach we developed to calculate the water solvation contribution to the free energy of bio-nano complex matter [3-7].

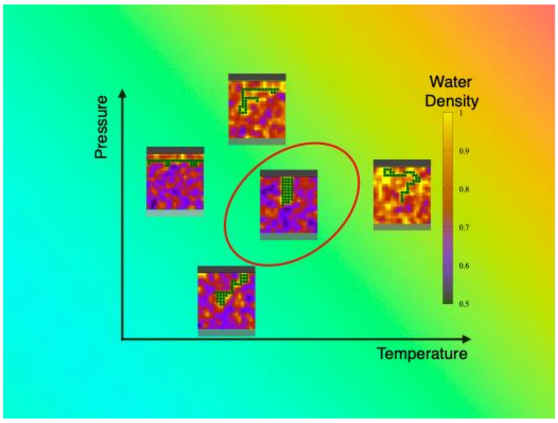

Figure 1: *Water solvation of an intrinsically disordered protein absorbing onto a nanointerface reveals an intriguing interplay with its coil-to-globule structural changes, depending on the confining and thermodynamic conditions [2].*

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[OC-48]

Insights into structure and dynamics of biomolecules by multi-wavelengths UV Resonance Raman spectroscopy

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Raman spectroscopy is an inelastic scattering technique that allows to detect the vibrational spectra of molecular systems and it has been widely implemented from several years as valuable tool for the non-invasive characterization of several kind of materials. Thanks to the so-called resonance effect, multi-wavelengths UV Resonance Raman (UVRR) spectroscopy enables to overcome the limitations of conventional visible Raman technique. Besides the significant increment of the detection limit, resonance condition leads to significant enhancement of signal from the absorbing species and thereby enables the selectivity needed to incisively monitor specific chromophoric segments within the sample [1].
In this seminar, we would like to give an overview on the opportunities offered by the unique in the world UVRR setup working with the synchrotron radiation (SR) source available at the BL10.2-IUVS beamline (Elettra synchrotron facility, Trieste, Italy) [2]. The SR-based UVRR set-up at Elettra enables to perform UVRR experiments with a fine tuneable source in the range of excitation wavelengths 200-270 nm. This provides a label-free technique very useful especially for studying complex systems such as bio-solutions by the probing of structure, local environment, and hydrogen-bonding of biomolecules [3].
Selected case studies will be discussed in order to show the usefulness of SR-based UVRR method and the areas of interactions with other research interests.

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[OC-49]

Plant absorption of metal nanoparticles cohabiting with arbuscular mycorrhizal fungi targeting for biomarker systems

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Nanoparticles (NPs) can be potential biomarkers if the NP surface is modified adequately to label the target part or disease. Zinc oxide (ZnO) NPs, which are non-toxic in nature, are candidates for such markers, as we have accumulated knowledge to modify the ZnO NPs' surface chemically. In the present study, we determined the uptake ratio, r_{upt}, of ZnO NPs to barley using electric microscopy and related techniques. With single ZnO NP administration, r_{upt} was 0% in the leaf part, whereas r_{upt} was 40% when barley was cultivated with arbuscular mycorrhizal fungi and a liquid fertilizer. The fungi are in mutualistic association with the root, which enhances water absorption because of the more efficient activities of the rhizosphere. Our previous study [1] found that ZnO and TiO_2 NPs are taken up to Poaceae family plants with appropriate surface modifications.

In the present contribution, we studied the ZnO NP r_{upt} in barley, where r_{upt} was determined using Energy-dispersion spectroscopy–scanning electric microscopy (EDS-SEM). Barley was chosen as a typical crop from Poaceae and ZnO as a representative non-toxic NP with the potential as an emitting device with a modified surface. The ZnO NPs employed have a diameter d = 20–40 nm, as determined using transmission electron microscope (TEM). Figure 1 indicates an TEM image of ZnO we used for uptake.

The barley was grown in a hydroponic culture in which ZnO NPs were dispersed in the cultivation field. Arbuscular mycorrhizal fungi and liquid fertilizer were added to the field. The EDS-SEM results indicated that ZnO NPs were absorbed into the root, stem, and leaf parts and detected around the vascular bundles. Both arbuscular mycorrhizal fungi and liquid fertilizers enhanced ZnO uptake in plants.

For instance, r_{upt} was higher in the leaf when both arbuscular mycorrhizal fungi and liquid fertilizer were added than when liquid fertilizer alone was added and was zero without them. The arbuscular mycorrhizal fungi were in mutualistic association with the root. An apparent increase in r_{upt} is attributed to better water absorption from the root, which pushes up water-dispersed ZnO NPs, even to the stem and leaf.

In future studies, the ZnO NP surface could be modified with functional groups connected to a disease antibody. Moreover, further studies on NPs regarding efficient nanoscale biomarkers are needed and can provide a more detailed elucidation of uptake mechanisms.

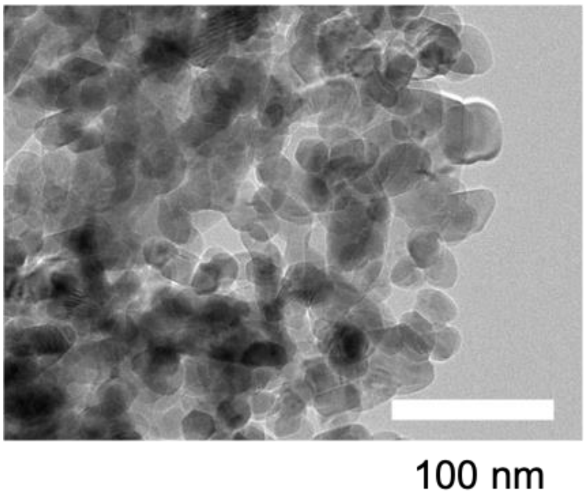

Figure 1: *TEM image of ZnO NPs used for uptake*

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Abstracts of Poster Contributions: [PC-01] → [PC-43]

[PC-01]
Aqueous solutions of heterocyclic amines: structure and thermodynamics

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Heterocyclic amines, such as piperidine and N-methylpiperidine aggregate in aqueous solutions due to hydrogen bonds between hydration water molecules [1,2]. No such aggregation occurs in the mixtures of these amines with other hydrogen-bonded solvents, such as methanol or ethanol. This difference highlights the active role of water solvent in promoting the self-aggregation. However, the role of various contributions in thermodynamic functions due to specific interactions, van der Waals forces, and the effect of the size and shape of the molecules remains open. In the present communication we discuss the family of solutions of pyrrolidine, piperidine, and their methylated counterparts in water and in methanol, as revealed by thermodynamic measurements as well as by direct visualization of the mesoscopic stucture employing small-angle neutron scattering.

The limiting partial molar enthalpies of solutions of pyrrolidine, N-methylpyrrolidine, piperidine, and N-methylpiperidine in methanol follow closely the trend assessed from theoretically calculated molecular interaction energies. However, their behavior is markedly different in water solutions, and can be described by taking into account an empirical hydrophobic hydration term [3].

Small angle neutron scattering evidenced that the aqueous amine solutions are microheterogeneous on the nanometer length scale. Various models are considered to describe the structural arrangement of the hydrated amine molecules. The tendency of approaching phase separation increases in the order:
N-methylpiperidine < N-methylpyrrolidine < piperidine < pyrrolidine.

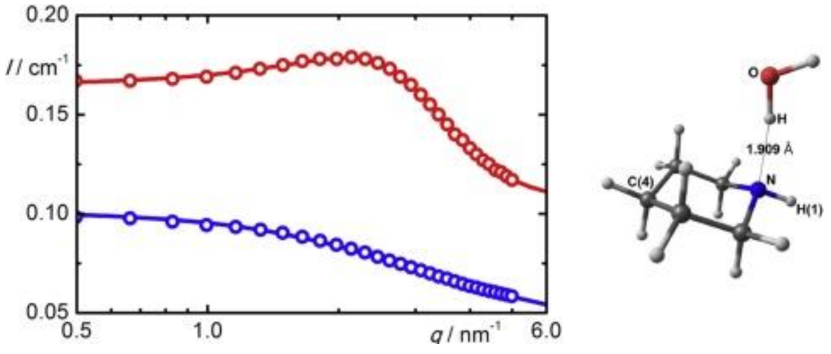

Figure 1: *Small angle neutron scattering of piperidine clusters in water and ab initio structure of piperidine-water complex in vacuum.*

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[PC-02]

Phase behavior of aqueous levulinic acid in trioctylamine solution using at different temperatures

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Carboxylic acids can be produced through chemical processes of fossil raw materials as well as by the microbial fermentation of naturally occurring biomass. Levulinic acid is typically produced by separating and purifying a complex aqueous mixture. Among different separation methods, the reactive extraction process has received increasing attention as an alternative and effective method of carboxylic acid separation [1]. In this study, the reactive extraction method was used to investigate the liquid extraction of levulinic acid from water using trioctylamine (TOA). For that, liquid-liquid equilibrium (LLE) data were experimentally determined for Levulinic acid (LA) + trioctylamine (TOA) + water (H_2O) system at T = (293.15, 313.15, and 333.15) K. For this purpose, the analytical and cloud point methods were used to determine tie-line and binodal values. High acid concentrations enable higher extraction efficiency, as seen by the slope of the determined tie-lines. Infrared spectroscopy (FT-IR) was used to analyze the potential interactions and complex formation in the solutions. Figure 1 illustrates how tie-lines deviate from the lever rule because the acid-extractant complex in the solution is not detectable by the GC technique. Finally, the experimental data were correlated with the NRTL model at all the measured temperatures. Although there are some publications on the phase behavior of ternary aqueous carboxylic acids in ionic liquid solutions [2, 3], there are no experimental data on the phase behavior of ternary aqueous systems including levulinic acid and trioctylamine as an extractant in a wide concentration range.

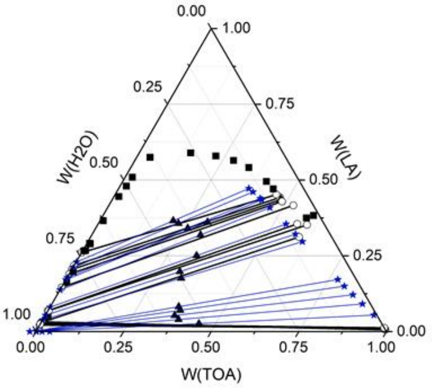

Figure 1: Phase diagram of the trioctylamine (TOA) + levulinic acid (LA) + Water (H_2O) system at T = 293.15: (■) experimental binodal, (—○—) experimental tie-lines, (▲) initial experimental points, (★) calculated tie-lines.

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[PC-03]

Towards microfluidic separation processes using Switchable Hydrophilicity Solvents

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Solvent engineering aims at controlling the solubility and transport properties of a solvent medium, in order to optimize the chemical or physical processes performed. Among the strategies of Solvent Engineering, reversible CO_2-switchable hydrophilicity solvents (CO_2-SHS) represent a promising route to reversibly switch the properties of a solvent.

The final goal of this work is to combine microfluidic technologies and CO_2-SHSs to perform liquid-liquid separation processes at microscale and in optimized experimental conditions. 2,2-Dibutylaminoethanol (DBAE) was chosen as this solvent is able to switch from a tertiary amine (hydrophobic form), to the corresponding bicarbonate salt (hydrophilic form) at room conditions [1]. The reaction scheme is presented in Figure 1(a).

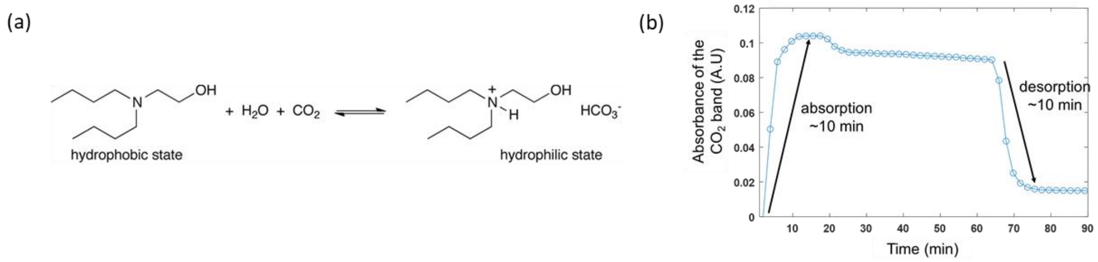

Figure 1: (a) Reaction scheme of the hydrophilicity switch. (b) Results of the Attenuated total reflectance infrared (ATR-IR) spectroscopy measurements about the kinetics of CO_2 absorption and desorption of the solvent under CO_2 atmosphere.

In a first step, we studied the kinetics of CO_2 absorption and desorption in DBAE through ATR-IR spectroscopy measurements. Those measurements were performed using a home-made ATR accessory suitable for high temperature and high pressure coupled to an FTIR spectrometer (see details in [2]). After the injection of carbon dioxide up to a desired pressure into the sample chamber containing pure DBAE, the CO_2 sorption process was followed during a given time period. Figure 1(b) shows a plot of the absorbance of the band associated with the antisymmetric stretching mode of CO_2 over time, once a pressure of 5 bar of CO_2 is imposed over the DBAE sample. After 60 minutes the pressure was released and the CO_2 desorbed.

Then, we developed microfluidic chips made of poly(dimethylsiloxane) (PDMS) using soft lithography (typical channel height 10-50µm), PDMS being the material of choice, not only for the versatility and simplicity of microfabrication, but also for its permeability to gasses. We developed two-level PDMS chips made of a bigger channel stick on the top of the main one. The membrane between these two elements has thickness of ~200 µm. This configuration allowed us to impose either a CO_2 or an N_2 flow in a channel superimposed to a fluidic channel in which we created an interface between DBAE and water. Because of the permeability of PDMS to gasses, we were able to induce the phase change of the SHS and modulate its solubility into water. We are currently exploiting these microfluidic experiments to design a liquid-liquid separation process in a microchannel.

