Title of the publication: 38th International Conference on Solution Chemistry
9–14 July, 2023, Belgrade, Serbia
Book of Abstracts

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Published by: University of Novi Sad, Faculty of Sciences
Trg Dositeja Obradovića 3, Novi Sad, Serbia

For publisher: Prof. Dr. Milica Pavkov Hrvojević, dean
University of Novi Sad, Faculty of Sciences

Prepress design: Tijana Adamov

Printed by: Zola štampa, Novi Sad

Number of copies: 150

CIP - Каталогизација у публикацији
Библиотеке Матице српске, Нови Сад

544.35(048.3)

INTERNATIONAL Conference on Solution Chemistry (38 ; 2023 ; Belgrade)
Book of abstracts / 38th International Conference on Solution Chemistry, Belgrade, Serbia, July 9-14, 2023 ; [editors Slobodan Gadžurić, Marija Bešter-Rogač, Sanja Belić]. - Novi Sad : Faculty of Sciences, 2023 (Novi Sad : Zola štampa). - 152 str. : ilustr. ; 25 cm

Tiraž 150.

ISBN 978-86-7031-624-9

а) Хемија раствора – Апстракти

COBISS.SR-ID 118371081

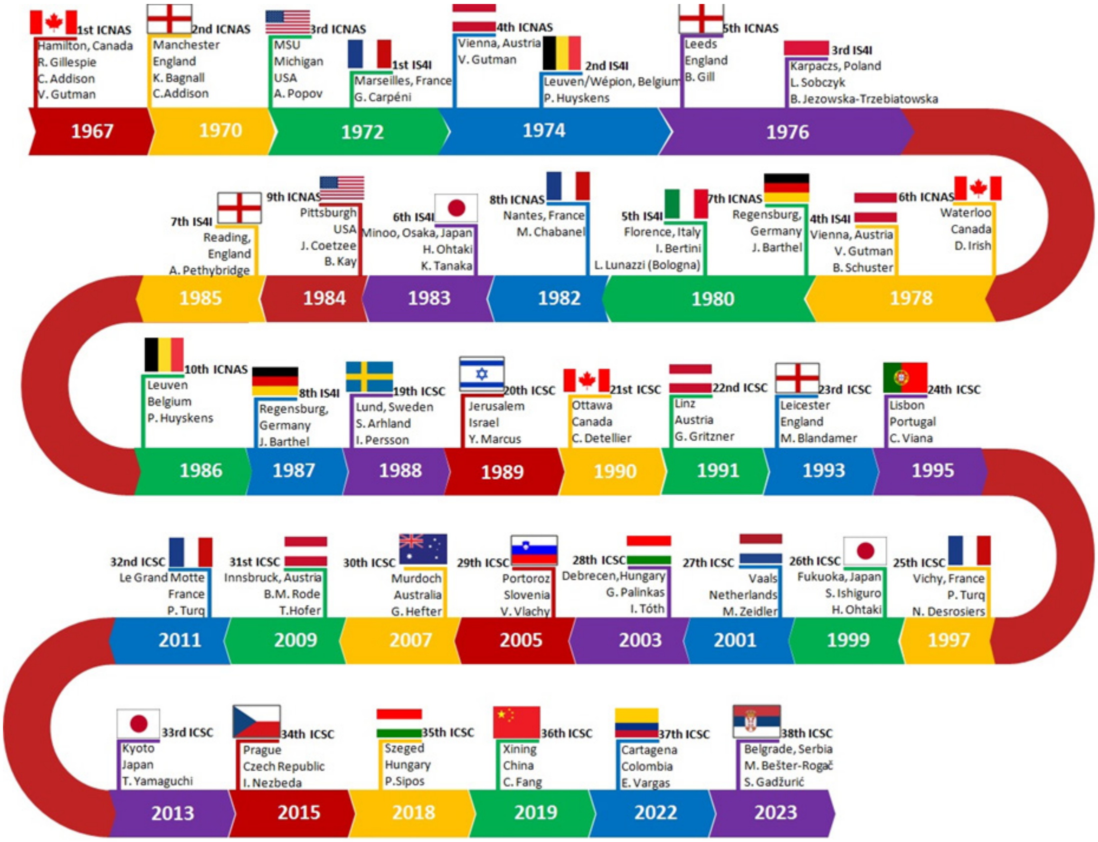
38th International Conference on Solution Chemistry

Book of Abstracts

Belgrade, Serbia, July 9–14, 2023

Dear friends and colleagues,

It is our great pleasure to organize and chair the 38th International Conference on Solution Chemistry (38ICSC) in Belgrade, Serbia, July 9-14, 2023. ICSC is a traditional conference founded in 1967 as the International Conferences on Non-Aqueous Solutions, with the first event held in Hamilton, Canada.



After a successful and productive previous meeting in Xining (2019, China), the conference was moved to South America and announced for 2021 in Cartagena, Colombia. Due to the COVID -19 pandemic, the conference was postponed to 2022 and organized as a virtual meeting. Nevertheless, the ICSC aims to continue the tradition and promote interaction between the different research communities worldwide. For the first time, ICSC is organized by two universities from two European countries (College of Ljubljana, Slovenia and College of Novi Sad, Serbia). Belgrade, the capital of Serbia and one of the best kept secrets in Europe, was chosen as the venue for the conference. With its rich cultural heritage, traditions and diversity, youthful vibrancy and multicultural creativity, Belgrade will surely impress you and make this event an unforgettable experience.

Solution chemistry is a broad and interdisciplinary field of chemistry, physics and biology, as well as pharmaceutical and medical sciences. With the advent of new theories, analytical methods, computers, and technologies, the research field of solution chemistry has expanded widely and profoundly and holds great promise for industrial applications such as biomaterials, proteins, and nanotechnology. The 38ICSC will cover fundamental aspects, applied research and various applications of solutions, divided into different topics. Over 120 researchers from all continents and 30 countries will gather to present their latest scientific results orally in three parallel sessions or as poster presentations in two afternoon poster sessions during the five days.

The goal of ICSC is to present new results of our scientific work and to introduce and discuss new findings on various scientific and technological issues related to solution chemistry. Let us come together and share our thoughts that will shape the future in this field. Welcome to Belgrade.

Marija Bešter-Rogač & Slobodan Gadžurić,

Chairs of the 38ICSC

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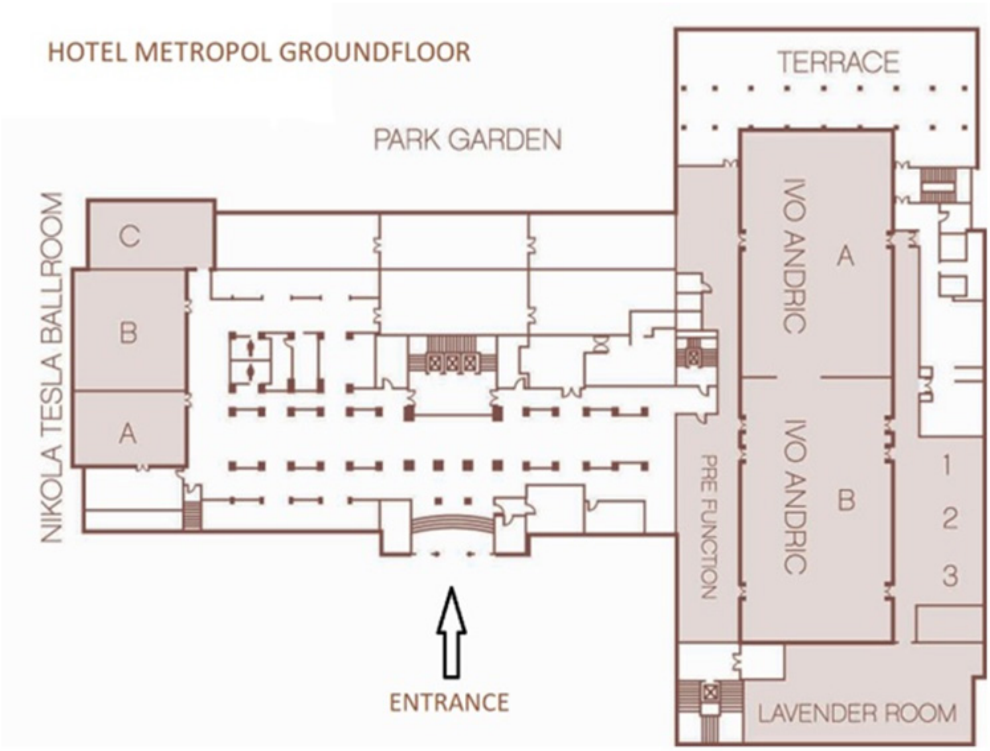
General Information

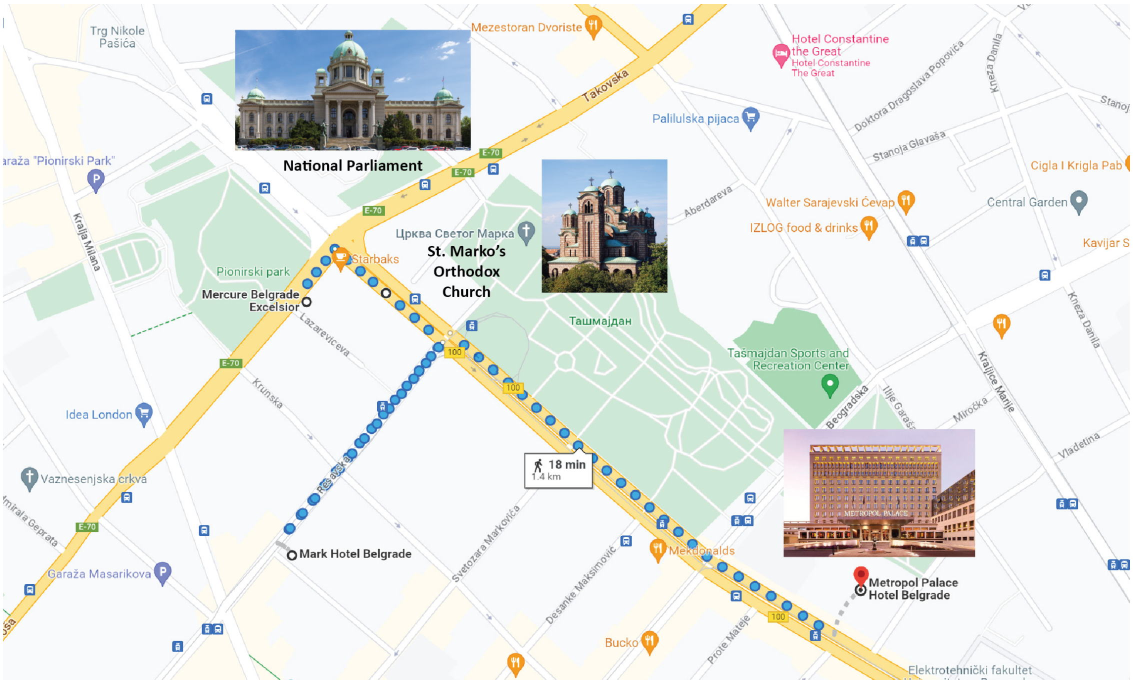
Venue

Hotel Metropol Palace, Bulevar kralja Aleksandra 69, 11000 Belgrade, Serbia

The venue of the 38ICSC is located in the heart of the city of Belgrade. The place is an ideal starting point to discover the capital of Serbia. The main sights such as Kalemegdan Fortress, Knez Mihajlova pedestrian street, St. Sava Orthodox Temple, Nikola Tesla Museum or Skadarlija bohemian street are easily accessible from here. The Serbian capital offers a variety of attractions and a relaxed atmosphere to experience and enjoy. The hotel's various venues - ballrooms, conference rooms, restaurants, lobby, bar and park garden - provide space for all kinds of business and leisure events. Our lectures are organized in three parallel sessions in the conference halls Ivo Andrić A, Ivo Andrić B and Lavender, all located on the ground floor of the hotel.



The venue is within walking distance (about 10 minutes, 800 m) from two other recommended hotels - Hotel Excelsior and Mark.



Registration

The registration desk will be open on Sunday, July 9, 2023, from 2:00 pm to 7:00 pm and every day during the conference from Monday to Friday from 9:00 am in front of the Ivo Andrić Conference Hall.

Welcome party

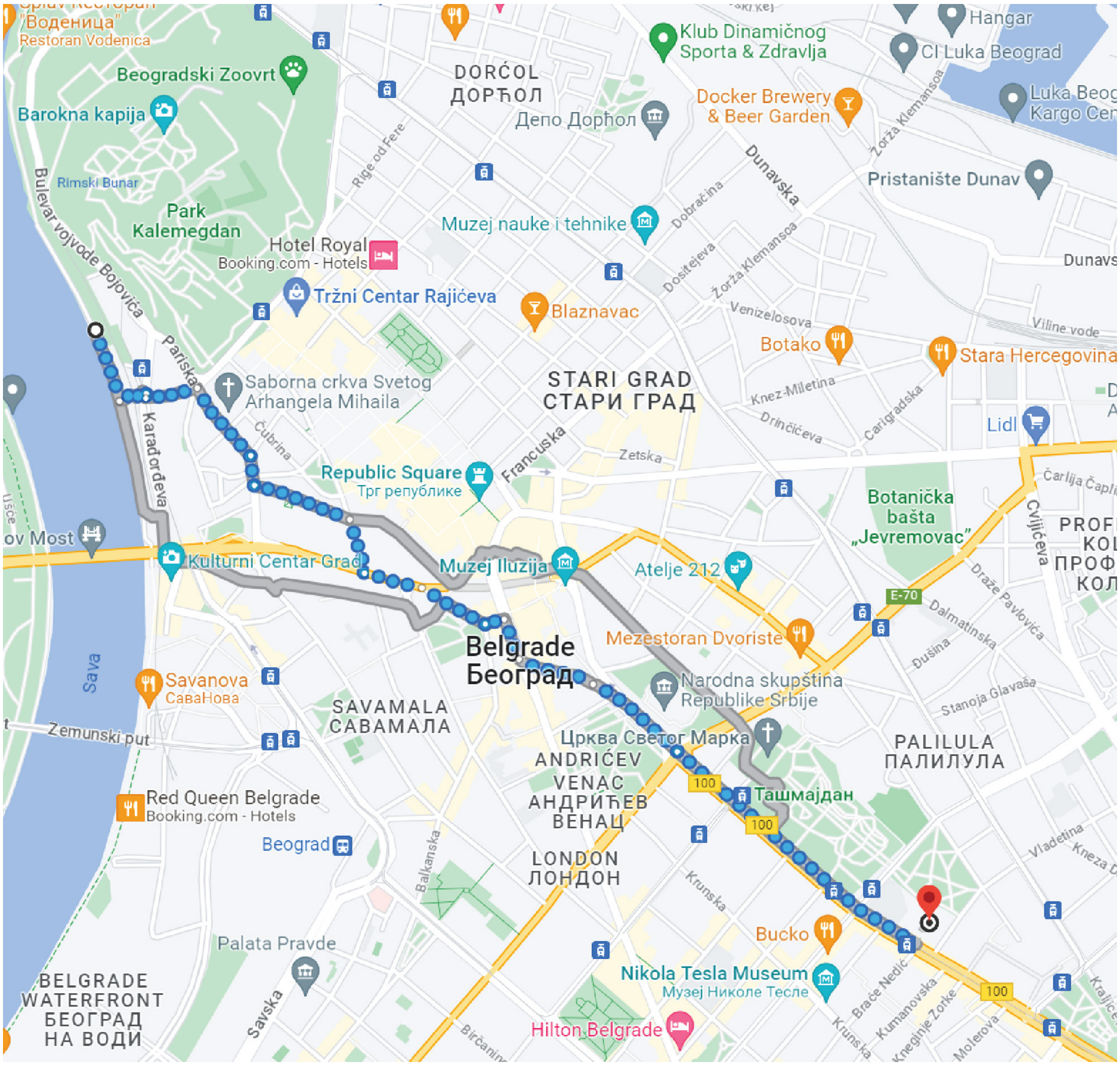
The welcome party will be held on Sunday, July 9, 2023, starting at 7:00 pm in one of the hotel restaurants. Drinks and snacks will be served.

Conference excursion

The excursion to the medieval fortress of Golubac is scheduled for Wednesday, July 12, 2023 in the afternoon for all participants. The busses will depart from the plateau in front of the Metropol Hotel at 2:00 pm, directly after lunch. Golubac is a well-preserved fortress located 130 km from Belgrade in the rugged landscape at the head of the Iron Gate (Serbian Đerdap) gorge. The total of nine towers, each between 20 and 25 meters high, as well as the exciting location of the fortress leaning over the Danube, make Golubac undoubtedly one of the most beautiful castles along the 2850 km Danube odyssey from its source to the Black Sea.

Conference dinner, Ambar restaurant, Karađorđeva 2, 11000 Belgrade, Serbia

The conference dinner will be held on Thursday, July 13, 2023 at 8:00 pm in the modern Ambar Restaurant, where you can enjoy traditional Serbian cuisine. The restaurant is located in one of the most attractive places in Belgrade - at the foot of Kalemegdan Fortress on the bank of the Sava River, where we can enjoy the unique concept of traditional Serbian cuisine. It is the first modern international chain of restaurants serving Balkan cuisine with locations in Washington DC and Belgrade, offering exceptional gourmet dishes. The easiest way to reach the restaurant is on foot (30-35 minutes from Hotel Metropol) or by taxi. For all participants who would like to walk to the restaurant, the meeting point is at 7:15 pm in the lobby of the hotel.



Topics

Ionic liquids **ILS**
Solution thermodynamics **TER**
Biochemical effects in solutions **BIO**
Solubility phenomena and phase equilibria **SOL**
Solution structure and dynamics **STR**
Supercritical fluids and solutions under extreme conditions **FLU**
Colloids and interfaces **COL**
Computational solution chemistry **COM**
General solution chemistry **GEN**
Industrial applications of solutions **IND**

Program of the 38ICSC, July 9-14 2023, Belgrade, Serbia

Sunday July 9, 2023

14:00-19:00	REGISTRATION
19:00	Welcome party

Monday July 10, 2023 (all plenary lectures are in the conference hall Ivo Andrić A+B)

8:00-9:00	REGISTRATION		
9:00-10:00	Opening ceremony		
10:00-11:00	Chairman: Toshio Yamaguchi **PL1** T. Welton - **Why are ionic liquids so viscous?**		
11:00-11:30	Coffee break		
11:30-12:30	Chairman: Glenn Hefter **PL2 Y. Jiang - Probing interfacial ion-water interaction with atomic resolution**		
12:30-14:00	Lunch		
	Hall Ivo Andrić A	Hall Ivo Andrić B	Lavender hall
	Chairman: Tom Welton	Chairman: Ying Jiang	Chairman: Earl Waghorne
14:00-14:40	**KN1** C. Schröder **Charge and proton transfer in polarizable molecular dynamic simulations of ionic liquid**	**KN2** N. Malikova **Organisation of charged nano-platelets in liquids and gels**	**KN3** E. Enyedy **Coordination modes and substituents of tridentate thiosemicarbazones modulating the solution chemical properties and cytotoxicity**
14:40-15:00	**ILS1** I. Polishuk **About interrelation between PVT of ionic liquids and phase equilibria in their systems**	**COL1** M. Jaklin **The effect of glycine buffer on the β-lactoglobulin amyloid fibrillization tendency**	**GEN1** S. Gupta **Advancements in the sustainable development of bio-based nanomaterials for wastewater treatment and desalination**
15:00-15:20	**ILS2** A. Melchior **Structure and formation thermodynamics of cobalt(II) complexes with nitrate and chloride anions in $[C_4mim][Tf_2N]$ ionic liquid**	**COL2** Sz. Sáringer **Effect of the surface properties on the stability and activity of catalase-latex composites**	**GEN2** M. Amara **Membrane process using complexation properties used to enhance separation between chemical species**
15:20-15:50	Coffee break		
	Chairman: Christian Schröder	Chairman: Natalie Malikova	Chairman: Éva Enyedy
15:50-16:10	**ILS3** E. Safonova **Structurally modified alkylimidazolium ionic liquids in aqueous and aqueous-salt solutions**	**COL3** B. Katana **Halloysite nanotube-based nanomaterials as efficient radical scavengers in colloidal dispersions**	**GEN3** E. Waghorne **Analysis of Catalan hydrogen bond acceptor and donor parameters SB and SA using computational chemistry and comparison with corresponding Kamlet and Taft, Abraham and Gutmann parameters**

16:10-16:30	**ILS4** M. Bogdanov **A new definition and extended set of constants to predict densities of ionic liquids by using the residual volume approach**	**COL4** A. Pulikkal **Solubilization of aqueous-insoluble phenothiazine drug in TX-100 micellar solution and its interactions with cationic surfactants**	**GEN4** Y. Szabó **Katoite synthesis from tricalcium aluminate via isomorphic substitution of silica**
16:30-16:50	**ILS5** R. Kanzaki **Ionization thermodynamics of poly(acrylic acid) in ionic liquids**	**COL5** A. Campos **On the colloidal stability of magnetic core@shell nanoparticles in ionic liquid-based solvents for thermoelectric applications**	**GEN5** É. Böszörményi **Formation of heteronuclear complexes in the ternary Ca(II)–Nd(III)–gluconate system**
16:50-18:00	Poster session P1-P22		

Tuesday July 11, 2023

9:00-10:00	REGISTRATION		
10:00-11:00	Chairman: Edgar Vargas **PL3** L. Vega - **Hunting sustainable energy – the role of solution chemistry and computation on finding optimal solvents for CO_2 capture**		
11:00-11:30	Coffee break		
	Hall Ivo Andrić A	Hall Ivo Andrić B	Lavender hall
	Chairman: Andrea Melchior	Chairman: Abdenacer Idrissi	Chairman: Johannes Hunger
11:30-11:50	**ILS6** J. Panić **The nature of interactions in mixtures of pharmaceutically active ingredient ionic liquid and natural deep eutectic solvents**	**COL6** R. Bouzaiene **Experimental and theoretical studies of the influence of cross interaction effects on the structure, CMC, and mobility of SDS and TTAB micelles in aqueous mixtures**	**SOL1** M. Skripkin **Effect of water addition on the formation of copper/zinc terephthalate MOFs**
11:50-12:10	**ILS7** M. E. di Pietro **Towards safer electrolytes for lithium-ion batteries: the curious case of DBUH-IM14 protic ionic liquid**	**COL7** D. Takács **Heteroaggregation of microplastics with anionic clays in aquatic environment**	**SOL2** J. Skvara **Thermodynamics and structure of water-alcohol mixtures at the level of simple models**
12:10-12:30	**ILS8** S. Papović **Improving the thermal and electrochemical stability of lithium-ion battery electrolytes safety using the ionic liquids and zwitterionic additives**	**COL8** E. Leontidis **Calorimetric measurements of complexation and transfer of a europium salt in colloidal liquid-liquid extraction systems**	**SOL3** B. Kutus **Hydrolytic and neutralization processes of hydroxysodalite**
12:30-14:00	Lunch		