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[PC-04]

Extraction of natural compounds by green solvents: a comparative study by COSMO-RS

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In the recent years, different alternative solvents to the conventional organic solvents have been employed to extract natural compounds from many types of samples. These "green solvents" can come from different sources such as water, carbon dioxide, bio-sourced solvents, ionic liquids and eutectic mixtures, fluorinated solvents, among others [1]. A tool that has been used recently in the preselection of these solvents is the theoretical model COSMO-RS (COnductor-like Screening Model-Real Solvent). By considering the solvent as a dielectric continuum, the COSMO-RS model uses the σ-profile and thermodynamic properties to predict the activity coefficient of a chemical species in a solvent or mixture [2]. The objective of this work is to use parameters such as σ-profile similarity, σ- potential similarity and activity coefficient at infinite dilution (Υ^{∞}), to predict which type of green solvent can be used for the extraction of a specific type of natural compound. Two types of green solvents will be evaluated: carbon dioxide and bio-based solvents as 2-methyltetrahydrofuran, for example. Moreover, a comparison with conventional solvents such as water, ethanol or glycerol will also be performed. Some comparisons with some experimental systems already evaluated for our group will be presented. Phenolic acids, polyphenols, flavonoids, fatty acids, terpenes, aminoacids will be considered as natural compounds to be extracted.

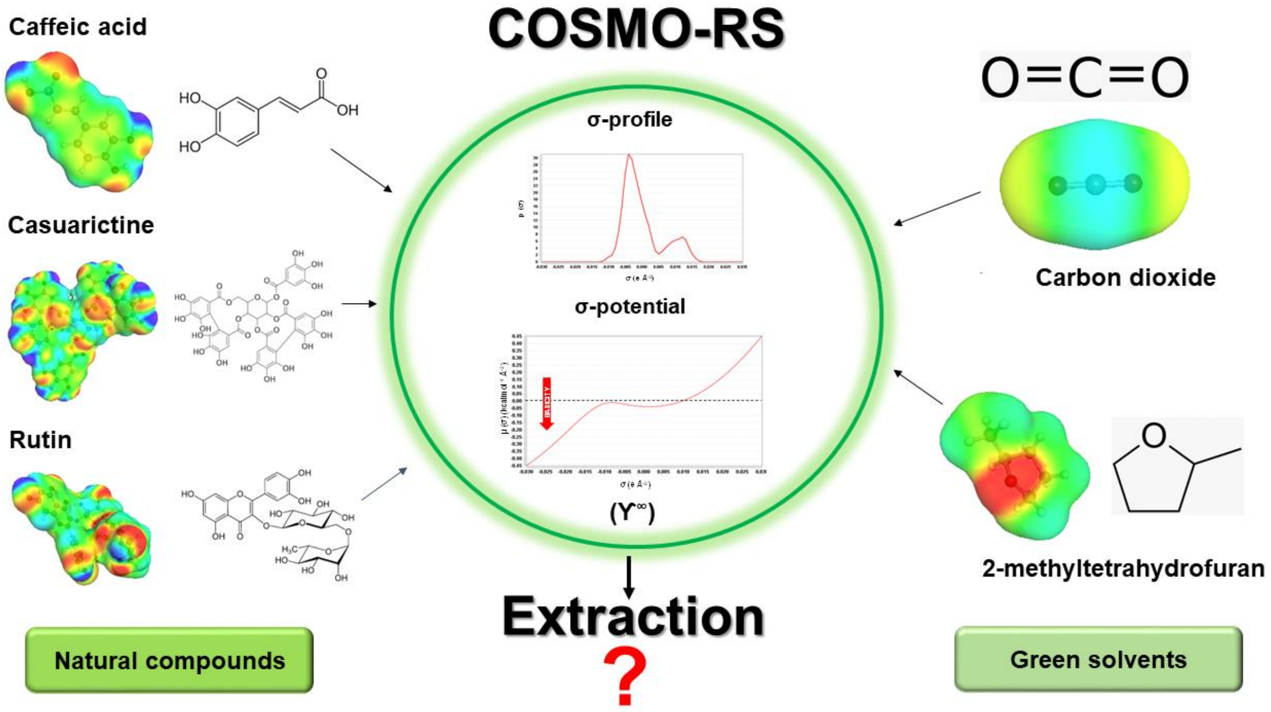

Figure 1: Employed approach to evaluate the possibility of extraction for natural compounds with different "green solvents" (Shown molecules as examples)

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[PC-05]

Adsorption of HCN on Amorphous Ice under Interstellar Conditions

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The adsorption of hydrogen cyanide (HCN) on low density amorphous (LDA) ice is investigated under interstellar conditions by grand canonical Monte Carlo (GCMC) simulations. HCN is known to be present in the interstellar medium, and its reactivity on icy surfaces might lead to the spontaneous formation of several building blocks of large biomolecules, such as proteins and nucleic acids. Thus, for example, adenine is formally a pentamer of HCN, and such an oligomerization reaction can occur under interstellar conditions, given that the local concentration of HCN is large enough. A potential mechanism of such HCN enrichment is its adsorption on LDA ice, known to cover the surface of comets and interstellar dust. To investigate the problem of HCN adsorption, we have performed a set of GCMC simulations, in which we have systematically varied the HCN chemical potential, and calculated, as its function, the number of adsorbed molecules. This way, we determined the adsorption isotherm at three different temperatures, namely, at 50 K, 100 K, and 200 K. To distinguish between the HCN molecules that are dissolved in bulk LDA ice, those forming the first molecular adsorption layer, and those belonging to outer adsorption layers, the Identification of the Truly Interfacial Molecules (ITIM) method [1] has been used, as implemented in the freely available Pytim software [2]. We have found that a considerable fraction of the HCN molecules are dissolved in the bulk LDA phase, however, while the adsorption becomes stronger, the dissolution becomes weaker with decreasing temperature. Thus, while adsorption of HCN is an exothermic, its dissolution is an endothermic process. To characterize the adsorption layer, we have calculated the density profile of the adsorbed molecules, as well as the orientational and binding energy distributions of the first layer HCN molecules. Our results reveal that adsorbed molecules prefer to stay more or less parallel with the ice surface, and their stay is stabilized by up to 2 hydrogen bonds with the surface water molecules and their HCN neighbors.

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[PC-06]
Anisotropic Molecular Reorientation of Methanol Unravelled

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Based on its tendency to form linear hydrogen-bonded aggregates in the condensed phase, the reorientaional motion of methanol shows a significant degree of anisotropy. The reorientation of different molecule-fixed vectors can be addressed with NMR relaxation experiments of specific quadrupolar nuclei such as ^{2}H and ^{17}O. However, the accurate determination of reorientational motions in liquids from those experiments requires precise knowledge of the respective quadrupolar coupling constants (QCCs) and the orientation of the electric field gradient principle axis system (EFG-PAS) at the position of the nuclei within the molecular frame.

In this study, we present a procedure for computing those quantities for ^{2}H- and ^{17}O-nuclei for the gas-phase, liquid, and solid-state and the ^{1}H chemical shifts of the hydroxyl proton for liquid methanol. The properties are computed *ab initio* using clusters sampled from MD simulations for two different force field models. We can directly relate their absolute magnitude, temperature, and model dependence to changing local structural features. Moreover, the magnitude of the quadrupolar coupling depends on the proton chemical shifts. Our calculations additionally provide nearly model-independent relationships between the diffusion coefficient and the ^{2}H- and ^{17}O EFG-correlation times addressing different intramolecular motions. The accurate computation of the correlation times in combination with the knowledge of the quadrupolar coupling strength for ^{2}H- and ^{17}O-nuclei allows the description of quadrupolar relaxation processes in nearly quantitative agreement with experimental data [1,2]. This allows us to reinterpret existing experimental data and provide new, and better justified "experimental" reorientational correlation times for various molecule fixed vectors in liquid methanol.

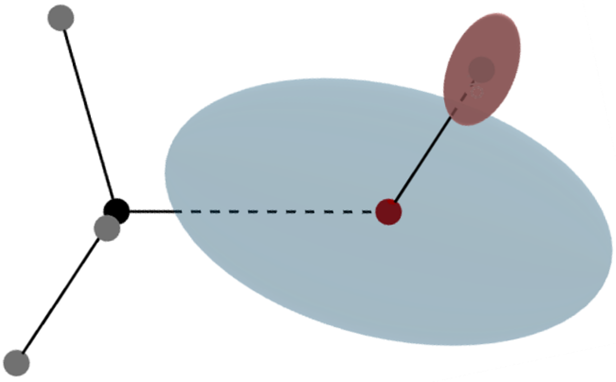

Figure 1: Representation of the EFG-PAS for ^{2}H and ^{17}O in methanol. The vectors defining the PAS within the molecular frame are computed from averaging over the sampled quantum-chemically derived EFG-PASs.

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[PC-07]

Supercooled water in two dimensions: Structure and thermodynamics of the Mercedes - Benz model

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Simple models have played an important role for the understanding of matter at the molecular level. Particularly for such a substance as water with its number of anomalies. Among such models there belongs the two-dimensional (2D) Mercedes-Benz (MB) model introduced in 1971 by Ben-Naim [1]. It is one of the earliest models accounting explicitly for the phenomenon of hydrogen bonding (H-bonding). In the model the molecule is represented by a soft disk with three arms in the arrangement resembling the logo of MB cars. The strongly orientation dependent short-range attraction between the arms mimics then H-bonding. The model was intensively studied, both theoretically and numerically [2,3,4]. Despite all the effort invested so far, the phase behavior of the MB model is not fully understood yet. A part the phase diagram obtained from molecular simulations was reported long time ago by Silverstein et al. [4] and Urbic reported both simulation and theoretical results in his recent review [5]. Melting of 2D systems is known to follow not only the common first order solid-liquid transition but also the melting via the hexatic phase [6]. Moreover, in the last two decades there was also interest in the behavior water in the supercooled region with a potential existence of a second critical point. We are not aware of any study dealing with these phenomena in the case of the MB model.

In this work, the MB model has been studied by molecular simulations over a wide range of thermodynamic conditions as an attempt to locate the supercooled region where a liquid-liquid separation and, potentially, also other structures may occur. Both the correlation functions and a number of local structure parameters have been used to identify different structural arrangements. These arrangements were recognized as an sets of hexagons, pentagons, and quadruplets. All these structures result from the competition between the hydrogen bonding and Lennard-Jones interactions and their effect at different temperatures and pressures.

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[PC-08]

Interfaces between Metal Organic Frameworks and Ionic Liquids Probed by Molecular Dynamics Simulations

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Type III porous liquids are defined as porous solid hosts dispersed in size-excluded liquids. These multiphase fluids have potential in processes such as gas storage, ion transport, energy storage, separation, and catalysis.[1] In this work the interactions on Type III porous liquids were characterized using classical Molecular Dynamics (MD) simulations. For this purpose, the mobile phase consisted of Ionic Liquids (ILs), while the solid substrate comprised Metal-Organic Frameworks (MOFs).

The ILs chosen in this study were $[P_{6\,6\,6\,14}][NTf_2]$, $[C_{14}C_1im][NTf_2]$, $[N_{14\,1\,1\,2OH}][NTf_2]$ and $[C_{14}C_1im]Cl$ representing different possible arrangements of cations and anions interacting with MOFs (Figure 1). The MOF used was the crystalline structure of ZIF-8, consisted of zeolitic imidazolate frameworks.

The MD analyses indicate that $[P_{6\,6\,6\,14}][NTf_2]$, $[N_{14\,1\,1\,2OH}][NTf_2]$ and $[C_{14}C_1im][NTf_2]$ are affected by the presence of the MOF, while $[C_{14}C_1im]Cl$ show no deviation in comparison with its bulk phase results. Near the ZIF-8 surface the first three ionic liquids are settled in a chessboard-like pattern formed by the cation headgroups and anions. This pattern is less defined for $[P_{6\,6\,6\,14}][NTf_2]$, that has a more pronounced non-polar part attached to the cation. In addition, the Cl^- anion changes radically the behaviour of $[C_{14}C_1im]Cl$ polar part near the ZIF-8 interface.

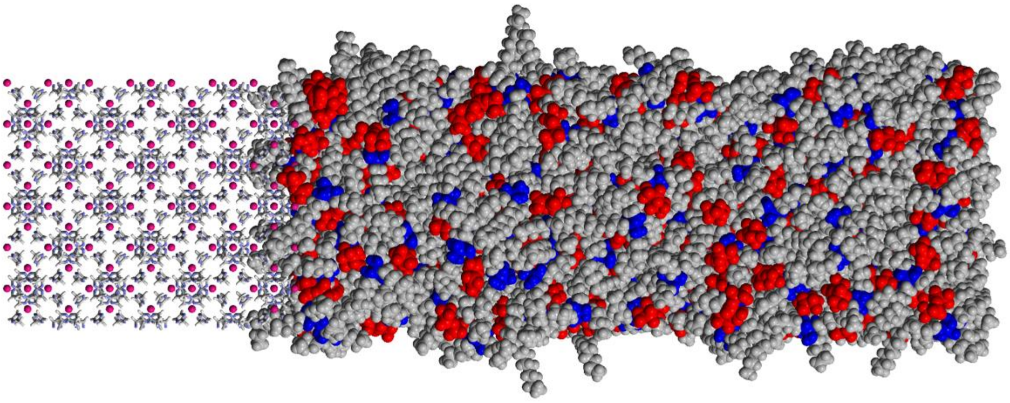

Figure 1: *Snapshot of the ZIF-8/$[P_{6\,6\,6\,14}][NTf_2]$ system simulated at 350 K.*

Acknowledgments: Fundação para a Ciência e a Tecnologia (FCT – Portugal) through contracts IST-ID/100/2018 (K.S.) and IST-ID/93/2018 (A.A.F.). Projects UIDB/00100/2020, UIDP/00100/2020, LA/P/0056/2020, PTDC/QUI-QFI/29527/2017 and CPCA/A1/470169/2021.