	Chairman: Robin Rogers	Chairman: Richard Buchner	Chairman: Marina Fedotova
14:00-14:40	**KN4** M. J. Lourenço **Complex and not so complex systems for SDG's solutions**	**KN5** Y. Zhou **Ion hydration, ion recognition and applications in salt lake resources separations**	**KN6** E. Vargas **Resorcinarenes, solvation in water and organic solvents**
14:40-15:00	**IND1** Zs. Árok **Solution properties of scleroglucan: a promising biopolymer for enhanced oil recovery**	**STR1** W. Alves **On the electroactive species in rechargeable Mg battery electrolytes: a vibrational study on solution chemistry**	**SOL4** M. Lukšič **Salt-specific effects on the phase stability of BSA-PEG solutions below and at the isoionic point of BSA**
15:00-15:20	**ILS9** M. Seitkalieva **A study of biological activity of bio-based ionic liquids**	**STR2** I. Persson **Structure of complete hydration shells of metal ions in aqueous solution**	**SOL5** E. Kása **Neutralization of tricalcium aluminate hydrates with hydrochloric acid**
15:20-15:50	Coffee break		
	Chairman: Tamal Banerjee	Chairman: Sofia Gama	Chairman: Tadafumi Adschiri
15:50-16:10	**ILS10** U. Domańska--Żelazna **Extraction of metals from waste by ionic liquids, DESs and organophosphorous--based acids**	**STR3** Z-W. Yu **Solution Structures of a lithium-containing electrolyte system**	**TER1** R. Dey **New, simple and highly effective models for predicting thermodynamic and transport properties for binary and multicomponent solutions**
16:10-16:30	**ILS11** D. Lazarević **Pluronic-based biocompatible ternary systems for extraction of parthenolide**	**STR4** J. Han **Speciation of aluminum ions in $AlCl_3$-glyme solutions**	
16:30-16:50	**ILS12** A. Kovačević **Separation of components of rare-earth magnets using phosphonium based ionic liquids**	**STR5** K. Lin **Ion pairs in the sodium-ion aqueous solution by IR ratio spectra and Raman excess spectra**	**TER2** J-L. Gómez Estévez **About the use of the compressibility equation from Kirkwood-Buff theory to the study of electrolyte solutions with a concentration dependent dielectric constant (Adelman's theory)**
16:50-18:00	Poster session P23-P46		

Wednesday July 12, 2023

9:00-10:00	REGISTRATION
10:00-11:00	Chairman: Yongquan Zhou **PL4** H. Torii - **Roles of electrostatics and intermolecular electronic motions in the structural and spectroscopic features of hydrogen- and halogen-bonded systems**
11:00-11:30	Coffee break

	Hall Ivo Andrić A	Hall Ivo Andrić B	Lavender hall
	Chairman: Urszula Domańska-Żelazna	Chairman: Jalel Mhalla	Chairman: Ranjan Dey
11:30-11:50	**ILS13** T. Mu Properties of deep eutectic solvents	**COM1** M. Fedotova New treatment of hydrated protein complexes in silico	**TER3** J-N. Jaubert Coupling an equation of state and the entropy scaling concept to correlate the transport properties of pure fluids
11:50-12:10	**ILS14** H. Mori Machine learning-boosted functional liquids design and experimental verification: An example for CO_2 absorption liquid	**COM2** R. Liu The hydration of Li^+ and Mg^{2+} in subnano carbon nanotubes by multiscale theoretical approach	**TER4** B. Šarac Thermodynamics of the association of KCOSAN in different solvents
12:10-12:30	**ILS15** A. Bronusiene Synthesis, characterization and the use of tin-ascorbate complex as precursor for tin sulfide nanoparticles	**COM3** L. Antonov Are there water-free solvents in general: the “sudden” behaviour of tautomeric switching systems in organic solvents	**TER5** S. Markarian Thermodynamic study of binary mixtures of aliphatic nitriles (acetonitrile, propionitrile, butyronitrile and acrylonitrile with dimethylsulfoxide (or diethylsulfoxide)
12:30-14:00	Lunch		
14:00	Conference excursion		

Thursday July 13, 2023

9:00-10:00	REGISTRATION		
10:00-11:00	Chairman: Pál Sipos **PL5** S. Ražić - **Between green and white analytical chemistry - Greener solvents, from solutions to applications in complex matrices**		
11:00-11:30	Coffee break		
	Hall Ivo Andrić A	Hall Ivo Andrić B	Lavender hall
	Chairman: Slavica Ražić	Chairman: Tomaž Urbič	
11:30-11:50	**TER6** G. Hefter Physicochemical properties of aggressive acid solutions at elevated temperatures	**STR6** F. Castiglione Xenon NMR spectroscopy: structure and dynamics of simple liquids, ionic and porous liquids	
11:50-12:10	**TER7** N. Espitia Galindo Volumetric properties of ionic aminated resorcin[4]arenes	**STR7** Y. Umebayashi Two dimensional Raman and dielectric relaxation correlation analysis for $LiCF_3SO_3$ – propylene carbonate solutions	
12:10-12:30	**COL9** R. Kashapov Supramolecular assembly of polymers with calix[4]resorcin for design of drug delivery systems	**STR8** R. Buchner The effect of added ions on hydration and ion binding of aqueous glutamate	

12:30-14:00	Lunch		
	Chairman: Ingmar Persson	Chairman: Maria J. Lourenço	Chairman: Thierry Tassaing
14:00-14:40	**KN7** S. Gama Chelators and (radio)metals: Speciation and thermodynamic studies	**KN8** T. Banerjee Molecular modelling studies on deep eutectic solvents as novel separation media for aromatic extraction	**KN9** T. Adschiri Supercritical hydrothermal reactions – Basics and applications
14:40-15:00	**TER8** Ž. Medoš Atypical micellization of closo-dodecaborate--based dianionic surfactants in water	**STR9** Y. Zhou Hydration of Hofmeister ions	**FLU1** A. Idrissi The inhomogeneous locale structure of water at ambient and supercritical conditions: Voronoi polyhedral and density-based spatial clustering analysis
15:00-15:20	**TER9** T. Ivanović Activity coefficients of the system $\{y\mathrm{NaCl}+(1-y)\mathrm{Na_2PO_4}\}(\mathrm{aq})$ at $T = 298.15\,\mathrm{K}$	**STR10** M. Busato A multidisciplinary approach to unveil the structural arrangement of deep eutectic solvents: from local order to nanoscale organization	**FLU2** T. Yamaguchi Verification of the structure-making/breaking concept of ion solvation from the structure of aqueous MCl (M=Li, Na, K, Rb, and Cs) solutions in the gigapascal pressure range
15:20-15:50	Coffee break		
	Chairman: Miha Lukšič	Chairman: Carlos Nieto de Castro	Chairman: Lourdes Vega
15:50-16:30	**KN10** J. Hunger On the origin of asymmetric hydrogen--bonds in water: Anti--correlated hydrogen-bonds of D_2O evidenced by 2D-IR spectroscopy	**KN11** T. Urbič An electric and magnetic field effects water's anomalous properties	**KN12** T. Tassaing Investigating the selective solvation of organic materials in supercritical CO_2 through advanced vibrational spectroscopy
16:30-16:50	**TER10** D. Galindres Study of interaction between sulfonated resorcin[4]arenes and bovine serum albumin	**STR11** S. Hosokawa Improved data analysis for molecular dynamics in liquid benzene	**SOL6** I. Shumilin Modifying macrocycle stability and supramolecular chemistry in a deep eutectic solvent
16:50-17:10	**COM4** N. Stamenković Solvent topology in bond decomposition analysis: The path to natural intrinsic acidity	**STR12** P. D'Angelo The Complex Story Behind a Deep Eutectic Solvent Formation as Revealed by L-Menthol Mixtures with Butylated Hydroxytoluene Derivatives	**SOL7** T.T. Borović The effect of methyl salicylate as an additive on the solubility and self-aggregation of caffeine - a thermodynamic and computational approach
20:00	Conference dinner		

Friday July 14, 2023 (all lectures today are in the conference hall Ivo Andrić A+B)

9:30-10:30	Chairman: Jiri Skvara **PL6** R. Rogers - **Solution processing of terrestrial and marine biopolymers can overtake melt processing of plastics and lead to more sustainable materials**
10:30-11:00	**IUPAC Representative** Glen Hefter
11:00-11:30	Coffee break
	Chairman: Tatjana Trtić-Petrović
11:30-11:50	**ILS16** I. Čobanov-Marinković **Thermodynamic studies of micellization of surface active ionic liquids**
11:50-12:10	**STR13** C. Nieto de Castro **Molecular insight on the properties of ionic liquid + water mixtures: From experiment to modelling**
	Chairman: Toshio Yamaguchi
12:10-12:50	**KN13** J. Mhalla **Importance of the dielectric friction effect on the conductivity of polyelectrolytes**
12:50-13:00	**Presentation of ICSC2025**
13:00	Closing ceremony

Book of Abstracts

38th International Conference on Solution Chemistry

PL1

Why are ionic liquids so viscous?

Frederik Philippi[1], Daniel Rauber[2], Kira Lieberkind Eliasen[3], Nathalie Bouscharain[4],
Kristine Niss[3], Christopher Kay[2]
and Tom Welton[1]

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[2]Department of Chemistry, Saarland University, Campus B2.2, Saarbrücken, Germany
[3]"Glass and Time", IMFUFA, Department of Science and Environment, RoskildeUniversity,
P.O. Box 260, DK-4000 Roskilde, Denmark
[4]University of Lyon, INSA Lyon, CNRS, LaMCoS, UMR 5259, 69621 Villeurbanne, France
Presenting author email: t.welton@imperial.ac.uk

Room temperature ionic liquids are considered to have huge potential for practical applications such as batteries. However, their high viscosity presents a significant challenge to their use changing from niche to ubiquitous. The modelling and prediction of viscosity in ionic liquids is the subject of an ongoing debate involving two competing hypotheses: molecular and local mechanisms versus collective and long-range mechanisms. To distinguish between these two theories, we compared an ionic liquid with its uncharged, isoelectronic, isostructural molecular mimic. We measured the viscosity of the molecular mimic at high pressure to emulate the high densities in ionic liquids, which result from the Coulomb interactions in the latter. We were thus able to reveal that the relative contributions of coulombic compaction and the charge network interactions are of similar magnitude. We therefore suggest that the optimisation of the viscosity in room temperature ionic liquids must follow a dual approach.

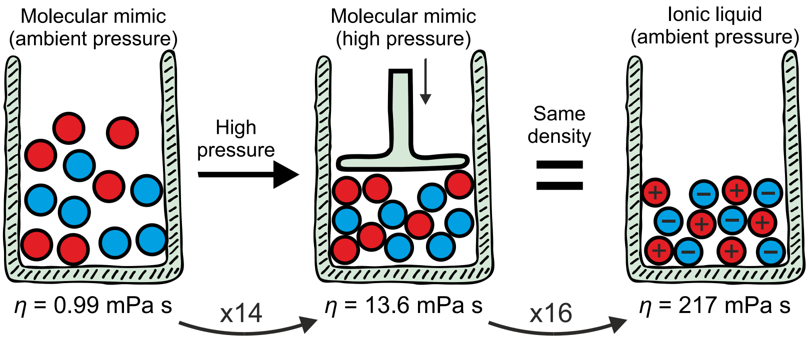

Figure 1. Separating the effects of solvent density and charges.

PL2

Probing interfacial ion-water interaction with atomic resolution

Ying Jiang

International Center for Quantum Materials,
School of Physics, Peking University, Beijing 100871, P. R. China
Presenting author email: **yjiang@pku.edu.cn**

Ion hydration and transport at interfaces are relevant to a wide range of applied fields and natural processes. Interfacial effects are particularly profound in confined geometries such as nanometre-sized channels, where the mechanisms of ion transport in bulk solutions may not apply. To correlate atomic structure with the transport properties of hydrated ions, both the interfacial inhomogeneity and the complex competing interactions among ions, water and surfaces require detailed molecular-level characterization. Using a noncontact atomic force microscopy (AFM) system, we were able to image the individual ion hydrates and their assemblyat surfaces with atomic resolution [1-3]. We found that the alkali ion with specific hydration numbers diffuses orders of magnitude more quickly than other ion hydrates, arising from the degree of symmetry match between the hydrates and the surface lattice. In addition, we found that the alkali ions can come into close contact with each other through the dehydration and water rearrangement process, which is driven by the effective ionic attraction due to the interplay between the water-ion and water-water interactions. These results not only help us to understand the nature of biological ion channels, but may also provide general design principles for artificial ion channels towards high permeation rate and selectivity.

[1] Peng *et al., Nature*, 2018, **557**, 701.
[2] Tian *et al., Nature*, 2022, **377**, 315.
[3] Tian *et al., Under revision*.

PL3

Hunting sustainable energy – the role of solution chemistry and computation on finding optimal solvents for CO_2 capture

Lourdes Vega, Ismail Alkhatib and Daniel Bahamon

Research and Innovation Center on CO_2 and Hydrogen (RICH Center) and Department of
Chemical Engineering, Khalifa University, PO Box 127788, Abu Dhabi, United Arab Emirates
Presenting author email: lourdes.vega@ku.ac.ae

Providing sustainable energy to meet the demands for quality of life and economic growth without compromising the environment is one of the greatest challenges we are facing today. Recognizing this challenge and the need to address it, several countries have already launched their net zero strategies. According to the International Energy Agency, achieving net zero emissions requires a radical technological transformation of the energy sector with carbon capture, utilization and storage (CCUS) identified as a key technology to achieve it. The same conclusion is extracted from the IPCC Working Group III report, Climate Change 2022, where it is stated that CCUS is a route to decarbonize the energy and industrial sectors in the short to medium term [1].

CCUS is not new; in fact, CO_2 has been traditionally captured from concentrated industrial sources for its current applications in food, fire extinctions, etc. However, the conventional chemical absorption-based post-combustion process using aqueous alkanolamines (e.g., monoethanolamine (MEA)) implies high regeneration energy requirements, as well as losses due to degradation and evaporation, posing a great challenge when using them at the scale required to mitigate change. Hence, there is a need to find alternative solvents, overcoming the limitations of traditional ones, in order to improve the efficiency of the process, making it economically viable and environmentally friendly [2]. Here is where understanding the chemistry of solutions plays a key role. In addition, and given the large amount of possible solvents and conditions to be addressed, a holistic approach based on a combination of experimental and modelling work is needed.

After a short overview on the topic, we will show the application of a multi-scale modelling framework to assess the potentiality of alternative amine-based solvents for CO_2 capture examining different solvents including aqueous amines from novel families such as alkyl-ethanolamines, amino-alcohols, dialkylamino-alcohols, and multiamines. Additionally, water-free and water-lean solvents formulated from MEA, with a wide array of organic diluents such as alcohols, glycols, glymes, and polar aprotic solvents are also examined. The multi-scale framework is built in a consistent manner establishing a direct link between the molecular structure of the solvent and its performance for CO_2 capture at industrial conditions. The core of the modelling framework relies on the application of a robust molecular-based equation of state (EoS), namely, soft-SAFT EoS [3,4], to provide all required thermodynamic information needed for an accurate process model and techno-economic evaluation, such as CO_2 solubility, solvent viscosity, density, surface tension, etc. The overall goal is to provide a framework to screen novel solvents for CO_2 capture at the required process conditions at which they will operate, speeding up the industrial implementation of these novel solvents.

Acknowledgements: Financial support for this work was provided by Khalifa University, through the RICH Center (RC2-2019-007).

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PL4

Roles of electrostatics and intermolecular electronic motions in the structural and spectroscopic features of hydrogen- and halogen-bonded systems

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The importance of electrostatic interactions in the structural and dynamical properties of liquids and biomolecular systems is widely recognized. In classical MD simulations of those systems, it is usual to place partial charges on the atomic sites to represent them. In the case of water, some more sophisticated models (such as TIP4P/2005) are widely known, but (aside from the inclusion of polarizability) is this the only case where it is essential to take an extended way of representing intramolecular charge distributions for intermolecular electrostatic interactions? In fact, in some cases, the anisotropic nature of the electron distribution around each atom is so significant that it manifests itself in the intermolecular structural configurations. In the present lecture, the principles will be discussed with some related case studies [1,2].

One way to probe the electrostatic situations in condensed phases is to measure vibrational spectra and to analyse the bands that are sensitive to electrostatic interactions. It is most fundamentally based on the response of the vibrational mode to the intermolecular electric field, and the molecular property in relation to this is the dipole derivative $\partial\mu/\partial Q$ (where Q is the vibrational coordinate of interest). However, the situation is not always so simple. In the case of the $C\equiv N$ stretch of a nitrile compound, it is known that a low-frequency shift is induced by dipolar solvation while a high-frequency shift is induced by hydrogen-bond formation (with water, etc.). Then, is there anything special about the hydrogen bonding of nitrile? In the present lecture, it is shown that, in fact, the spatial inhomogeneity of the electrostatic situation induced by the hydrogen-bond donating group is mainly responsible for this phenomenon [3,4].

According to the fixed atomic partial charge model, the dipole derivative $\partial\mu/\partial Q$ arises from the displacements of partially charged atoms. However, for many vibrational modes with large dipole derivatives, the electronic motions that do not faithfully follow the atomic displacements play an important role. In some cases, they stride over molecules. For example, in the case of the OH stretch of water, the extent of intermolecular partial charge transfer through the hydrogen bond is modulated significantly, so that the dipole derivative is greatly enhanced upon hydrogen-bond formation [5]. This kind of vibration-induced “intermolecular charge flux” plays an important role also in the intensity generation of the THz spectra of hydrogen-bonded systems [6]. In the present lecture, the way of analysing this phenomenon based on the features of electron density will be discussed.

Acknowledgements: This study was supported in part by JSPS KAKENHI Grant Numbers JP22H04534, JP20H05215, JP22K05020 and JP19K05384.

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PL5

Between green and white analytical chemistry - Greener solvents, from solutions to applications in complex matrices

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Green chemistry (GC) is nowadays highly recognized and considered as a holistic concept and exact science for a sustainable future. Considering the twelve GC principles [1], it must be emphasized that only some of them can be directly applied to analytical chemistry. The 12 principles of green analytical chemistry (GAC) were proposed a decade ago [2]. In fact, several GC and GAC rules relate directly to green solvents. The development of new generations of environmentally friendly solvents is one of the most active research areas in green analytical chemistry.

Based on current knowledge, the complete elimination of solvents,as the greenest choice in analytical procedures, is almost impossible. Therefore, eliminating hazardous solvents or replacing them with safer alternatives is a good way. If we need an ideal solvent with good dissolving properties, selectivity and extraction efficiency, it should definitely meet the following requirements: low toxicity, biodegradable, reusable, easy to obtain from renewable sources, low environmental impact and low cost [3]. From an analytical point of view, the main challenge in the future will be to find a compromise between the increasing requirements for the quality of the results (accuracy, LOD, reproducibility...) and the whiteness of the method and the improvement of environmental friendliness [4]. In this presentation, different classes of more environmentally friendly alternatives to conventional organic solvents, such as ionic liquids (ILs), deep eutectic solvents (DES), subcritical water (SCW) and supercritical fluids (SCFs), will be discussed with their basic chemistry and applications in food (natural products) and environmental analysis.

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PL6

Solution processing of terrestrial and marine biopolymers can overtake melt processing of plastics and lead to more sustainable materials

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Today's world is covered in oil in the form of non-degradable synthetic plastics which mar our landscapes and threaten our oceans, but simply eliminating their use with no viable alternatives would be catastrophic. Society is shifting its strategic emphasis on finding suitable renewable plastics replacements, not only because of limited petroleum reserves, but also because of a great amount of synthetic plastics polluting oceans and land. Thus, renewable, biodegradable replacements for plastics are being actively developed, however, they have come nowhere close to completely replacing plastics. Plastics enjoy technological maturity and an entrenched economy of scale that have kept new technologies from competing with plastics.Plastics also enjoy a relatively cheap and simple processing advantage; they are melt processable while most biopolymers are not.

The solubility of many natural biopolymers in ionic liquids, opens many new routes to plastics replacements, however, by solution processing rather than melt processing. In this presentation we will explore pros and cons and ins and outs of biopolymer processing in ionic liquid solution to determine if there is a viable, economic pathway to replacing plastics in the near future with biopolymers.

KN1

Charge and proton transfer in polarizable molecular dynamics simulations of ionic liquids

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Although non-polarizable molecular dynamics simulations successfully modeled the structure of various ionic liquids, the simulated dynamics tend to be one order of magnitude too slow compared to the experiment. Scaled charge approaches may accelerate the dynamics at the cost of abandoning hydrogen bonding and potentially introducing simulation artifacts [1].

Polarizable molecular dynamics simulations are computationally more expensive but offer various advantages [1]:

(1) The simulated dynamics usually come close to experimental data.

(2) The induced dipoles of the molecules may respond to their local environment offering new pathways which are not accessible by “fixed” charge approaches.

(3) The induced dipoles smooth the Coulomb energy in non-equilibrium events like charge and proton transfer.

Classical molecular dynamics simulations are restricted by fixed charges and the incapability to break or form new bonds. However, our novel polarizable molecular dynamics simulations include charge [2] and proton transfer [3-5] events, which are essential for understanding protic ionic liquids. Besides analyzing reduced charge and polarizability effects occurring simultaneously [2], proton transfers allow for the investigation of various conductivity mechanisms like Grotthus and vehicle transport [4,5].