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[PC-09]

Molecular Dynamics Simulations of Lithium-ion Transport in Concentrated Sulfolane-LiBF$_4$ Mixtures

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Nonaqueous polyelectrolyte solutions, aqueous Li^+-ion batteries, eutectic mixtures, superconcentrated or highly concentrated electrolyte (HCE) solutions have received increasing attention as strategies to overcome safety and environmental issues regarding conventional Lithium-ion batteries (LIBs) [1]. In this work we employed molecular dynamics (MD) simulations to explore the solvation behavior of sulfolane-$LiBF_4$ mixtures going to [$LiBF_4$] up to ca. 6 mol.L^{-1} (Figure 1). The results indicate that the relaxation dynamics of the contact ion pair and Li-sulfolane pair follows a Kohlrausch–Williams–Watts function. Also, the primary steps of the pair relaxation in $LiBF_4$-sulfolane mixtures are analogous to that seen in glass-forming materials at much lower temperatures [2,3]. At fully percolated conditions, i.e., in the presence of two continuous networks (cation-anion and cation-solvent), the relaxation of the contact ion pair is dictated by long-range Coulomb interactions, while density fluctuations play an important role in relaxation of the Li^+–sulfolane pair. The Li-ion transport changes from cage diffusion to hopping conduction, similar to the Grotthuss mechanism of proton transfer.

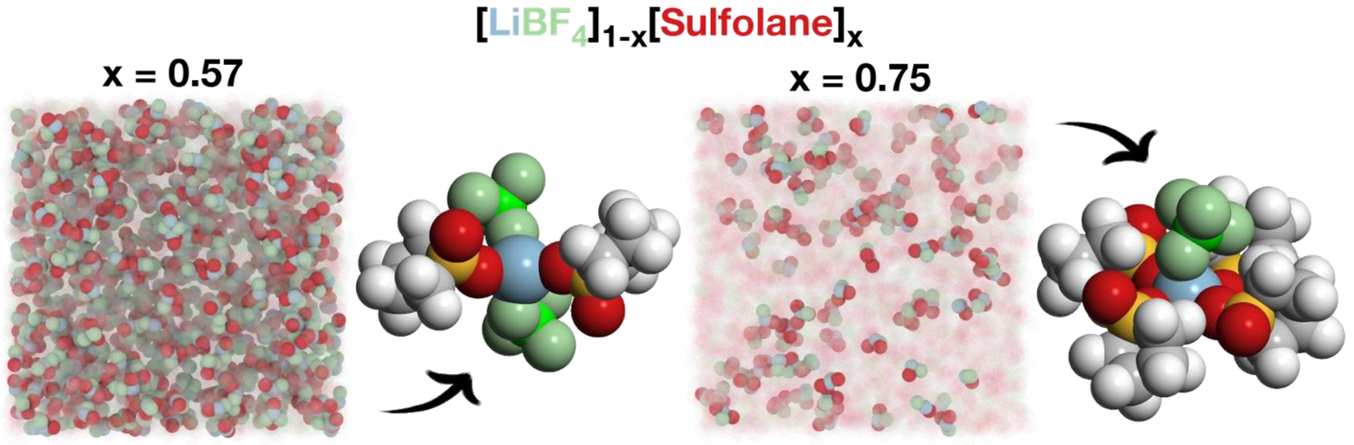

Figure 1: MD simulation snapshots depicting the polar networks of the sulfolane/$LiBF_4$ mixtures. Only the Li^+ ions shared simultaneously by O atoms from sulfolane and F atoms from BF_4^- are displayed. The highlighted structures show the vicinity of the Li^+ ions. The colors grey, red, yellow, blue, light and dark green represent C, O, S, Li, B and F atoms, respectively.

Acknowledgments: Fundação para a Ciência e a Tecnologia (FCT – Portugal) through contracts IST-ID/100/2018 (K.S.) and IST-ID/93/2018 (A.A.F.). Projects UIDB/00100/2020, UIDP/00100/2020, LA/P/0056/2020, PTDC/QUI-QFI/29527/2017 and CPCA/A1/470169/2021.

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[PC-10]
Calcium versus potassium selectivity in a nanopore: the effect of charge inversion at localized pore charges

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The Anomalous Mole Fraction Effect (AMFE) in negatively charged pores has been considered as a signature of Ca2$^+$ vs. monovalent ion (K^+, in this study) selectivity. Increasing the mole fraction of Ca^{2+} in the KCl/$CaCl_2$ mixture, the total conductance first declines as Ca^{2+} ions replace K^+ ions inside the pore, then it increases as Ca^{2+} becomes the main charge carrier. While the AMFE was first pointed out in calcium selective ion channels, in a previous study (Gillespie et al., Biophys. J. 95 (2008) 609–619.) we showed that it is also present in synthetic nanopores. Here we use the Local Equilibrium Monte Carlo method coupled to the Nernst-Planck transport equation to study a simple model of a finite nanopore in a membrane with ions being explicitly modeled as charged hard spheres and water as an implicit continuum. The novel component of the model is the treatment of the pore charges that are present in localized COO^- groups on the wall of the nanopore. Therefore, we study the effect of localizing the pore charges instead of smearing them as a continuous surface charge. Localized charges profoundly influence Ca^{2+} vs. K^+ selectivity because they enhance charge inversion at the pore wall. Ca^{2+} ions overcharge the pore wall at which the K^+ ions have a disadvantage in the K^+ vs. Ca^{2+} competition because the overcharged pore wall does not attract them so strongly.

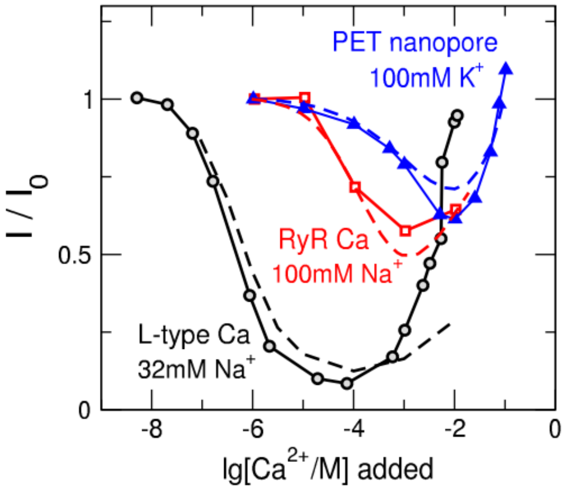

Figure 1: *The AMFE experiments for different nanopores [2]*

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[PC-11]

Pickup properties of water clusters developed in supersonic expansion

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The water clusters can be created experimentally via supersonic expansion of vapor.[1] An ability of picking up the molecules from the cluster vicinity can be quantified by the cluster pickup cross-section. The cross-section depends on substance of the cluster and on the picked molecule. This quantity can be measured in supersonic expansion experiment [2]. Our approach allows to determine the pickup cross-section using MD methods and to compare these measured values with the experiment.

The measurement procedure can be divided into three parts. At the first part, MD simulation of water vapor supersonic expansion is performed. The simulation runs in adiabatic regime without any external thermostat or barostat. The algorithm of this simulation has been published in [3, 4]. At the end of the simulation, the water clusters are created. These clusters are cut out of the simulation box and its translation motion is removed. The last step of whole procedure is the cross-section measurement. The cluster is placed at the center of the simulation box and a two dimensional molecular grid is created. The velocity with direction perpendicular to the grid is assigned to each molecule. The velocity magnitude is assigned randomly from the Maxwell-Boltzmann distribution to mimic a real experiment. Next, each molecule is shot to the cluster independently in a separate simulation. These simulations are evaluated and classified as sticky/nonsticky interaction. From the knowledge of molecules initial positions and the classification, the cluster cross-section can be evaluated. The results of these measurements for different molecules are compared with the experimental data.

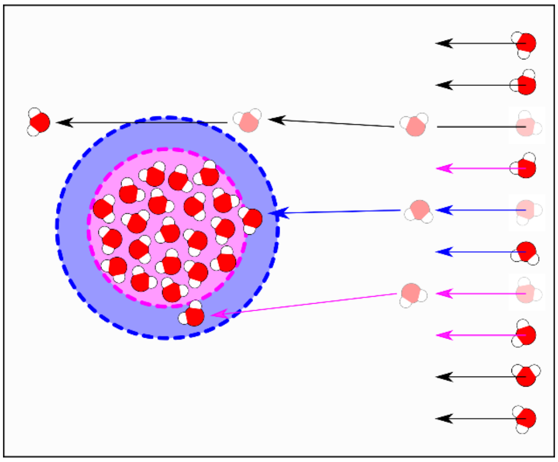

Figure 1: *Scheme of pickup cross section measurement. The cluster is placed in the simulation box center and a molecular grid is prepared. Molecules from the grid are shot to the cluster one by one with a given velocity.*

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[PC-12]

Viscosity of supercooled water under pressure and a proposed range for its putative liquid-liquid critical pressure

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Many of water's physical properties are anomalous compared to other liquids. Several thermodynamic scenarii have been put forward to explain those anomalies [1]. One of them is a putative liquid-liquid transition (LLT) between a low-density and a high-density phase, that would end at a liquid-liquid critical point (LLCP). According to simulations with the TIP4P/2005 model of water [2,3,4], the LLCP influences the temperature and pressure dependence of the Stokes-Einstein ratio, that relates dynamical characteristics of water (viscosity and self diffusion coefficient).

I will present the Stokes-Einstein ratio that we deduced from our measurements of the viscosity of deeply supercooled water under pressure [5,6] using existing self-diffusion data [7]. I will compare to the Stokes-Einstein ratio that we could deduce from our measurements on deeply supercooled heavy water [8,9,10] and conclude about the possible pressure of the putative LLCP.

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[PC-13]

Thermodynamic Description of Aqueous Mixtures of New, Less Toxic Green Antifreezes

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HGVs continuously become greater and their engines more powerful. Although combustion engines for motor vehicles will disappear on a long-term sight, this class of engines will still carry out a substantial role for the multifaceted applications for many years further. As a consequence of power increase leading to high local surface temperatures of up to 260 °C in a modern engine, also the requirements on coolants regarding stability and ability to maintain the dissipation of heat are increased. Recent developments for internal combustion engines expose the heat transfer fluid to increased thermal loads [1,2]. Since currently applied antifreezes (coolants) seem to be unstable at elevated temperatures, new systems are needed which fulfill the technical requirements but also those of sustainable chemistry that is not expensive, non-toxic, and efficient. In search for possible alternatives and to create an overview about freezing point depressants in use, several compounds are checked. In this work, aqueous solutions of five molecule classes are studied in a wide temperature and composition range. Diols: 1,2-propanediol and 1,3-butanediol; glycols: monoethylene glycol (EG), diethylene glycol, triethylene glycol and tetraethyleneglycol; glycerols: glycerol and diglycerol; carbonic acid salts: potassium acetate, sodium propionate and potassium propionate (KPro); lactones: γ-valerolactone (GVL). The latter is a new prospective, water-miscible solvent that could be synthesized from cellulosic biomass and successfully used in a variety of commercial products. It could be utilized in large-scale chemical processes and shows a very low toxicity towards environment. The solvent is rapidly biodegradable [3]. Vapor pressure osmometry measurements were applied to the systems EG + water, KPro + water, GVL + water for varying molalities ($m_{EG} = 2.0–24.0$ mol/kg, $m_{KPro} = 0.002–2.0$ mol/kg, $m_{GVL} = 0.2–165$ mol/kg) at T = 298.15 K. From vapour pressure osmometry, concentration dependent activities of water, activity coefficients of water and the corresponding osmotic coefficients of the mixtures have been calculated, both being directly related to the chemical potentials of the different species and therefore to their Gibbs energy. The densities of GVL + water mixtures are measured at T=278.15–328.15 K (in steps of 10 K) with the accuracy 0.00001 g/cm^3 in the composition range $x_2 = 0–1$. The data were generalized and systemized with interpolated data from literature or reported in previous works [4] as next database: osmotic coefficient values at m = 2–24 mol/kg for aqueous solutions of the diols and glycols and at m = 0.002–5 mol/kg for the solutions of the salts at the temperature 298.15 K, densities and viscosities measured at m = 2–14 mol/kg for the solutions of the diols and glycols and at m = 2–5 mol/kg for the solutions of the salts in the temperature range from 238.15 to 368.15 K; volumetric heat capacity and specific heat capacity values determined for m = 2–14 mol/kg for the solutions of the diols and glycols and at m = 2–5 mol/kg for the solutions of the salts in the temperature range from 298.15 to 368.15 K. The conclusions on applicability of liquids with the best flow behavior and thermal properties as antifreezes have been done.

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[PC-14]

Understanding the dynamics of ionic liquids by means of fast-field-cycling NMR relaxometry and molecular dynamics simulations

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We present a combined approach of Fast-Field-Cycling (FFC) NMR relaxometry and molecular dynamics (MD) simulations towards a better understanding of the dynamics in ionic liquids (ILs). Here, we focus on the IL triethylphosphonium bis(trifluoromethylsulfonate)imide ($[P_{222H}][NTf_2]$). In contrast to their ammonium-based analogues the dynamics of phosphonium-based ILs are little studied. Spin-lattice-relaxation rates for ^1H and ^{19}F have been recorded in the range of 0.01 kHz and 38 MHz using FFC-NMR. Since the proton nuclei are merely located on the cation and the fluorine nuclei on the anion, the physicochemical properties of both ions can be investigated separately from each other. Applying different analytical models, the relaxation rates have been dissected into their intra- and intermolecular contributions. While the intramolecular contribution allows access to rotational correlation times, the intermolecular part yields in translational correlation times as well as self-diffusion coefficients. [1] We want to point out that the well-known Bloembergen-Purcell-Pound approach, assuming isotropic rotational motion, is valid for the description of the cation, but not for the anion. [2] Here, based on the internal rotation of the CF_3-groups a more complex relaxation model has to be introduced. MD simulations based on a polarizable forcefield are used to complement our FFC-NMR experiments: We compute both the intra- and intermolecular frequency-dependent contributions to the dipolar NMR relaxation rates for the ^1H and ^{19}F nuclei. We find them in good agreement with our FFC-NMR experimental data. Moreover, our MD simulations provide detailed insight in the dynamical processes and emphasize the importance of considering internal rotations in the employed analytical models.