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KN2

Organisation of charged nano-platelets in liquids and gels

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Clay nanoparticles, main constituents of soil, occupy a very specific place in colloidal science: these negatively charged particles have a *plate-like* form. Shape anisotropy leads to a much richer phase diagram and to a more involved experimental and theoretical treatment of these systems. We have explored several aspects of clay organisation and their aggregation in both aqueous suspensions and in water-based gels (hydrogels).

Concerning clay suspensions, we studied clay aggregation by ionenes, a class of cationic polyelectrolytes/polyions with a regular charge density, which can be tuned to match/mismatch the clay charge density [1]. The multi-scale structure of these clay-polyions aggregates is determined by a combination o¬f small angle X-ray scattering (SAXS) and scanning transmission X-ray microscopy (STXM). Locally, we see clear evidence for the formation of clay tactoids (dense face-to-face platelet organisation), within the otherwise loose aggregates. The relative charge density of the polyions chains and clay surfaces is a key parameter for the repeat distance within these tactoids (of the order of 1nm), but also for tactoid abundance and possibly even for the macroscopic aggregate density [2]. The extent of stacking (5–10 platelets per tactoid) is a general feature of all the systems, and its origin remains unknown.

Interestingly, it is possible to form more extended clay-ionene tactoids (~ 20 stacked platelets) by starting with clay suspensions with multivalent atomic counterions, such as Ca^{2+} and La^{3+} (as opposed to monovalent ions). In such cases, extended tactoids held together by multivalent ions are present in the system from the start. After addition of ionene polyions, an equilibrium is established between two types of extended tactoids, those held together purely by multivalent atomic ions on one hand and by ionene polyions on the other. No mixed tactoids seem to be present. We suspect multivalent-ion-tactoids acting as “templates” for polyion-tactoids.

The face-to-face organisation of clay platelets is equally reproduced in ionene-based hydrogels, albeit at much larger clay separations (tens of nm), which is decided by the underlying mesh size of the polyelectrolyte hydrogel network [3-4]. Interestingly, the degree of nanoplatelet ordering in the hydrogel is very sensitive to the negative charge location on the clay platelet. Increased nanoplatelet ordering leads to an improvement of the elastic properties of the hydrogel, in particular close to the cgc (critical gel concentration). On the contrary, the presence of tactoids destroys the hydrogel network. We are currently exploring the possibility of a unique nanoplatelet orientation inside the hydrogel, in order to yield a versatile hydrogel system with potentially anisotropic permeability properties.

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KN3

Coordination modes and substituents of tridentate thiosemicarbazones modulating the solution chemical properties and cytotoxicity

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Thiosemicarbazones (TSCs) have a broad range of pharmacological effects and are promising drug candidates for anticancer therapy. Their mechanisms of action are often linked to their ability to form stable and redox active complexes with essential metal ions such as iron and copper [1]. 3-Aminopyridine-2-carboxaldehyde thiosemicarbazone (triapine) is the most well-known representative of the α-N-heterocyclic TSC compound family. It has been studied in *ca*. 30 phase I and II clinical trials in both solid and haematological tumours. Also other two orally available TSCs (code names: COTI-2, DpC) have entered clinical trials rekindling the research interest in this compound family. The tridentate α-N-pyridyl TSCs possess a $\{N_{pyridyl},N,S\}$ donor set, while the salicylaldehyde derivatives can offer an $\{O_{phenolato},N,S\}$ binding mode (Figure 1). Triapine is the effective inhibitor of the ribonucleotide reductase, an iron-containing enzyme, involved in the rate-limiting step of DNA synthesis. The $\{N_{pyridyl},N,S\}$ donor set provides the possibility to form stable complex with both Fe(II) and Fe(III) ions, which seems to be a crucial factor in the anticancer effect [2,3]. Additionally, intracellularly formed copper complexes of the tetramethylated triapine derivative were suggested to be responsible for the increased cytotoxicity as well as the potential to induce paraptosis [4]. In contrast, the salicylaldehyde TSC derivatives generally display weaker cytotoxic activity in comparison to the α-N-pyridyl TSCs, while their Cu(II) complexes often are more cytotoxic than the ligands alone.

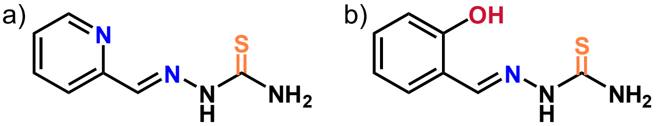

Figure 1. Chemical structure of the simplest a) α-N-pyridyl TSC and b) salicyladehyde TSC.

Herein, I am going to present an overview on how the structural diversity of the TSC ligands can affect the cytotoxic activity, the proton dissociation processes, lipophilicity, the stability in solution and redox properties of the complexes formed with Cu(II) and Fe(II/III) ions based on our results obtained in the least years. Impact of the variation of the chalcogen atom (S, O, Se), the substituentsat various positions and combination with the sterane backbone on the physical-chemical properties and the biological activity will be presented.

Acknowledgements: Special thanks to all the co-authors of our common papers published on thiosemicarbazones in the last years. This work was supported by the Eötvös Lóránd Research Network (LP2019-6/2019).

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KN4

Complex and not so complex systems for SDG´s solutions

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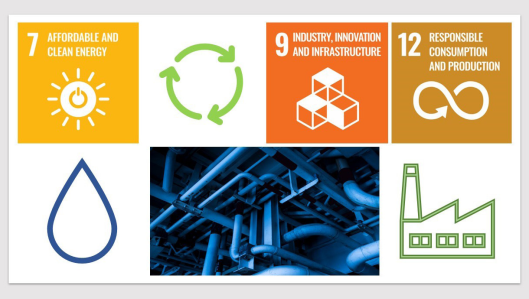
This keynote aims to show that the accurate measurement of thermophysical properties is a very important factor in making energy decisions, especially when working above 200°C. Possible systems used for heat transfer and storage are presented, in different temperature ranges, at low pressures, based on molten salts, ionic liquids, and nanofluids. The in-depth knowledge of these properties in molten salts and ionic liquids, with or without the addition of nanomaterials could quickly contribute to increase, for example, the performance of some solar systems, heat transfer fluids, heat storage and/or nuclear energy plants [1,2]. Society faces a complex mission in the development of energy-efficient, low-polluting systems (CO_2 footprint), with secondary resourceswhich should be based, whenever possible, on a sustainable circular economy without environmental damage or human risk. In fact, it is understood that the future of chemical industry must be mainly driven by the sun [3], which complicates the safety rules issue.It should be noted that most of the equipment operating with these materials (of which the purity, contaminants, concentration, toxicology, ecotoxicology are unknown) perform their function based on very old experimental/theoretical results, never questioning whether they are still the most appropriate.

Due to the main characteristics of molten salts, such as stability at high temperatures, low vapor pressure, liquid state over a wide range of temperatures, ability to dissolve many inorganic and organic compounds, generally low viscosity, and high heat capacity per unit volume [1], their use has increased in energy production plants with solar incidence. On the other hand, ionic liquids have a wide range of properties that give them enormous technological flexibility and make them convenient for applications in low and medium range temperatures, when mass flow is important,but they generally have higher viscosities and can degrade at temperatures higher than 250°C. Its industrial use depends on the cost/kg of its production, still high today. However, by blending the ionic liquid with water, significant decrease in viscosity is achieved and cost decreased [4].

Thus, the strictly measured thermophysical properties combined with the safety data of some nanosystems (synthetic and/or natural) are discussed for the near future, which is intended to be sustainable in terms of resources, health, and environmental protection, paving the way for more efficient industries, less polluting and recyclable, in the light of the 2030 UN Agenda.



Acknowledgements: This work was supported by Centro de Química Estrutural, UID/QUI/00100/2019, and UIDB/00100/2020, funded by FCT - Fundação para a Ciência e Tecnologia, I.P., Portugal.

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KN5

Ion hydration, ion recognition and applications in salt lake resources separations

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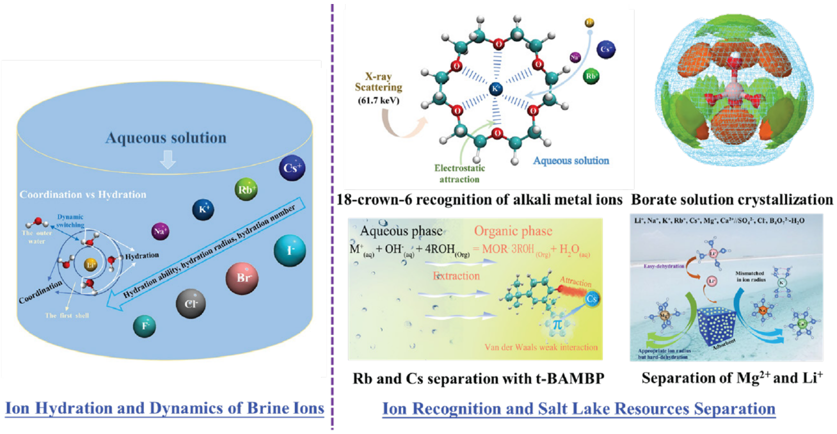
Salt lakes contain abundant mineral resources such as sodium (Na), magnesium (Mg), potassium (K), lithium (Li), boron (B), *etc*. In the past decades, great progress was achieved in salt lake resources separation [1], and researchers found the ion hydration and complex play important roles for the salt lake resource separation. However, solution structure, and the mechanism study at atomic level isn't an easy work [2]. In the present talk, the methods for solution structure at the atomic level with the neutron scattering (NS), wide angle X-ray scattering (WAXRS) and computer simulations will be presented. The micro-hydration structure [3] and dynamics of Li^+, Na^+, K^+, Rb^+, Cs^+ and F^-, Cl^-, Br^-, I^- were systematically studied at the atomic level by neutron scattering (NS), wide angle X-ray scattering (WAXRS) and molecular dynamics (MD) simulations to obtain the change rule of ionic hydration structure and dynamics with the ionic potential (q/r). Then, four application examples, *i.e.* (1) 18-crown-6 recognition of alkaline ions; (2) Aqueous borate solution and crystallization [4,5]; (3) Rb and Cs separation from salt lake brines with t-BAMBP [6]; (4) Mg^{2+} and Li^+ separation were discussed.



18-crown-6 recognition of alkali metal ions

Borate solution crystallization

Rb and Cs separation with t-BAMBP

Separation of Mg^{2+} and Li^+

Ion Hydration and Dynamics of Brine Ions

Ion Recognition and Salt Lake Resources Separation

Figure 1. The main contents in this talk

Acknowledgements: This work was financially supported by the National Natural Science Foundation of China (No.201973106) and the Innovation Platform Construction Project of Qinghai Province (2019-ZJ-T03). The authors are grateful for the J-PARC and SPring-8 teams for their help during the experiments.

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KN6

Resorcinarenes, solvation in water and organic solvents

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The resorcinarenes (RAs) have attracted attention in recent times due to their use in different fields of supramolecular chemistry. Appropriate synthesis methods have allowed systematic changes in the size of the molecule, allowing to vary the solubility of these compounds in common solvents. The physiochemical properties in aqueous and organic solvents of these macrocycles have received less attention compared to applications and uses as host molecules.

This contribution shows some studies related to the solvation of resorcin[4]arenes in aqueous and organic solvents, with special emphasis on the effect of systematic changes in the structure of these macrocycles. The physicochemical properties of anionic and cationic resorcinarenes have shown association phenomena and surface activity in aqueous solutions, while non-ionic resorcinarenes have showed aggregation in organic solvents. The thermodynamic properties in solution are also showed.