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[PC-15]

Towards understanding the structure and dynamics of localized high-concentration battery electrolytes

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In recent years high-concentration liquid electrolytes (HCEs) received much attention in the battery research due to the evident performance advancement achieved in lithium-based batteries. HCEs offer lots of advantages comprising, among others, broad electrochemical stability window, current collector protection, high safety, an effective solid electrolyte interface (SEI) formation, and therefore a high rate capability and stable galvanostatic cycling.[1] However, due to the high conducting salt content, HCEs are very viscous thus resulting in low ionic conductivity. This is why the concept of localized high-concentration electrolytes (LHCEs) was developed and first published by Chen et al. in 2018.[2] Here, a third component, the diluent, is added to the system to reduce the viscosity without participating in the ion solvation. Thus, the local environment of the ions, which is responsible for the described benefits of a HCE, remains unchanged and the main disadvantage, the low ionic conductivity, is improved.

However, the structural heterogeneity of the LHCEs and the complexity of their composition require further research to gain a profound understanding of the structure and ion dynamics in order to reach the full potential of this type of electrolyte formulation. Therefore, in this work a LHCE consisting of the conducting salt lithium bis(trifluoro-methanesulfonyl)imide (LiTFSI), the solvent 1,2-dimethoxyethane (DME), and the diluent 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) was investigated by systematically varying the molar ratios of the three components in order to gain information about the structure and lithium dynamics in the formulation. A combination of selected complementary spectroscopic methods, namely NMR, Raman, and impedance spectroscopy, was used and supported by molecular dynamics (MD) simulations. To further analyze the influence of the anion on the solvation, the obtained results were compared to an electrolyte formulation containing lithium bis(fluorosulfonyl)imide (LiFSI) as the conducting salt. It was shown that this small variation already has a significant impact on the lithium coordination structure and therefore lithium dynamics in the electrolyte formulation.

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[PC-16]

Propulsion from energy bursts for nitromethane in water

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Energy dissipation is of interest for the accurate generation and control of movement in micro and nano-particles. Studying molecular relaxation after a vibrational excitation has potential applications in multiple fields. We consider the nitromethane molecule, whose energy relaxation after vibrational excitation has already been studied in argon gas [1,2].

Prompted by the amphiphilic nature of nitromethane we study its relaxation in liquid water. We perform high energy excitations (200 kJ/mol) of individual modes and study energy relaxation via all-atom molecular dynamics simulations. Our results show that, as expected, some normal modes relax considerably faster than others. These faster modes have associated motions related to the nitro group, which is to be expected due to the hydrophilic nature of the functional group. To get more insight into the relaxation mechanisms we also studied the work performed by the nitromethane molecule on the surrounding water molecules [3]. Ourmain finding is that energy relaxation is remarkably asymmetric, favoring the nitro side (30% more work is performed to the nitro side).

To our knowledge this is the smallest molecule for which a marked asymmetry has been found, irrespective of the excited mode. Excitations of specific normal modes also induce a short time impulse in the symmetry axis. This response is linked to a high translational work, in addition to the fast relaxation and asymmetric relaxation.

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[PC-17]

Simulation and modelling of the dynamic structure of water with the BK3 potential

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The BK3 potential is a simple polarizable intermolecular potential of water based on a charge-on-spring model [1] which proved to be a good model to reproduce several properties of water, such as the density, the self-diffusion coefficient and the compressibility as a function of temperature and pressure [2,3]. In this work, we focus on the dynamic structure factor S(q,ω) and on the longitudinal and transverse current correlation spectral densities $C^L(q,\omega)$ and $C^T(q,\omega)$. MD results of atom-atom partial functions $C^L_{OO}(q,\omega)$, $C^L_{HH}(q,\omega)$, $C^T_{OO}(q,\omega)$ and $C^T_{HH}(q,\omega)$ are fitted using Generalized Collective Modes model involving relaxing modes occurring in the longitudinal component and propagating modes occurring in both components [4]. The effect of temperature is explored by comparing simulations results at 298 K and 350 K at ambient pressure.

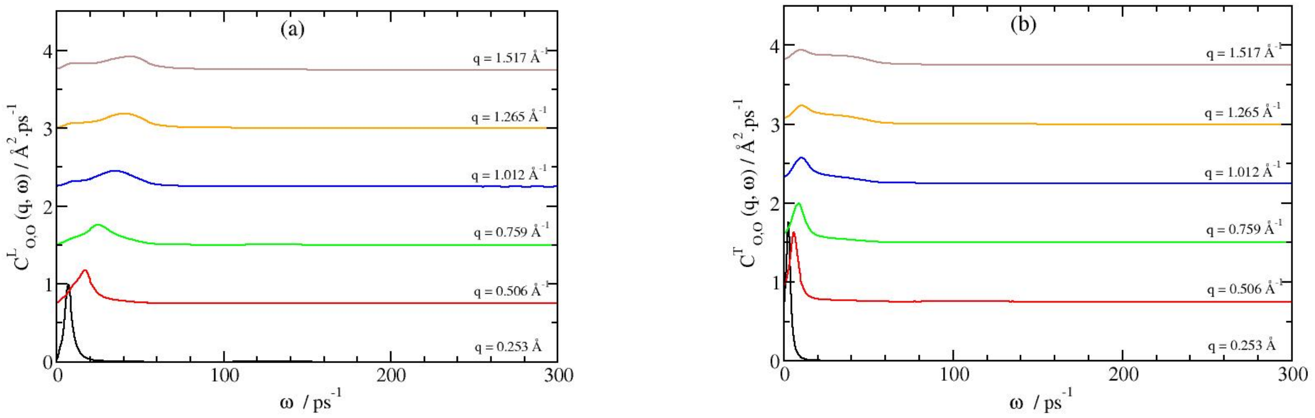

Figure: *Partial oxygen-oxygen current correlation spectral densities at 298 K for 6 values of the wave vector q.*
a) longitudinal part $C^L_{OO}(q,\omega)$ *b) transverse part* $C^T_{OO}(q,\omega)$

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[PC-18]

Medium- and Short-Range Structure of $LiNTf_2$-Water-in-Salt-Electrolytes from Molecular Dynamics Simulations

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The need for cheap and efficient energy storage systems is one of the most pressing issues of the 21st century. Due to their rather high conductivity and good stability, LiNTf2-water-in-salt systems have recently gained significant attention as an environmentally friendly electrolyte for large-scale energy storage applications. While a lot of research is focusing on the stabilization of the electrochemical window, our work aims at a better understanding of the microscopic properties and structural intricacies of those water in salt mixtures. By using Molecular Dynamics (MD) simulations [1, 2], we provide insights into the structure of the LiNTf2 water in salt mixtures for various mixture compositions and temperatures. Previous studies have shown that the water network is disrupted at sufficiently low water concentrations, whereas the anions themselves form a network by connecting to each other [3]. While the dynamics of these systems have been well-examined theoretically and experimentally, [4] we took a deeper look into the formation of Li-water and water-water clusters, their cluster-size distributions and fluctuations. In particular, we are interested in how these structural features affect the structure factor determined from neutron scattering experiments in the medium to small angle regime.

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[PC-19]

The effect of alkyl length of ionic liquids 1-alkyl-3-methylimidazolium acetate (alkyl length 2-7) on cellulose solubility

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Ionic liquids (ILs) are salts in the liquid state at room temperature and are mainly composed of asymmetric organic cations and organic or oriented anions. ILs exhibit unique properties such as nonflammability, high thermal and electrochemical stability, and low vapor pressure. ILs are expected to replace conventional strong acids and bases as solvents because of their ability to dissolve cellulose [1]. In particular, 1-alkyl-3-methylimidazolium acetate ([CnMIm][OAc])(Figure 1) is known to dissolve cellulose well, and it has been reported that the addition of dimethyl sulfoxide (DMSO) further increases the solubility of cellulose [2]. It has also been reported that the solubility of cellulose in [CnMIm][OAc]/DMSO mixtures reaches a maximum at a carbon number (n) of 4 in the alkyl chain, and that the cases of even numbers show relatively higher solubility than that of odd numbers, i.e. an even-odd effect was exhibited [2,3]. However, the molecular interpretation of such phenomena has not been fully understood. In this study, we investigate why the even-odd effect is exhibited in the solubility of cellulose by using MD simulations.

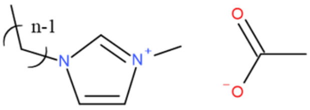

Figure1. Structure of [CnMIm][OAc]

Gromacs 5.0.7 [4] was used for the simulation, with using parameters by Sambasivaro [5] for [CnMIm][OAc] force field, charge AM1-BCC, and for DMSO, non-binding potential OPLS-AA/L binding potential GAFF. Glycam06 [6] was used for Cellulose (Degree of Polymerization 8).

As an indicate to evaluate solability of cellulose in the cases of IL solution or IL+DMSO solution (60 mol% of DMSO), the coordination number of anions to cellulose is shown as a function of the alkiyl length of [CnMIm] in Figure 2. Especially in the case of IL+DMSO conditions, alkyl chains of even numbers clearly showed higher coordination number than that with odd numbers. The result indicated that more anion can access to cellulose in the case of even number of alkil chain, and it supported the even-odd effect.

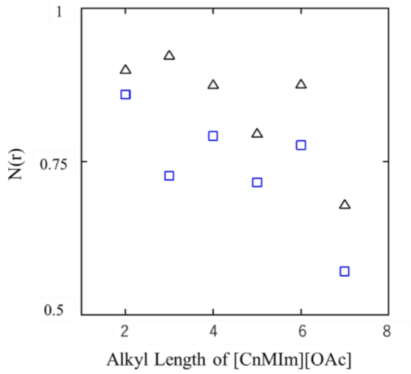

Figure 2. Coordination number of anions to cellulose
(△)Pure IL , (□)IL+DMSO(60 mol%)

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[PC-20]

Effect of Preparation Condition (Temperature and Hydrostatic pressure) on Physicochemical Properties of Cellulose Hydrogel Using Ionic Liquid

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Cellulose hydrogels (CHGs) are gels which are consisted of cellulose and water and have various advantages such as non-toxicity, biocompatibility, biodegradability, etc. Therefore, CHGs are expected to be used in wound dressings, tissue engineering, drug delivery systems, filtration separation, and other applications [1,2]. Because certain physicochemical properties such as mechanical strength and water content are required depending on the application, these properties are recommended to be tunable. In general, it is known that the preparation conditions can change gel properties.

In this study, the effect of “Temperature” and “Hydrostatic pressure” on physicochemical properties of CHGs such as mechanical strength, gel size, water content, and crystallinity were thoroughly investigated. In addition, the mechanism of how temperature and hydrostatic pressure affect the gel properties was elucidated using Nuclear Magnetic Resonance (NMR), Molecular Dynamic (MD) Simulation, and Density Functional Theory (DFT) calculation.

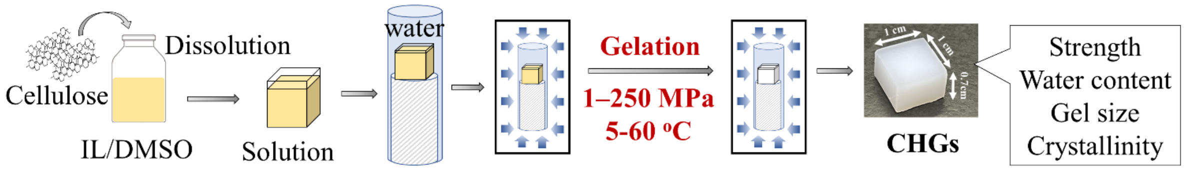

Fig. 1. Manufacturing process diagram of CHGs

Fig 1. shows the manufacturing process diagram of CHGs. CHGs (1 X 1 X 0.7 cm) were prepared by dissolving cellulose in 60 wt% Ionic Liquid (IL 1-butyl-3-methylimidazolium acetate) /dimethyl sulfoxide (DMSO) and gelating the resultant solution by displacing it in water at a temperature ranging from 5 to 60°C and hydrostatic pressures ranging from 0.1 to 250 MPa.

The result of gelation temperature revealed that with decreasing gelation temperature, the mechanical strength (compressive modulus, compressive strength, and fracture strength) and crystallinity increased whereas the gel size and water content decreased. Moreover, all gel properties exhibited highly cooperative two-state transitions, with the transitional midpoint at approximately 36°C according to the gelation temperature.

The result of hydrostatic pressure revealed that with increasing hydrostatic pressure, the mechanical strength (compressive strength, and fracture strength) increased whereas the gel size and water content decreased. Whilst, compressive modulus and crystallinity were not influenced by hydrostatic pressure.

The mechanism of how temperature and hydrostatic pressure affected gel properties was investigated using MD simulation, ^{1}H NMR, and DFT calculation. It was found that the lower the temperature is, the weaker the interaction between cellulose chains and ionic liquid which disturbs cellulose chains aggregating during gelation. For this reason, cellulose chains packed well at lower temperatures, and CHGs with high crystallinity, high mechanical strength, low gel size, and low water content were formed. In addition, MD simulation revealed that the higher the hydrostatic pressure is, the weaker the interaction between cellulose chains and ionic liquid, which promoted aggregation between the cellulose bundles that form the backbone of CHGs. For this reason, CHGs with low water content and high mechanical strength were formed.