Resorcin[4]arenes are suitable model solutes for the study the macrocyclic solvation processes and this information is useful to understand the interactions related to host-guest chemistry.

KN7

Chelators and (Radio)metals: Speciation and Thermodynamic Studies

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The use of nuclear techniques for the detection, follow-up and treatment of several pathologies is fundamental in nowadays medicine. In particular, the use of radioactive metal isotopes – radiometals – allowed remarkable advances in both diagnosis – using single photon emission computed tomography (SPECT) and positron emission tomography (PET) – and targeted radiotherapy with alpha-, beta- and Auger electron-emitting nuclei.

The leading method to use the advantages of metal isotopes is the use of radiometal-ligand complexes [1]. To this purpose, radiometal chelators need to be chosen and developed in order to form thermodynamically and kinetically stable metal-complexes with the target radiometal. Furthermore, as the final goal of the (new) radiometal-complexes is their use *in vivo*, the knowledge of their behaviour towards other metals (*e.g.*, Fe, Mo, Zn) and natural chelators present in biological fluids is fundamental. For all this, it is essential the knowledge of what species can be formed and their stability. In other words, their chemical speciation.

Speciation studies in aqueous solution are mainly performed through equilibrium data analysis based on stability constants. Potentiometry and UV/Vis spectrophotometry are the most widely used techniques in chemical speciation studies, and they still remain among the most adequate and accurate for the determination of the stability constants in solution. Nevertheless, the investigation of more and more complex systems (*e.g.*, ligands with several and different binding sites, very strong chelators, unconventional conditions, multicomponent solutions, etc.) opened up new challenges and questions for solution chemists. As such, other techniques and/or approaches are becoming even more necessary to get further information, for example, on the nature of species effectively formed, on their structure, and on their reactivity. It is worth of mention that the referred studies, when considering radiometal cations, are done using either the cold surrogate of the radioisotope of interest (*e.g.*, ^{69}Ga vs ☢^{67}Ga or ☢^{68}Ga; ^{63}Cu vs ☢^{64}Cu), or metal cations with very similar chemical properties (*e.g.*, La vs ☢^{225}Ac).

In this communication, some examples will be reported to evidence how these techniques and approaches have been exploited to complement potentiometric and/or spectrophotometric results to solve some issues related to the assessment of the chemical speciation of particularly complex systems [2-4]. Results relative to the binding ability of some multi-hetero-dentate ligands (namely natural and synthetic metallophores) towards metal cations of relevance will be presented.

Acknowledgements: The authors would like to thank the financial support from the National Science Centre (NCN), Poland, under the scope of the research project number 2020/39/B/ST4/03060 and COST (European Cooperation in Science and Technology), as this publication is based upon work from COST Action CA18202 – NECTAR, Network for Equilibria and Chemical Thermodynamics Advanced Research.

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KN8

Molecular Modelling studies on Deep Eutectic Solvents as Novel Separation Media for Aromatic Extraction

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The talk shall discuss Molecular Dynamics (MD) and Quantum Chemistry (QC) computations for aromatic extraction by Deep Eutectic Solvents (DES) from aqueous and hydrocarbon streams respectively. The three systems discussed shall be (a) high purity hexane isolation using phosphonium based DES, (b) extraction of pesticide component with menthol-based DES and (c) interfacial properties of DESs and water to extract phenolic compounds from water. The non-bonded interactions, radial distribution function, spatial distribution function, and hydrogen bonding topology of various components were explored via MD simulations that highlighted the enhanced and favourable interactions of aromatic compounds with DESs components. The stability of different DESs-water systems were also studied to understand the relative stability of solvents to extract the aromatic or phenolic compounds from water. The charge-transfer (CT) process in quantum calculation confirmed the direction of CT from DES to aromatic compounds, and the NBO analysis established the stability of DESs. The atom-in-molecules (AIM) and noncovalent interaction (NCI) analysis suggested a strong non-covalent interactions which is responsible for a higher extraction of aromatic compounds from water [1].

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KN9

Supercritical hydrothermal reactions -Basics and applications-

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This lecture will explain the supercritical water reactions and its related technologies that Tadafumi Adschiri has explored for more than 30 years. His research has focused on the fundamentals and applications of a flow reaction process that has enabled detailed kinetic studies of unusual reactions in supercritical fluids for both organic and inorganic reactions. The results of his research on supercritical water reactions have enabled various applications, such as the world first supercritical chemical recycling technology and continuous nanoparticle synthesis. His recent research features the creation of new materials (with new functions) using reactions in supercritical water, in which organic and inorganic reactions can be conducted simultaneously to create organic/inorganic composite nanomaterials. The high affinity of organic-modified nanoparticles toward organic solvents or polymers enables the fabrication of highly concentrated nano-inks or high-performance hybrid polymers. These nanoparticles have extremely high torsion inside their structure, which leads to high oxygen-ion mobility even at low temperatures, facilitating the development of a new, low-temperature steam cracking process for hydrogen production.

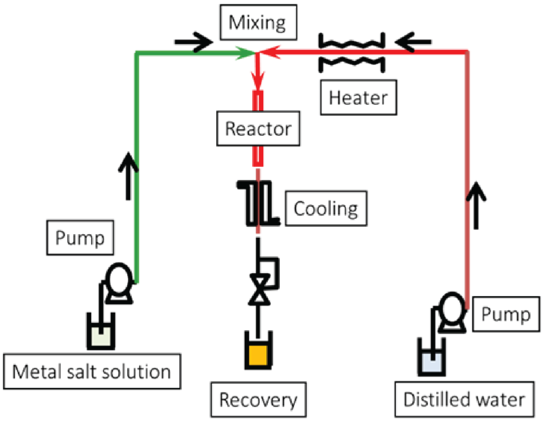

Figure 1. Two-fluids mixing flow system for particle synthesis in supercritical water.

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KN10

On the Origin of Asymmetric Hydrogen-Bonds in Water: Anti-Correlated Hydrogen-Bonds of D_2O evidenced by 2D-IR spectroscopy

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Liquid water is traditionally viewed to form a distorted tetrahedral hydrogen-bond (H-bond) network. Yet, this rather symmetric structure has been challenged by x-ray [1] and computer simulation [2] studies. These studies have revealed a highly asymmetric H-bond geometry resulting in chain- or ring-like configurations, relevant to understanding the various anomalies of water [2]. Here, we characterize the inherent H-bond structure of water by studying water diluted in dimethylformamide with two-dimensional infrared (2D-IR) spectroscopy. We characterize the distribution of local H-bonds via coupling and broadening of the OD stretching vibrations of HOD and D_2O. Experiments on the coupled OD stretch oscillators of D_2O – the asymmetric and symmetric vibrational modes – reveal a markedly narrower inhomogeneous line width for the coupled modes as compared to the uncoupled vibration of HOD. Frequency maps obtained from density functional theory calculations show that these differing line width scan be explained by anti-correlated H-bond strengths of water. This anti--correlation is confirmed by the cross-peaks in the 2D-IR spectra, yet, our results indicate that this anti-correlation is rather short-lived (~200 fs) and a mere results of the H-bond potential energy landscape. In fact, experiments on urea dissolved in dimethylsulfoxide provide evidence for a similar asymmetry of urea's N-H H-bonds. As such, our results suggest that asymmetric H-bonding is an inherent feature of XH_2 groups (X=N,O), but the structural consequences are rapidly smeared out at ambient conditions.

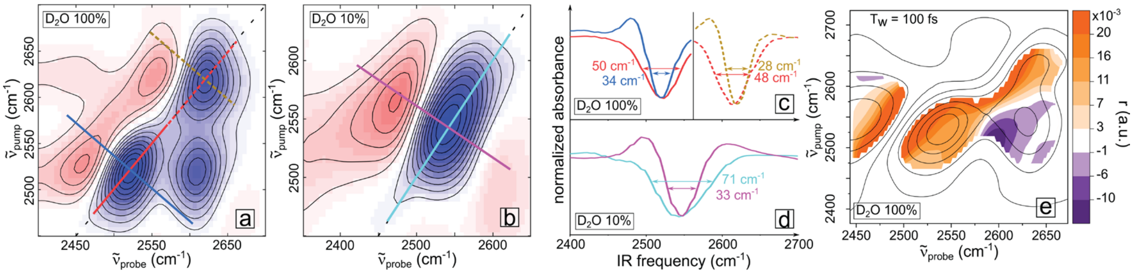

Figure 1. Isotropic 2D IR spectra of a) D_2O and b) $D_2O:H_2O$ 1:9 in dimethylformamide with diagonal and anti-diagonal slices indicated and displayed in c) and d). e) Map of the local correlation coefficient (color map) together the 2D-IR spectrum (contour plot).

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KN11

An electric and magnetic field effects water’s anomalous properties

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We have modelled influence of the electric field on water properties. We use the MB and rose model of water, two simple two-dimensional statistical mechanical models in which waters are represented as Lennard-Jones disks plus interactions mimicking formation of hydrogen bonds. We modified the original models by adding charges for particles to with electric and magnetic field.

The Monte Carlo simulations were performed to explore how water molecules are organized in the electric and magnetic fields of different strengths. The small strength of the electric and magnetic fields does not affect properties of water and position of phase transitions, while the strong strengths shift boiling and melting points as well as position of the density anomaly. From certain strength on the density anomaly disappears.

KN12

Investigating the Selective Solvation of Organic Materials in Supercritical CO_2 through Advanced Vibrational Spectroscopy

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Investigating the mutual solubility of organic materials with supercritical CO_2 ($ScCO_2$) is of primary importance to understand and control $ScCO_2$-assisted processes such as extraction, separation, impregnation, foaming, etc... Until now, most of the solubility studies focused on the solubility of a single compound in $ScCO_2$ or the CO_2 sorption in an homogeneous polymer. In contrast, much less works have been published on the solubility of multicomponent systems (i.e. mixture of compounds) in $ScCO_2$ [1-3] and on the CO_2 sorption in polymer blends and the resulting swelling of the polymer [4, 5]. Nevertheless, many $ScCO_2$-assisted processes involve multicomponent systems. For example, the extraction process of natural products using $ScCO_2$ leads to the withdrawal of few up to hundreds of compounds from the natural substrate [6]. On the other hand, the emerging trend in $ScCO_2$-assisted impregnation is to load natural multicomponent extracts in polymeric matrices to obtain functional materials that exhibits the bioactivity of this extract, which is generally higher than that of a single compound [7]. In addition, some co-solute effects may be observed that could lead to an enhanced or lower solubility in $ScCO_2$ of a given compound of a multicomponent system in comparison with the binary system (compound/$ScCO_2$). Thus, in order to put in evidence these cooperative effects, it is necessary to characterize the mutual solubility of these multicomponent materials with $ScCO_2$. To this aim, we have developed an FTIR/Raman spectroscopy and microscopy set-up that allows to perform in situ experiments under high pressure conditions in order to determine the solubility of organic materials in $ScCO_2$ as well as the CO_2 sorption into polymers and their resulting swelling. Through various examples, we will illustrate how using these advanced vibrational spectroscopic techniques it is possible to determinethe solubility in $ScCO_2$ of each compound in multicomponent systems and detect specific solubility enhancement of some compounds in comparison with the binary system. On the other hand, we will show how Raman microscopy allows to detect inhomogeneous distributionat the microscale of the CO_2 solubility in polymer blends.

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KN13

Importance of the dielectric friction effect on the conductivity of polyelectrolytes

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Unlike simple dilute electrolytes, theories of dilute polyelectrolyte solutions are not yet fully described and remain a challenge for the future, especially for the following reasons:

1-The absence of universal limit laws analogous to those of Debye-Hückel-Bjerrum-Onsager for dilute electrolytes.

2-The simulation of polyelectrolytes by molecular dynamics concerns only justly concentrated solutions with polyions of rather limited sizes.

3- Manning's model [1], even corrected, concerns only one configuration (rod-like chain), and has some lacks: a) It predicts degrees of ionic condensation of counterions independent on the concentration, which is in contradiction with the Ostwald dilution principle. b) It cannot interpret the dependence of the mobility of the polyion with the nature of its counterions, (particularly in the case of deviations from Kohlrausch's law of additivity). c) It only takes into account three frictional forces (hydrodynamic, electrophoretic and ionic relaxation friction) and therefore completely ignores the dielectric friction.

4-Manning's model has recently been extended on the basis of scaling concepts for the description of polyelectrolyte chain conformation in terms of electrostatic blobs and correlation blobs. However, the composition and size of these blobs are approximated for a given solvent, assuming that all energies involved are of the order of thermal energy [2].

In addition, the degrees of ionic condensation of the counterions are determined empirically by adjusting the equivalent conductivities calculated according to Manning's general expression, with the experimental data without taking into account the dielectric friction.

Therefore, the main objective of this lecture is to summarize the essence of our new contribution in order to model and evaluate the thermodynamic and transport properties of dilute polyelectrolyte solutions. The general ellipsoidal configurations of the polyion and its ionic atmosphere are quantized mathematically via the "generating functions" g(R,L) and g(d,L) between two limits: spheroid conformations and partially or completely stretched configurations (Pearl-Necklace or Chain of Charged Spheres). The degrees of ionic condensation are determined according to the statistical model of the two states taking into account electrostatic and specific interactions. The four friction coefficients are also quantified. The results for different types of polyelectrolytes show a complex interdependence between conformation, condensation and the four frictions. The important role of dielectric friction undergone by the moving polyion is very sensitive to conformation, ionic condensation, ionic solvation, specific interactions and hydrophobicity via blobs size [3-4].

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ILS1

About interrelation between *PVT* of ionic liquids and phase equilibria in their systems

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This study demonstrates that the solubilities of different compounds in Ionic Liquids (ILs) could be explained by the remoteness between the critical points of solutes and the imaginary critical points of ILs. A growing difference between them increases the systems' asymmetry and, therefore, results in wider ranges of phase splits, which also means lower solubilities. These basic Global Phase Diagram considerations emphasize the primary importance of rigorous obeying of the critical constants of the ordinary compounds on one hand and precise modelling *PVT* of ILs in a wide range of conditions on the other. The latter allows robust estimation of the imaginary critical constants of ILs. The Critical Point-based modification of the Perturbed-Chain Association Fluid Theory (CP-PC-SAFT) [1] fits these criteria and, therefore, can be characterized by a far-going predictive potential even while neglecting association, polar and electrostatic interactions occurring in IL systems. It is demonstrated that using the k_{12} value obtained for a certain IL system, CP-PC-SAFT truthfully predicts VLE, LLE and LLVE in a wide variety of systems of similar ILs with non-associating compounds such as various gases, refrigerants, aliphatic and aromatic hydrocarbons. The LLE in ternary systems are considered as well.

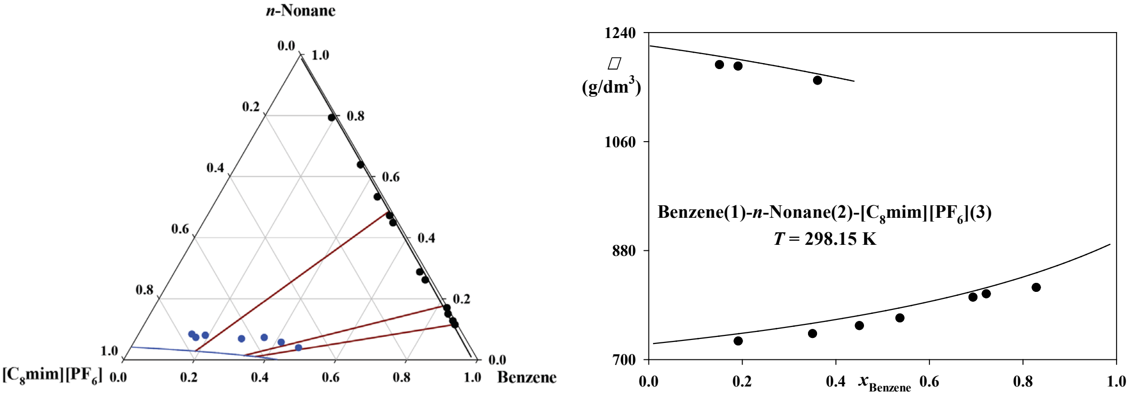

Figure 1. LLE and density of phases in the system n-nonane-benzene-[C_8mim][PF_6]. Points – experimental data [2]. Dotted lines – experimental tie-lines. Solid lines – predictions of CP-PC-SAFT with $k_{12}=0.04$, which was obtained for the system CO_2 -[C_4mim][BF_4].

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ILS2

Structure and formation thermodynamics of Cobalt(II)complexes with nitrate and chloride anions in [C_4mim][Tf_2N] ionic liquid

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Room temperature ionic liquids (RTILs) have emerged and attracted increasing interest in the past few years as “green” substitutes of volatile organic solvents in hydrometallurgical recovery processes of “critical” materials deriving from mining or high-tech waste [1]. In this field, the recycling of cobalt assumed a growing importance due to the increasing demand related to its use in strategic technologies, such as Li-ion batteries or motors for electric mobility [2]. Among the hydrophobic RTILs, those based on the alkylimidazolium ($C_nC_m$im$^+$) cation and bis(trifluoromethylsulfonyl)imide (Tf_2N) anion (Figure 1.) have been widely studied for metal extractions in recent years [3-6]. However, only few works were focused on the nature of the dissolved metals and their speciation in RTILs [6], despite these are fundamental data to understand the metal coordination properties in the RTIL and the separation processes.

In the present communication, we report a thermodynamic and structural study of the species formed between Co(II) and two important coordinating anions, chloride and nitrate, which are often present in RTIL and aqueous solutions in separations applications. To simplify the system in study, water was removed from in [C_4mim][Tf_2N] by keeping it under vacuum at 70°C for several days and preparing the solutions in a dry box. Then, complex formation has been studied by UV-Vis titrations and isothermal titration calorimetry (ITC). The analysis of UV-Vis titrations evidence that the CoX_j species correspond to j = 1-3 with NO_3^- and j = 1-4 with Cl^-. The species with Cl^- present a much higher stability and also a change in the metal coordination geometry from the starting octahedral $[Co[Tf_2N]_6]^{4-}$ [6] to tetrahedral complexes. This different behaviour is also reflected in the ITC plots in Figure 1 which show a clearly different heat evolution at increasing ligand/metal ratios. We find that the 1:2 species with chloride is enthalpy disfavoured and stabilized by a very positive entropic term, which can be associated to the change of coordination of the metal. Theoretical calculations (DFT) provided the structures of the $[CoX_j[Tf_2N]_{6-i}]^{i-j-4}$ complexes ($X^- = NO_3^-$, Cl^-) and showed that 1) two $[Tf_2N]^-$ are replaced by each NO_3^- 2) for Cl^-, the change of coordination occurs when the 1:2 species is formed and corresponds to $CoCl_2[Tf_2N]_2^{2-}$. Molecular dynamics (MD) simulations provided also information on the changes in the outer solvation shell of the Co(II) complexes.

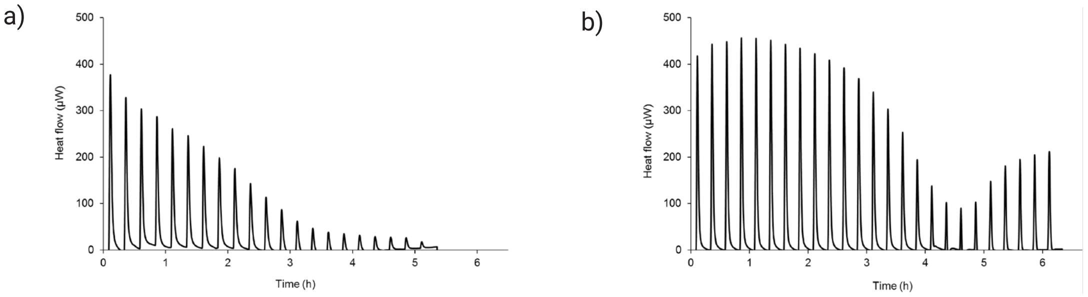

Figure 1. ITC of Co(II) solutions in [C_4mim][Tf_2N] with solutions of: a) [C_4mim][NO_3] and b) [C_4mim][Cl].

Acknowledgements: MIUR PRIN “CHIRALAB” (#20172M3K5N).

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ILS3

Structurally modified alkylimidazolium ionic liquids in aqueous and aqueous-salt solutions

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Ionic Liquids (ILs) occupy a special place among solvents. Their well-known features, such as a wide liquid range, low volatility, high thermal stability etc., make many ILs promising, in particular, as an alternative to traditional organic solvents in liquid-liquid extraction of high-value substances [1]. Aqueous biphasic systems (ABSs) that may provide more eco-friendly extraction media are of special interest. In 2003, Rogers and co-workers, for the first time, used the ABSs formed by adding inorganic salts to water-miscible ILs [2]. By varying the chemical structure of ILs it is possible to obtain the required change in their properties (phase behavior, extraction capacity, self-organization etc.). Among the modified ILs, ILswith amino acidic anions attract attention,particularly due to their low toxicity and likely biocompatibility [3]. Recently, polymerized ILs have been shown to be promising agents for enhanced bioextraction [4].

In this work, we obtain new data (viscometry, light scattering, titration calorimetry, LLE studies) and analyze structural and phase behavior of aqueous and aqueous-salt solutions of 1-alkyl-3-methylimidazolium ILs with different amino acid anions (leucinate, lysinate and valinate) in comparison with the behavior of the halide ILs based systems. Partitioning of L-tryptophan (taken as a model biocompound) between the liquid phases is studied in these ABSs. ILs with bromide anion and modified cation, 1-butyl-3-vinylimidazolium and poly(1-butyl-3-vinylimidazolium), Figure 1., is considered next. Special attention is given to the structural behavior of this highly amphiphilic polyelectrolyte in aqueous-salt media.

We conclude by discussing structural design of ILs to control phase split in the ABSs and to improve the performance of liquid-liquid extraction systems.

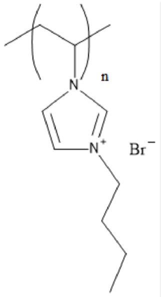

Figure 1. Chemical structure of poly(1-butyl-3-vinylimidazolium) bromide.