These results provide deep insight into the dependence of gel properties on “Temperature” and “Hydrostatic pressure” during gelation and a platform to expand applications.

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[PC-21]

Towards universal integration scheme for molecular dynamics

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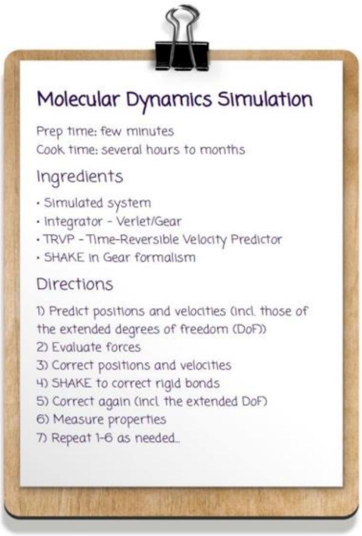
Currently, the most frequent molecular dynamics (MD) integration methods use the Verlet integrator, which seems simple [1]. However, it is not straightforward to implement some ensembles (like isothermal-isobaric) within the extended Lagrangian framework because the equations of motion contain velocities [2]. These factors complicate simulation software development. Here, we propose a universal integration scheme for solving the currently used sets of equations of motion in MD. To achieve this, we adapted the traditional SHAKE method for treating rigid bonds [3] to a predictor-corrector (PC) integration scheme and combined it with the existing Time-Reversible Velocity Predictor (TRVP) [2]. This new approach enables the use of both the time-honoured Verlet method and the recently improved Gear methods [4]. We tested the resulting universal integration scheme on two systems: SPC/E water and a relatively complex ionic liquid (1-ethyl-3- methylimidazolium tetrafluoridoborate). Trajectories in microcanonical, Nosé–Hoover canonical and MTK isobaric ensembles were generated. The results were in excellent agreement with those obtained using conventional integration methods. Thus, our universal approach provides a significantly simpler route to devise new integrators and maintain existing simulation software.



Molecular Dynamics Simulation

Prep time: few minutes
Cook time: several hours to months

Ingredients

- Simulated system
- Integrator - Verlet/Gear
- TRVP - Time-Reversible Velocity Predictor
- SHAKE in Gear formalism

Directions

1) Predict positions and velocities (incl. those of the extended degrees of freedom (DoF))
2) Evaluate forces
3) Correct positions and velocities
4) SHAKE to correct rigid bonds
5) Correct again (incl. the extended DoF)
6) Measure properties
7) Repeat 1-6 as needed.

Figure 1: *A universal “recipe” for MD simulation.*

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[PC-22]

Study on the relationship between alkyl chain length of 1-alkyl-3-methylimidazolium bromide and hatchability of Artemia eggs

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Ionic liquids are salts composed of anions and cations with melting points below 100°C. They have potential applications in various fields. However, it is important to obtain information on the toxicity of ionic liquids because of their potential impact on aquatic organisms. Previous studies have reported that ionic liquids become more toxic as the carbon number of the alkyl chain of the cation increases, but most of these studies were conducted with even carbon numbers, mostly in adult Artemia and adult zebrafish [1].

Therefore, in this study, we systematically investigated the effects of ionic liquid concentration and the number of carbons in the alkyl chain (2-10) of an aqueous 1-alkyl-3-methylimidazolium bromide/NaCl solution on the hatchability rate of Artemia eggs.

Nine different 1-alkyl-3-methylimidazolium bromide in alkyl chain length ([C_nMIM]Br (n=2~10)) ionic liquids were used. Artemia eggs were incubated at a water temperature of 28°C in a mixture of NaCl solution with a salinity of 3.5 wt% with a series of concentrations of each ionic liquid. The number of hatched Artemia individuals was measured, and the hatchability rate after 24, 48, and 72 hours was determined using the formula (Nauplius larvae hatched) / (eggs fed). Based on the relationship between hatchability and ionic liquid concentration, EC_{50} concentration of ionic liquid that inhibited the hatching of half of the eggs was determined.

Figure 1 shows the EC_{50} obtained from the hatchability rate at 72 hours. The hatching inhibition was increased with an increase of the number of carbon up to 4, where the maximum was obtained. Then beyond the carbon number of 4, the effect decreased with an increase of the carbon number.

In the presentation, we will discuss the dependence of the hatching inhibition effect of [C_nMIM]Br on the carbon number of the alkyl chain, comparing with the EC_{50} of dimethyl sulfoxide, which is commonly used for cell preservation, and other ionic liquids.

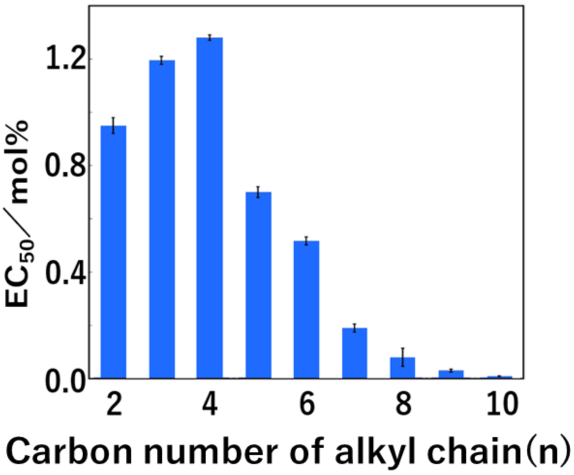

Figure 1: EC_{50} of [C_nMIM]Br (n=2~10)

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[PC-23]

Spectroscopic Investigations of Amino acid based Ionic Liquids for Carbon Capture

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Spectroscopy and quantum computational calculations provide an excellent way to investigate subtle changes in the environment of ionic liquids. Minor influences in the chemical surroundings are often enough to see subtle changes in the electronic configuration. Within this work, we report the investigation of different 1-Ethyl-3-Methyl-Imidazole amino acid based ionic liquids [EMIm][AA] and their mechanistic capability in the capture of carbon dioxide.

Since the amine moieties alone already have the capacity in binding CO_2 by forming carbamic acid or carbamate the C2 position in the Imidazole is claimed to have a similar effect, depending on the anion. [1, 2, 3]

Structural investigations in advance are inevitable for the elucidation of such loading processes. Since physisorption alone cannot deal with large-scale uptake chemisorption comes into focus, especially with the tunability of ionic liquids in mind. [1, 4] Synthetically the corresponding ionic liquids can be obtained by acid base reactions as shown before allowing a broad facet of tailored ILs. [5]

Spectroscopic methodologies shell shed more light onto the hydrogen-bonded network of the respecting ionic liquids [EMIm][AA] and their CO_2-loaded counterparts leading to a better understanding of the ongoing mechanisms.

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[PC-24]
Liquid Dynamics in Metal-NHC Complex Formation

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N-heterocyclic carbenes (NHCs) are ligands, often used in transition metal catalysis.[1] For the preparation of those complexes from the metal compound and the azolium cation there exist several pathways, e.g. transmetalation or by using strong bases. In this work, a pathway using weak bases to from the metal-NHC complex is investigated. This specific pathway has lots of advantages compared to the other ones, like not requiring inert atmosphere of harsh reaction conditions and it even shows much broader applicability in terms of the metals that can be used.[2] In earlier works, quantum chemical methods were already applied in order to understand the underlying mechanism of this reaction. It was discovered that in this pathway, no free carbenes are formed, but rather the reaction happens in a concerted fassion, cleaving the C-H bond simultaneously with the formation of the C-M bond.[3] Herein, the mechanism is also labeled as the "associative pathway".

The mechanism of metal-*N*-heterocyclic carbene (NHC) complex formation from imidazolium salts in the presence of weak bases was investigated through theoretical methods. Quantum chemical calculations revealed that the two bases considered here, sodium acetate and trimethylamine, both facilitate complex formation. In contrast to previous experiments, these calculations indicated a slightly lower barrier with the amine. Molecular dynamics simulations showed that the ionic nature of the $[AuCl_2]^-$ and imidazolium ions, as well as the sodium acetate base keep these species associated in the reaction mixture through ion pairing. This pre-association of the components produces those clusters that are essential for the metal complex formation reaction. The neutral amine, however, remains mostly separated from the other reaction partners, making it a significantly less effective base.

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[PC-25]

CONAN - A novel tool to create and analyze liquids in confined space

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Modeling of complex liquids at solid surfaces and in confinement is gaining attention due to increase in computer power and advancement of simulation techniques.

Therefore, tools to set up structures and analysis are needed. We present CONAN[1] --- a program that allows to generate solid structures such as carbon surfaces and boron nitride analogues, as well as to carry out several structural property analyses of the confined or interfacial liquids. At the case of the ionic liquid 1-butyl-3-methylimidazolium acetate ($[C_4C_1Im][OAc]$) in carbon nanotubes of different sizes, we demonstrate the abilities of our tool. The average density within the confinement highly depends on the carbon nanotube size, and it is generally lower than the density of the bulk liquid. The arrangement of the individual species within the tube also depends on size, with radial layers forming within the tubular confinement. The density is largely increased in the respective layers, while it is drastically reduced between the layers.

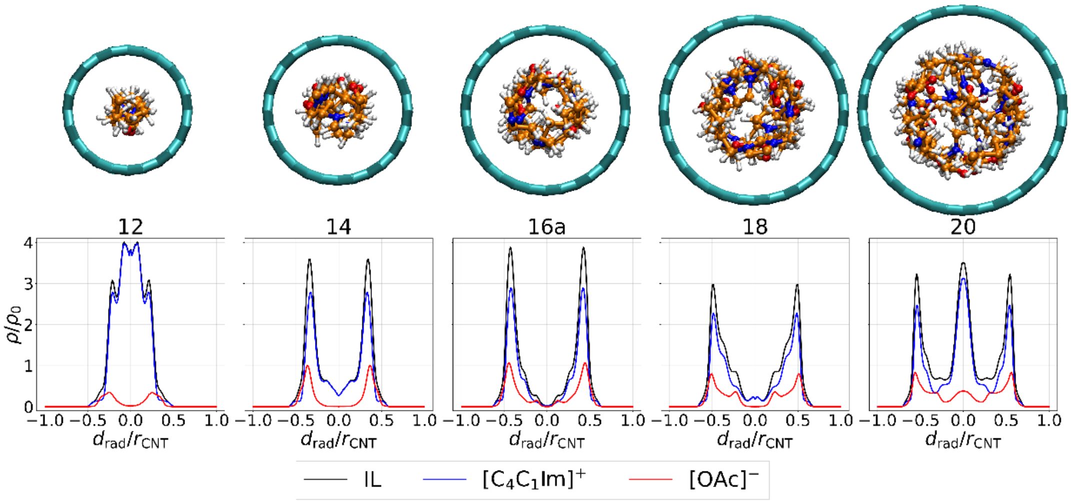

***Figure 1:** Radial mass density distributions of the IL inside CNTs of differing size computed using CONAN. The overall density profile is shown in black, the individual contributions from the cation in blue and from the anion in red. The upper panels show the IL in the respective tubes, cut from a snapshot of the trajectory of a given system using CONAN. The CNTs are shown in a bond model (blue), the ions in a ball and stick representation (color code: carbon = orange, hydrogen = white, nitrogen = dark blue, oxygen = red)*

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[PC-26]

Charge transport in protic ionic liquids: Effect of protonation state in 1-methylimidazolium – acetate/trifluoroacetate mixtures

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Protic ionic liquids (PILs) are a promising class of materials for electrochemical applications as slow diffusive charge transport in ionic liquids can be overcome by faster proton transport in PILs.[1-3] Although several studies have attempted to elucidate the underlying molecular-level details, the distribution of protons and their transport in PILs is not yet fully understood.[4,5] Such fundamental understanding of the molecular level dynamics in PILs is, however, crucial for an application-oriented rational design.

Here, we investigate the molecular-level dynamics of 1-methylimidazolium acetate [MimH][AcO], which has been suggested to be dominated by electro-neutral molecular species.[4,6,7] To investigate the effects of the charge state of the molecules on both dynamics and transport properties, we vary the acid gradually from acetic to trifluoroacetic acid. To gain insights into the proton distribution and molecular dynamics in the PILs, we use dielectric relaxation spectroscopy (DRS) to probe the dynamics of ions and molecular dipoles, and nuclear magnetic resonance (NMR) spectroscopy to obtain information on the chemical environment of the molecular-level species and their mobilities. DRS experiments show that with increasing trifluoroacetate content the hydrogen-bonded structure of the PIL breaks up and – together with NMR chemical shifts – that the fraction of charged species increases, resulting in enhanced electrical conductance. Remarkably, diffusion-ordered NMR spectroscopy indicates a decoupling of the proton mobility from the mobility of the molecular species – consistent with an enhancement of Grotthuss-type proton transport.

Although we find that the fraction of ionic molecular species also increases with trifluoroacetate content for solutions of the PILs in molecular solvents, the nature of the molecular solvent can dramatically impact electrolyte behaviour: solvation of ions in methanol and methanol's active role in proton transport can boost conductance, while in dimethylformamide ion-pairing is enhanced and thereby conductivity suppressed. Our findings highlight that electrolyte dynamics are governed by the subtle balance between protonated and deprotonated species, which are very sensitive to the acidity and the immediate environment of the constituting molecular species. As such, tuning these equilibria provides routes to enhance proton conductivity.

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[PC-27]
Theoretical investigation of novel ionic liquid-salt electrolytes

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The evaluation of reduction potentials is fundamental to determine the feasibility of novel electrolyte systems, as well as to guide the design of electrolytes for novel battery technologies. In order to potentially focus experimental screening of electrolytes on promising candidates, we present a theoretical study obtaining structure-property relationships and estimated reduction potentials of several solvent-salt combinations for use as electrolytes in energy storage applications. Two ionic liquids (ILs), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2C_1Im][NTf_2]$) and 1-ethyl-3-methylimidazolium tetrafluoroborate ($[C_2C_1Im][BF_4]$), are investigated as potential solvents. For the solvated salt within the ILs, monovalent s-block metal cations lithium and sodium in conjunction with fluorohydridoborate ($BH_{4-n}F_n^-$, n = 0 − 4) and cyanohydridoborate ($BH_{4-n}(CN)_n^-$, n = 1 − 3) based anions are employed. All combinations of the respective constituents are studied to obtain data regarding the influence of each component on structural, dynamical, and electrochemical properties. This is done by performing classical molecular dynamics (MD) simulations to model the dynamics of each individual solvent-salt combination. The first solvation shell of the respective central metal cation is harvested from the MD simulation, which subsequently is used to compute the reduction potential using static quantum chemical calculations according to Reference [1].

Investigation of the systems shows that in the presence of fluorohydridoborate anions, a metal cation dependency regarding the reduction potential is observed, as systems containing Na^+ cations yield lower reduction potentials than systems containing Li^+. For cyanohydridoborates however, lower reduction potentials are observed in $[C_2C_1Im][BF_4]$ compared to $[C_2C_1Im][NTf_2]$ pointing towards a solvent dependency when cyano-based borates are present.

Additionally, we are currently working on analyzing differently sized clusters using the quantum cluster equilibrium (QCE) approach to derive electrochemical stability windows for pure and mixed electrolytes in varying concentrations using the Peacemaker program.[2] Also, further efforts are made to improve existing parameters for commonly used forcefields regarding electrolyte systems.

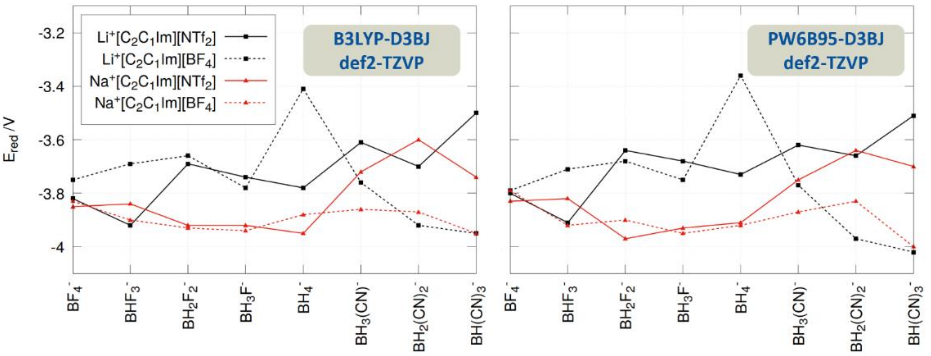

Figure 1: Computed reduction potentials versus the standard hydrogen electrode for all solvent-salt combinations.

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[PC-28]

An Explicit Solvation Neighbors Approach: Toward the Understanding of the Non-covalent Interactions in the Mixtures of Imidazolium-based Ionic Liquids with Molecular Solvents

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Non-covalent interactions in ionic liquid-molecular solvent binary mixtures determine the microscopic organization in these systems. In this regard, we propose the Explicit Solvation Neighbors Approach. It combines the advantages of classical molecular dynamics simulations (provides a statistical distribution of geometrical descriptors of hydrogen bonding)[1] with quantum-chemical calculations (permits to analyze the electron density distribution between the nearest neighbor interacting components). This approach allowed calculating the ^{1}H NMR chemical shifts and their favorable comparison with the experimental ones. It was found that for weakly coordinated anions (PF_6^- and $TFSI^-$), the dominant preferential anion localization around the imidazolium cation is disrupted and subsequently replaced by the solvent molecule. In contrast, strongly coordinated anions (Cl^-, BF_4^- and TFO^-) form bifurcated H-bonds both with anion and solvent molecule. Hence, a low cation solvation is a result of a competitive nature of interionic and ion-molecular interactions in such systems.

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[PC-29]

Solvent effects of choline and geranate-based ionic liquid on organic catalysts

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Ionic liquids (ILs) are being increasingly studied with over 3000 publications in the last 3 years alone. Aside from their traditional applications, they have shown promising applications in the biomedical context. Recently, new ILs composed by choline and geranic acid, named CAGE, have shown remarkable potential due to their ability to permeate membranes, leading to success in transdermal and oral drug delivery. This work considers the delivery of photoactivatable anticancer complexes by CAGE; in particular our aim is to shed light into the solvents effects CAGE exerts in the photocatalytic reduction of Pt(IV) complexes by organic compounds. Solvation effects, which effectively manifest in the case of ILs, can cause shifts in the peaks, intensities and shape of the absorption spectra. [1,2,3]

Modeling ILs at the molecular level is challenging due to the fact that they are formed by large organic ions with delocalized electrostatic charge, conformational flexibility, and asymmetric molecular shapes. Moreover, its properties are defined by a subtle balance between Coulomb interactions and van der Waals forces. Recently, a transferable, general, polarizable force field for ILs and their mixtures with molecular compounds has been developed. The new force field, CL&Pol, takes polarization into account explicitly in the form of Drude-induced dipoles, but in order to avoid a double counting of the induction effects, the Lennard-Jones parameters are scaled. [4]

We employ the CL&Pol force field to study the solvation of selected organic catalysts (flavin and methylene blue, for example) to sample the solute-solvent configurations and get an overall picture of the interactions present between the photoactivatable organic catalyst and the solvent. Different ratios of choline and geranic acid have been considered, together with variable water concentration. Once the solute-solvent configurations have been characterized, we have studied the optical properties by means of time-dependent DFT and compared the results with experimental spectra.

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[PC-30]
Choline chloride-water mixtures : as new generation of green solvents

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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, ChCl-water mixture was recently introduced as an auspicious and low-viscosity (Deep) Eutectic Solvent. We investigated the behaviour of different ChCl:H_2O mixtures at different molar ratios (1:n, with n=2-7, 10, 20) in terms of different physicochemical properties (density, viscosity and refractive index) and thermal behaviour via DSC measurements, together with NMR analysis. DSC has been used to explore the solid-liquid equilibrium and the Deep Eutectic nature for ChCl:H_2O 1:4 (termed as A*quoline*) was identified [1]. 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 [2].

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[PC-31]

Supramolecular cyclodextrin-based DES: From self-organization to molecular recognition

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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.

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[PC-32]

Al-Speciation Analysis in Non-aqueous Solutions via ^{27}Al NMR and Raman spectroscopy

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Using a non-aqueous solution is inevitable for electrochemical deposition of aluminum (Al) electrodeposition because the reduction deposition reaction of Al has a lower potential than the decomposition potential of water. Recently, non-aqueous solutions such as γ-butyrolactone have also shown promise as electrolytic bath solvents that can be electrodeposited at room temperature [1]. Kitada and Murase et al. reported that in the electrochemical reaction of Al with glymes (CH3O(CH2CH2O)n CH3, Gn), only diglyme (n = 2: G2) system showed good Al dissolution and deposition reactions, which is expected to be a next-generation electrolyte solution for electrochemical deposition of Al. [2] We have found that $AlCl_3$ is soluble in both acetonitrile (AN) and sulfolane (SL) with a mole fraction of more than 0.15. However, the aluminum electrodeposition behavior, its molecular factors, and the Al^{3+}-Cl^{-} complex formation reaction are unknown. In this study, we investigated the electrochemical behavior of the non-aqueous solutions, and the Al^{3+}-Cl^{-} complex formation reaction is studied by Raman spectroscopy, ^{27}Al NMR, and molecular orbital calculations.

The Raman spectra of $AlCl_3$-SL solutions in the range 150-600 cm^{-1} revealed the presence of both $[AlCl_4]^{-}$ and $[Al_2Cl_7]^{-}$. The average solvation number of Al^{3+}-Cl^{-} complexes decreased from 2 to 1 with increasing $AlCl_3$ concentration by the analysis of the Raman band assigned to SL. Figure 1 shows ^{27}NMR observed spectra and simulation spectra of $AlCl_3$-SL solutions. Three peaks were observed in the 27Al NMR: a sharp peak at 104 ppm attributed to the 4-coordinated structure of Al^{3+}-Cl^{-} complex, a broad peak at –13 ppm attributed to the 6-coordinated structure of Al^{3+}-Cl^{-} complex, and a sharp peak at –18 ppm assigned to $[Al(SL)_6]^{3+}$.The half-widths of the sharp peaks for the 4- and 6-coordinated structures increased with increasing concentrations of $AlCl_3$, indicating the chemical exchange effects. To assign the chemical species in the observed NMR spectra (upper spectra), spectral simulations were performed for each peak considering chemical species, labelled as A, B, and C from the low-magnetic field side. The middle and bottom spectra in Figure 1 shows the simulation assuming peak B to be $[AlCl_2(SL)_4]^{+}$ and $[AlCl(SL)_5]^{2+}$, respectively. The simulations considering peak positions, half-widths, fractions, and rate constants generally exhibited a good agreement with the measured spectra. As the theoretical NMR chemical shifts from the DFT calculations, it is determined that peak A corresponds to the exchange between $[AlCl_4]^{-}$ and $[Al_2Cl_7]^{-}$, peak B and peak C were attributed to $[AlCl(SL)_5]^{2+}$, and $[Al(SL)_6]^{3+}$,respectively. The average solvation number estimated by determining the fraction of each peak area ratio in the measured NMR spectra was in close agreement with that obtained from Raman analysis and decreases from 2 to 1 with increasing $AlCl_3$ concentration.

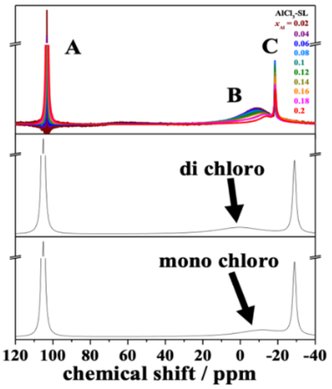

Figure 1: *27Al NMR observed spectra (upper) and simulation spectra (middle and bottom) of $AlCl_3$ —SL solutions.*

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[PC-33]

Prediction of heterodyne detected VSFG spectra from molecular dynamics simulations

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Charged interfaces attract a lot of scientific attention due to their omnipresence in a wide range of natural and industrial environments, since the surface of any material is the principal pathway for its interaction with its surroundings. The specific orientation of water molecules in proximity to the air/water or solid/water induced by the interface significantly varies properties of the environment in comparison with the homogenous (bulk) behavior. During last decades, nonlinear optics experiments, namely Sum Frequency Generation (SFG), Second Harmonic Generation (SHG) and Second Harmonic Scattering (SHS), also referred to as hyper-Rayleigh scattering (HRS), as representatives of the second-order nonlinear optical techniques, became respected and powerful tools for exploring a variety of topics ranging from fundamental questions of molecular dynamics at liquid interfaces to more applied problems of material surfaces. These techniques are highly suitable to study processes at surfaces and interfaces since the signal arises solely from the non-centrosymmetric regions at the interface. They provide direct information about the average orientation of the water molecules at the interface; monitor ion adsorption at the surface with micromolar sensitivity; infer interfacial electrostatic potentials, or even monitor the time-resolved evolution of interfacial processes.

We present a MD trajectory processing software to predict vibrational SFG non-linear optics spectra from classical molecular dynamics simulations of solid-liquid and solid-air interfaces. The computational method requires as input ab initio calculated parameterizations of change of dipole moment and polarization tensor of a water molecule upon its vibration. However, the trajectory to analyze is calculated by classical molecular dynamics simulations of non-polarizable flexible water models. This strongly reduces computation cost compared to ab initio calculations [1] and opens the possibility to study larger systems for long periods of time. The analysis allows detailed investigation of the origin of the SFG spectra, including contributions from water molecules differing in distance from the interface. The role of various parameters affecting the calculation, as well as inclusion of so far often neglected cross-correlation terms in evaluation of the necessary time-correlation functions [2] on water in contact with self-assembled monolayers (SAM) [3] composed of poly(ethylene glycol) (PEG) and octadecyltrichlorosilane (OTS) will be discussed.

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[PC-34]

Surface Affinity of Tetramethylammonium Iodide in Aqueous Solutions

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The surface affinity of tetramethylammonium iodide (TMAI) in aqueous solutions is investigated by surface tension measurements and molecular dynamics computer simulations. Experiments, performed in the entire composition range of solubility using the pendant drop method with two different setups (KRÜSS apparatus and a homemade version) clearly reveal that TMAI is a weakly capillary active salt.

Computer simulations performed with the AMBER force field reproduce the experimental data very well, while two other major force fields (i.e., CHARMM and OPLS) can still reproduce the experimental trend qualitatively. However, even qualitative reproduction of the experimental trend requires scaling down the ion charges according to the Leontyev-Stuchebrukhov correction[1]. On the other hand, the GROMOS force field fails in reproducing the experimentally confirmed capillary activity of TMAI.

Molecular dynamics simulation results show that, among the two ions, iodide has a clearly larger surface affinity than tetramethylammonium (TMA+). Further, the adsorption of the I- anions is strictly limited to the first molecular layer beneath the liquid-vapor interface, which is followed by several layers of their depletion. On the other hand, the net negative charge of the surface layer, caused by the excess amount of I- with respect to TMA+, is compensated by a diffuse layer of adsorbed TMA+ cations, extending to, or beyond the fourth molecular layer beneath the liquid surface.

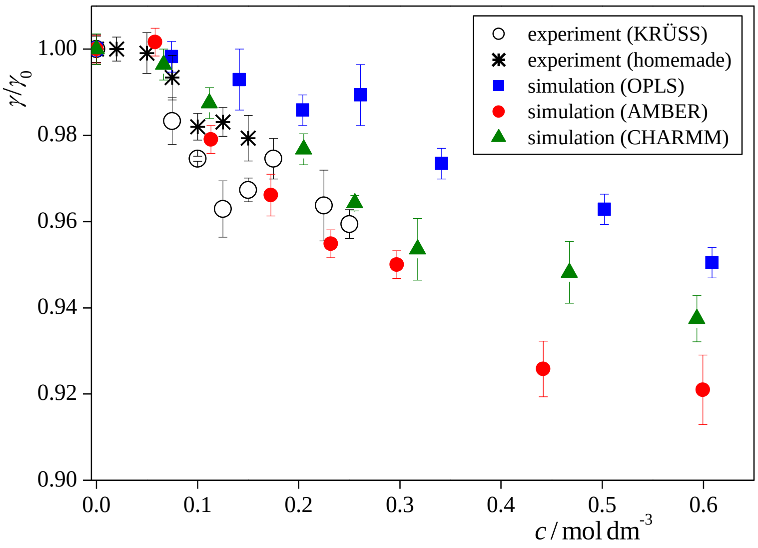

Figure 1: Surface tension of aqueous TMAI solutions, normalized by that of neat water, as obtained from experiments (KRÜSS apparatus - black open circles; homemade equipment - black asterisks), and from simulations using three different force fields (OPLS - blue filled squares; AMBER - red filled circles; CHARMM - green filled triangles).

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[PC-35]

Structure and free energy profiles of NaCl solutions in graphene-based single digit nanopores

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Capacitive deionization (CDI) has emerged as a promising technique for efficient and sustainable desalination [1]. This study aims to provide detailed insights into the underlying molecular mechanisms of CDI. Through molecular dynamics simulations, we investigate the behavior of ions and water molecules, focusing on their interactions with the nanopore surface [2]. By calculating the Potential of Mean Force (PMF) profiles using the Adaptive Weighted Histogram Analysis Method (AWH) implemented in GROMACS software, we elucidate the energetics and driving forces governing ion properties under confinement [3]. Our findings shed light on the ion selectivity and the effects of various system parameters, such as surface charge, pore size, and pore length, on the transport properties. The molecular modeling approach employed in this study offers valuable insights into the ion sorption and desorption processes, aiding in the optimization of CDI electrode materials and system performance [4]. These findings contribute significantly to the advancement of water treatment technologies and provide crucial guidance for the design and optimization of CDI systems, thus addressing the global water scarcity challenge effectively. By utilizing these insights, more efficient CDI systems can be developed to alleviate the growing water scarcity issues worldwide.

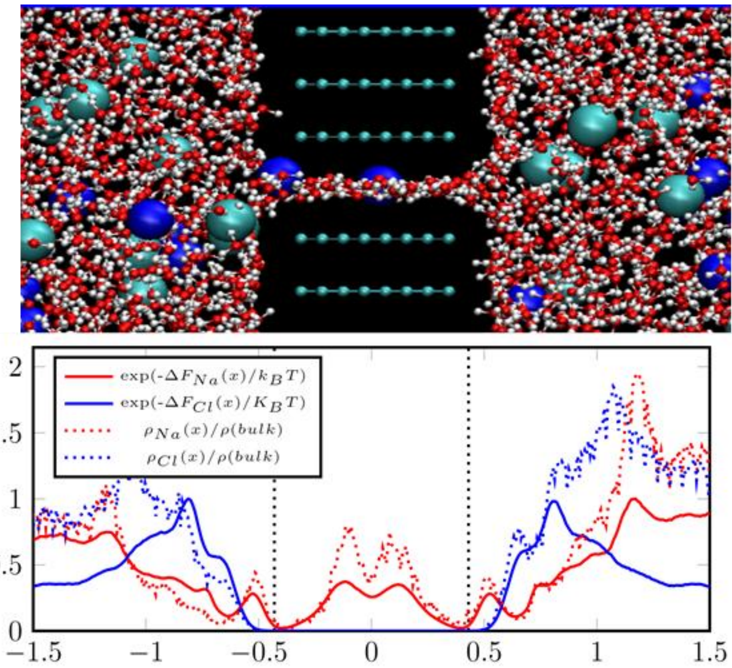

Figure 1: Snapshot of a positively charged graphene nanochannel of length 10 Å and length 7 Å filled with NaCl solution (Na^+ blue, Cl^- cyan) and the corresponding densities of ions observed directly and predicted from the potential of mean force calculations, explaining the surprising presence of Na^+ in the positive channel.

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[PC-36]

Molecular dynamics simulation study of charge inversion phenomena in nanopores

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Nanopores are facilitating the controlled transport of various molecules across several types of membranes, thus creating a possibility to exchange ions between both sides of the membrane. In this work, we aim to study the so-called charge inversion phenomena on a molecular level with the help of Molecular Dynamics simulations. There are several experimental situations when a nanopore changes its conductance properties as an effect of charge inversion. For example, as multivalent ions are present in the system the initially cation-selective pore becomes anion-selective [1]. In a mole fraction experiment, where monovalent ions compete with divalent ions, charge inversion causes anomalous behavior [2]. The peculiar behavior of the pore arises if the strong correlations between the multivalent cations and pore charges causes overcharging and a changed preference between various ions. Multivalent electrolytes are less studied so investigating these are at the spearhead of our study.

We use all-atom models of water, ions, and a carved-out silica block, attaching functional groups to its inner surface. So, in our case, the above-mentioned strong correlations (that is absent in mean-field theories) can be an ion-ion or ion-wall type interaction. We are especially interested in the role of water, so we compare our results to the outcomes of the simulations using implicit water models [3,4]. If we understand the underlying molecular mechanism of charge inversion on the atomic level better, then we can influence the fabricated channels emergent properties at the macroscale.

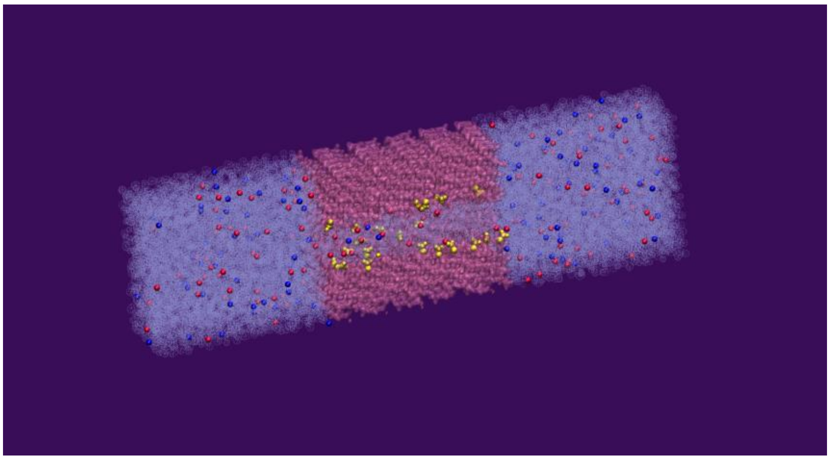

Figure 1: *A schematic snapshot of sliced charged silica pore sandwiched between two reservoirs*

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[PC-37]
Molecular Study of Solvent Effects on Polymer Materials

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Introduction

The film of polymer particles disintegrates into individual particles and dissolves when exposed to certain solvents. Other than the film of polymer particles, polymer materials also dissolve in specific solvents. Furthermore, solvents reduce mechanical stability. This relationship between polymers and solvents has been understood through solubility parameters. In other words, it has been assumed that solvents with a high affinity for polymers cause these phenomena. However, some phenomena cannot be explained by affinity alone. For example, a polymer material that is insoluble in a 100% alcohol solution with the highest affinity becomes soluble in an 80% alcohol solution. Water molecules with very low affinity for polymers reduce the mechanical strength of the polymer material. It is necessary to discuss solvent effects on polymer materials from the molecular level to clarify these phenomena. Therefore, we focused on the solvent-induced changes in polymer mechanical properties to elucidate the solvent effect on polymers and performed an all-atom molecular dynamics study.

Methodology

Since the target phenomenon often occurs in amorphous polymers, PMMA, a typical amorphous polymer, was used. Water and methanol were used as solvents. MODYLAS [1] and GROMACS were used as molecular dynamics calculation software. Uniaxial tensile fracture simulations were performed after PMMA was exposed to water or methanol.

Results and Discussion

Long-time simulations at 1 μs showed that both methanol and water molecules penetrated the PMMA interface, but methanol molecules penetrated deeper than water molecules. The stress-strain curves obtained for the uniaxial tensile fracture simulation are shown in Figure 1. Compared with the stress-strain curves without solvent, the stresses were lower when methanol and water were in contact. This result is in agreement with our immersion tensile test.

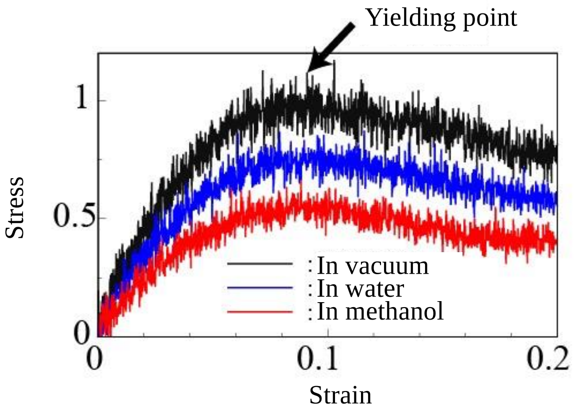

Figure 1: *Calculated stress-strain curves of PMMA in vacuum (black), water (blue), methanol (red). Stress were normalized by the stress value at the yield point in vacuum.*

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[PC-38]
Characterizing electrospun 3D matrices; the effect of humidity

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Polymers play a crucial role in medical and pharmaceutical applications, offering improved functionality and novel opportunities. Polysuccinimide shows promise for medical use. Nanotechnology enables the creation of artificial matrices with nanoscale fiber diameters resembling natural organisms. Electrospinning is a versatile technique for modifying fiber properties using nanoparticles, salts, and target geometries.

However, understanding the underlying mechanisms of the electrospun 3D structures remains elusive, limiting reproducibility and applications. Standardized methodologies and unified explanations are lacking due to the field's novelty. This study aims to synthesize biocompatible 3D structures, characterize them using vibrational spectroscopy and scanning electron microscopy. Additionally, evaluating optimal salts and concentrations to enhance pore size and create 3D structures. Solid polymer fibers were electrospun with different Polysuccinimide (PSI) and salt concentrations (CaCl2, MgCl2, and LiCl). Mechanical strength, chemical composition, fiber surface, and average diameter were analyzed.

Results show that 20 w/w % PSI concentration yields thinner fibers than 25 w/w %. Salts eliminate bead formation and induce new peaks in infrared spectra. Higher solution concentrations improve sample durability. Varying humidity levels during sample preparation affect structure and porosity, with a critical threshold of 48% humidity resulting in thinner samples below the threshold and the formation of loose, three-dimensional structures induced by salts above the threshold.

This work reveals the significant impact of salts on electrospun fiber morphology and diameter, as well as the critical humidity threshold for scaffold formation.

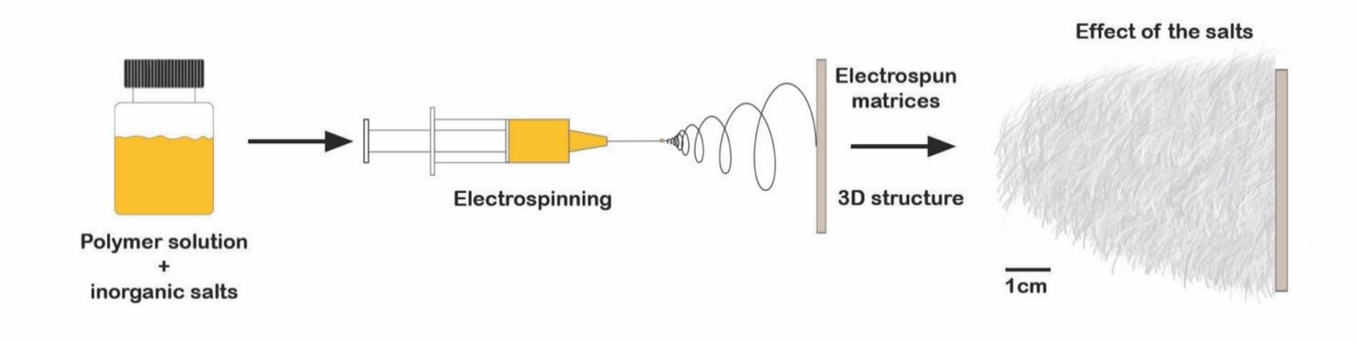

Figure 1: *Different steps of creating a three-dimensional fiber structure*

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ACKNOWLEDGMENT

This research was supported by NKFIH FK 137749. TKP2021-EGA-23 has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund. The research was further financed by Campus France.

[PC-39]

Liquid-Vapour Phase Behaviour of Patchy Colloids in a Patchy Porous Matrix

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We report a theoretical study of the phase behaviour of patchy colloids confined in a disordered porous material with a functionalized pore surface. Patchy colloids and matrix particles are modelled as hard spheres bearing interacting sites with the square-well pair potential. The matrix particles are frozen, i.e. free of translational and rotational degrees of motion, while the patchy colloids can move in the void not occupied by the matrix. To describe the thermodynamic properties of the considered system, we propose a semi-analytical approach based on a combination of the scaled particle theory [1] and Wertheim's thermodynamic perturbation theory [2,3], which enables us to take into account both the porous matrix presence and the associative effects appearing due the patch-patch interactions. A series of computer simulations is performed to assess the accuracy of our theoretical results, which appear to be in good agreement. At different number of patches at colloidal and matrix particles the phase diagrams are built. We demonstrate that the competition between a formation of bonds between fluid particles, and between fluid particles and matrix obstacles, leads to a re-entrant phase behaviour, which exhibits in three critical points and two separate regions of liquid-gas phase coexistence. Also the network-forming phenomena occurring in confined patchy colloids are investigated using the Flory-Stockmayer theory, and the corresponding percolation lines are calculated at different model parameters. An extension of the proposed theory to the case of two-component patchy colloids confined in a patchy matrix is considered as well within this study.

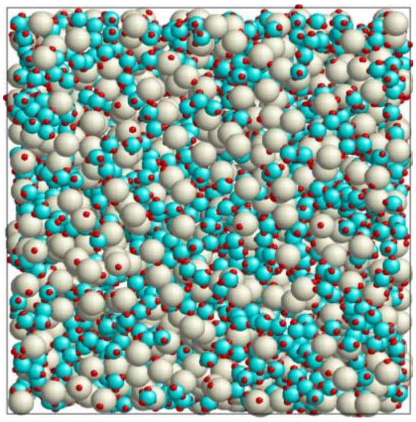

Figure 1: *Patchy colloids (cyan colour) in a patchy porous matrix (pale colour).*

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[PC-40]

Optical Properties of a Bipyridine Diol in Water: A Multilevel Computational Approach

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2,2’-bipyridyl-3,3’-diol ($BPOH_2$), originally proposed as a model of a base pair, is well known for giving rise to excited state intramolecular proton transfer in solution.[1] The complex photochemical properties of this chromophore are increasingly investigated in the literature but most theoretical studies have focused on the mechanism of proton transfer in the excited state.[2] On the other hand, the evolution of the absorption spectrum in the presence of a solvent and, in particular, the existence of a di-zwitterionic (diketo) form to explain the spectroscopic behavior in water, have not been fully examined yet.[3] In this work, we used a theoretical methodology based on the application of the Joyce protocol [4] and on the computation of RESP charges to provide quantum mechanically driven force fields (FFs) describing the different tautomers of $BPOH_2$ in water. Such FFs were used to run classical molecular dynamics simulations, from which a large number of configurations were extracted, then used to compute a statistically averaged spectrum of the molecules surrounded by explicit water molecules. Simulations also provided thermodynamic estimates of the Boltzmann factors to be used to reconstruct the total spectrum from the computed spectra of each tautomer. The excellent agreement thus found with the experimental measurements [3] allowed us to conclude that a diketo form of $BPOH_2$ is present in water, in addition to the diol form. Moreover, we showed that the use of quantum calculations with a continuum solvation model largely overestimates the population of the diol compared with the other tautomers.

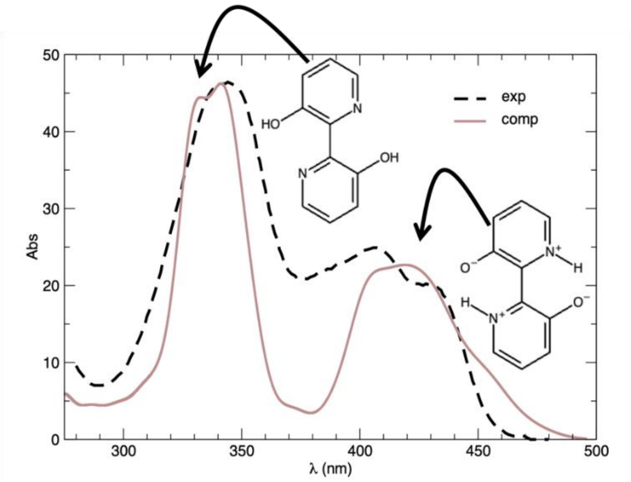

Figure 1: *Experimental (Ref. [3]) and computed (this work) absorption spectrum of 2,2′-bipyridyl-3,3′-diol.*

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[PC-41]

Quantitative *in situ* analysis of complex fluids by co-localized IR/Raman spectroscopy for the study of the chemistry of hydrothermal vents

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Hydrothermal smokers present unique physico-chemical conditions, suspected of having contributed to the emergence of life on Earth [1]. We present here the development of a high-pressure, high-temperature reactor specially designed to simulate the flow chemistry of deep-sea hydrothermal environments (Figure 1), and thus study the formation of prebiotic compounds. Sapphire portholes along the length of the reactor enable the application of Raman and infrared spectroscopy, and thus in-situ, real-time monitoring of the evolution of the system, composed of solid, gaseous, liquid and supercritical phases.

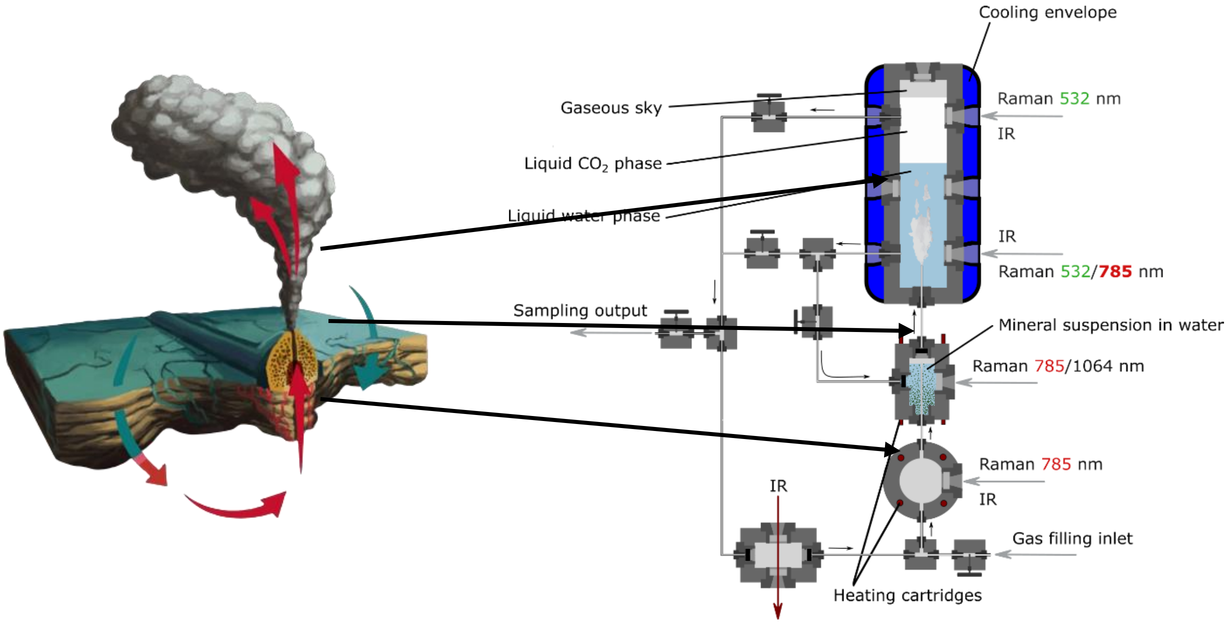

Figure 1: *Hydrothermal Deep-see vent scheme and the high-pressure high-temperature experimental set-up coupled with IR and Raman spectrometer for the co-localized in situ investigation of these environments.*

The development of a complete in-situ quantification method for monitoring the CO_2 phase is presented here. Diatomic mononuclear molecules are active in Raman scattering but inactive in infrared, while other gases such as CO_2, CO, CH_4, NH_3, etc. can be monitored by both techniques. Co-localized infrared/Raman spectroscopy offers an innovative approach to the in situ quantitative analysis of complex gas mixtures at high pressures (H_2, N_2, CO, CO_2 and CH_4 in our example). By combining the infrared and Raman spectra of a species observed in both spectrometric techniques, we have proposed a new methodology for calibrating Raman spectra to overcome the fact that Raman intensities are arbitrary (laser power, instrument response, integration time, fluorescence).

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[PC-42]

Assessment of the solubility of a highly fluorophillic photoredox catalyst in *sc*CO_2

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The use of supercritical CO_2 as a green solvent has been broadly studied since the last decades.[1,2] Among all of the uses, *sc*CO_2 was shown to solubilize heavy fluorinated molecules including perfluoropolymers.[3,4] In the same time, the rise of catalysis has emerged on organo-photocatalysis.[5,6] This methodology, using photons as reagents and catalysts without metals, is widely studied due to their stunning reactivity in organic chemistry.[7]

Being interested in the development of organic photoredox catalysts that could be recycled, we have prepared highly fluorophilic derivatives of the 4CzIPN fluorophore, such as compound **1** presented below. Exploiting *in situ* infrared spectroscopy. the assessment of solubility in supercritical CO_2 of fluorophilic 4CzIPN derivatives will be presented and compared with non-fluorinated analogues. In particular, we show that the highly fluorinated photocatalyst **1** is remarkably soluble in *sc*CO2, and that the amount of perfluoroalkylated chains on the molecule has a direct impact over the solubility.

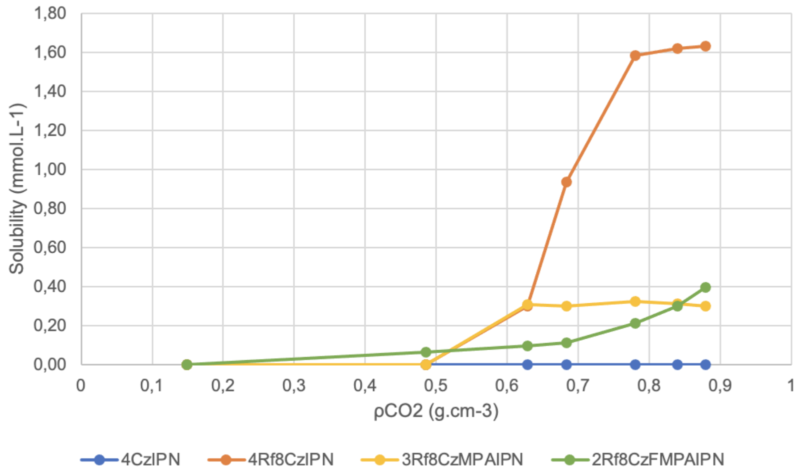

Figure 1 *– Evolution of the solubility of differently tuned photocatalysts with the CO_2 density at 40 °C.*

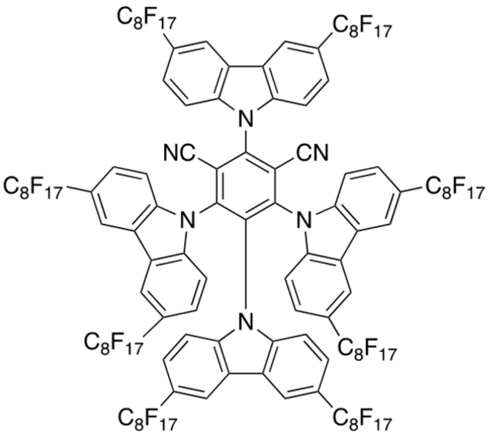

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Figure 2 *– Structure of the highly fluorophillic organophotocatalyst 1.*

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[PC-43]

Imidazolium-based polymerized ionic liquids as versatile stabilizers for ruthenium nanoparticles

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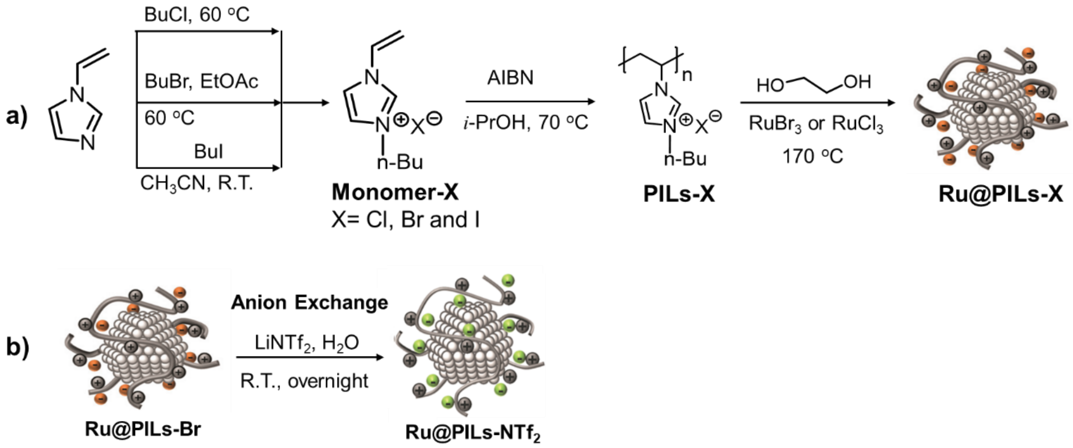
Key advances in the synthesis of metal nanoparticles (MNPs) in recent years have successfully led to the development of a variety of applications including sensing, imaging, catalysis, diagnosis, and therapy.[1] To obtain stable MNPs, considerable efforts have been directed towards designing versatile stabilizers, because they play a crucial role in controlling the size, shape, and surface properties of MNPs.[2] Nowadays, polymerized ionic liquids(PILs), especially those based on the imidazolium cation have emerged as intriguing stabilizers due to their unique properties.[3,4] Meanwhile, imidazolium-type PILs stabilized MNPs have proved to be promising catalysts for various chemical transformations such as Suzuki, Sonogashira-type coupling, hydrogenation reactions[5,6]

In this work, a group of simple imidazolium-type PILs with different anions have been smoothly fabricated and applied to stabilize ruthenium nanoparticles (RuNPs, **Scheme a**). Here, ethylene glycol acts as both the solvent and reductant. In addition, the anion exchange reaction allows water-soluble Ru@PILs-Br nanoparticles to be easily converted into RuNPs with bis(trifluoromethyl)sulfonimide (Ru@PILs-NTf_2) as the counter anion (**Scheme b**), which are not soluble in water any more but in organic media. Of particular interest, those exchange reactions could be harnessed to tune the catalytic properties (activity and selectivity) of MNPs catalysts in hydrogenation reactions,[5,6] which is what we will investigate in our following work.



Scheme 1. Synthetic route of PILs-X by a polyol process and PILs-Y-stabilised RuNPs by the anion exchange reaction (X = Cl, Br, I; Y = NTf_2).

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