Acknowledgements: We thank Russian Science Foundation (project 20-13-00038) for financial support; measurements were partly performed at the Research park of St. Petersburg State University (Center for Magnetic Resonance, Center for Chemical Analysis and Materials Research, Center for Thermogravimetric and Calorimetric Research, Center for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics).

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ILS4

A new definition and extended set of constants to predict densities of ionic liquids by using the residual volume approach

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The Residual Volume Approach (RVA), an empirical model for the prediction of physicochemical properties of ionic liquids (ILs) utilizing simple linear correlations between given property and the residual volume of the substituents within given homologues series, was proposed a decade ago [Bogdanov & Kantlehner, Z. Naturforsch. 64B (2009) 215] and was proven successful for predicting properties such as density, viscosity, ionic conductivity, the heat capacity of a large number, and a variety of ILs. A set of constants (β^X) which stands for the residual volume of the substituents X was initially defined for normal alkyl substituents from C1 to C12. In continuation of these studies, we propose a new definition and extend the set of constants to 45, which includes branched and functionalized substituents. Moreover, we put forward a mechanism for additional fine-tuning of the existent and calculation of new β-constants, allowing continuous improvement and enrichment of the set when novel experimental or theoretical data is available. The applicability of the improved RVA was tested for 4580 total data points (188 ILs at temperature range 293-363 K) and showed excellent predictive ability with an average absolute relative deviation (%AARD) of 0.18%. Furthermore, we demonstrated that RVA could successfully be applied to predict density regardless of the cation-anion combination. It can be utilized to widen the scope and improve the performance of other predictive methods. All this can contribute to the more straightforward and proper selection of ILs for a given process.

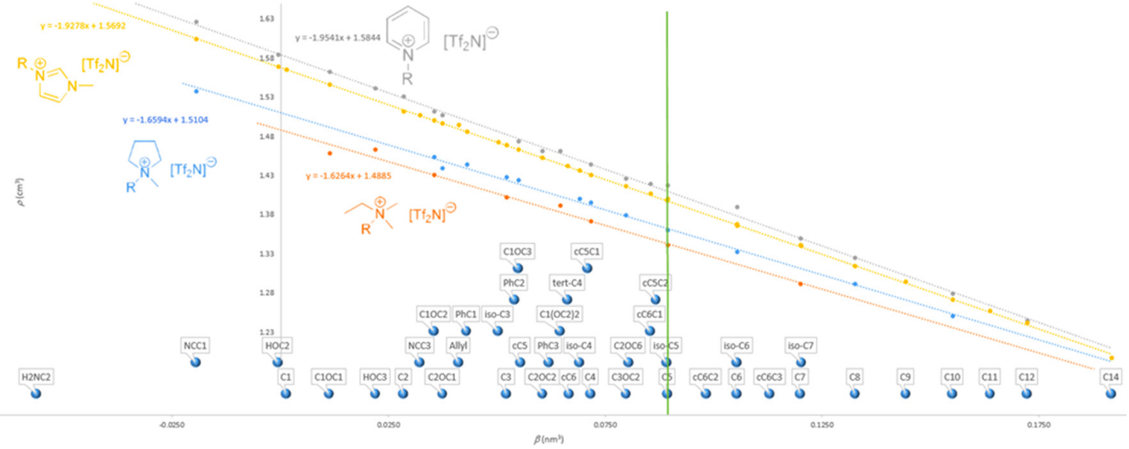

Figure 1. Graphical representation of the RVA

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ILS5

Ionization thermodynamics of poly(acrylic acid) in ionic liquids

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Ionic liquids, regarded as extremely condensed electrolyte solvents, are also attracting attentionas colloidal dispersion media. According to DLVO theory, the addition of electrolytes is generally the primary cause for reduced colloidal stability for charged nanoparticles in water. Therefore, ionic liquids could not be "good" dispersing media of colloids. Despite those predictions, techniques to yield stable dispersions of nanoparticles have already been obtained in various ionic liquids. We so far investigated the pH response of the colloidal stability of maghemite magnetic nanoparticles, whose surface is functionalized with polyacrylic acid (pAA), namely coated nanoparticles (CNps) [1,2]. In aqueous solutions, CNps aggregate to precipitate in an acidic condition, showing a single threshold pH, while the same CNps aggregate in both acidic and basic conditions and flocculate in the medium pH region in protic ionic liquids (PILs), ethylammonium nitrate (EAN) and *N,N*-diethylethanolammonium trifluoromethanesulfonate ($Et_2HyNH^+ \cdot TfO^-$), showing two switching pHs.In the current study, the ionization thermodynamics of pAA in ionic liquids are studied in order to reveal the role of pAA on the dispersion of CNps.

Figure 1(a) shows the enthalpogram of pAA ionization titration, and Figure 1(b) shows that of CNp in EAN. CNps disperse under the acidic condition (titration ratio < 0), flocculate when the titration ratio exceeds zero, and then redisperse when the titration proceeds (titration ratio > 0.8) to achieve an adequate degree of ionization. These enthalpograms are very similar, indicating that the ionization behavior of the surface pAA on CNp resembles that in the bulk. Interestingly, this works out even in the flocculation pH region, implying that the chemical potential of bulk pH penetrates inside the CNp aggregation to govern the ionization equilibria of the inside pAA. Figure 3(c) shows the pAA titration curve in $Et_2HyNH^+ \cdot TfO^-$. Prior to the ionization of the pAA, a heat generation not to be attributed to the ionization was observed. This has also been observed for CNp in the same PIL [2], which may arise from the condensation of the solvent cation at the vicinity of the surface pAA.Since the entropy of the subsequent ionization was large and negative, further condensation of the solvent cation around CNps may occurwith the increasing degree of ionization. Thanks to such strong solvations of the surface pAA of the CNps, the pH region of the stable dispersion of the CNp is considered to be wider than that in EAN.

In both PILs, the ionization thermodynamics of CNp resemble those of pAA in each solvent, and thus, the ionization and solvation of pAA are confirmed to contribute to the dispersion stability of CNps. Notably, the dispersion mechanism of CNps in EAN and $Et_2HyNH^+ \cdot TfO^-$ is different, even though both are PILs.

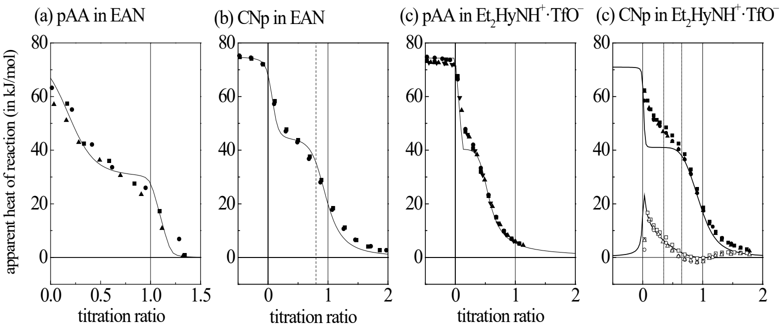

Figure 1. Enthalpogram of ionization of pAA and CNp in PILs.

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ILS6

The nature of interactions in mixtures of pharmaceutically active ingredient ionic liquid and natural deep eutectic solvents

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In past years, the third generation of ionic liquids (ILs) made from active pharmaceutical ingredients (APIs) has emerged, with extremely low toxicity, designed lipophilicity, and the possibility of cation and anion synergistic effect, thus enabling their use as potential medicines. Obtaining APIs in a liquid aggregate state at room temperature solves numerous problems, such as polymorphism, facilitates industrial manufacturing and opens up the possibility of direct topical application. Enhancement in the permeability APIs through ILs synthesis via transdermal or topical routes is conducted due to low dissociation of the API-based ILs, as a consequence of ion pairs formation. Namely, ion-pair formation in ionic liquid structure increases the drugs' lipophilicity enough to pass through the skin and manifest its pharmacological action but reduces their ability to further absorb into the bloodstream. However, although many room-temperature ionic liquids are based on local anesthetics and nonsteroidal anti-inflammatory drugs (NSAIDs), numerous combinations remain solid-state with melting temperatures below 100ºC. Since they still belong to ionic liquids and could significantly enhance the physicochemical and pharmacological properties of APIs, finding an adequate solvent for their topical application is necessary. One of the innovative approaches would be using natural deep eutectic solvents (NADESs). NADES is a mixture of two or more active pharmaceutical compounds, typically solid at room temperature. When combined in a specific molar ratio, they link by hydrogen bonds, achieve a significant melting point depression, and remain liquid at room temperature.

Herein, API-ILbenzocainiumibuprofenate with a melting point above room temperature was synthesized and characterized using infrared and nuclear magnetic resonance spectroscopy and differential scanning calorimetry (DSC). For the benzocainium ibuprofenate solution preparation, NADESs prepared from menthol and decanoic acid in different molar ratios of 1:2, 1:1 and 2:1 were selected as solvents, and their structure was confirmed using DSC. Benzocaine is a drug for local anaesthesia, ibuprofen is an NSAID, menthol is used for pain relief, and decanoic acid has a role as an antibacterial agent. The densities, speeds of sound, and viscosities of the investigated ionic liquid in a mixture with NADES as a solvent were measured in the temperature range from 293.15 to 318.15 K at different IL molalities. Based on the obtained results, the influence of solvent composition on interactions in mixtures of API ionic liquid and natural deep eutectic solvents was investigated. The system that stands out is the one with an excess of decanoic acid M:D/1:2, while the remaining two systems M:D/1:1 and M:D/2:1 behave quite similarly. In those systems, interactions via hydrogen bonds between menthol and decanoic acid are dominant, so adding the ionic liquid does not significantly disturb solvent organization order. This behaviour is especially noted in the system with an equimolar ratio of menthol and decanoic acid, where practically all solvent molecules are inhibited by hydrogen bonds between themselves and therefore do not show important solvation properties.

On the other hand, the system in which menthol is in excess behaves similarly because, as previously indicated, one molecule of decanoic acid can bind two molecules of menthol and thus effectively bind excess menthol. However, a system where decanoic acid is in excess leaves the possibility that its excess makes interactions with cations and anions from the IL. The variation of the apparent molar volume at infinite dilution, the apparent molar isentropic compressibility at infinite dilution, the limiting apparent molar expansibility with temperatures and DES composition, as well as the lowest values S_v coefficients, point out the weakest interactions between cations and anions of IL in M:D/1:2 system.

Acknowledgements: The acknowledgement for the support of the Cost Action CA18202 " NECTAR - the Network for Equilibria and Chemical Thermodynamics Advanced Research", and the Secretariat for Higher Education and Scientific Research of the Autonomous Province of Vojvodina, Serbia (Grant No. 142-451-2545/2021-01/2).

ILS7

Towards safer electrolytes for lithium-ion batteries: the curious case of DBUH-IM14 protic ionic liquid

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The development of high energy density, safe, cheap and environment-friendly energy storage devices is key to the energy transition. Although lithium ion batteries (LIBs) currently dominate the global energy storage market, their safety, cost, and environmental impact arouse concern, due to the highly flammable and toxic state-of-the-art electrolytes [1]. Protic ionic liquids (PILs) recently emerged as potential electrolyte solvents, thanks to their low flammability and easy synthesis [2]. Little is known, however, on the structure and dynamics of the systems, and how these molecular properties affect and correlate to the macroscopic behaviour.

Here, we target a family of PILs based on the super-base 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) and three super-strong acids (HIM14, HTFSI and HTFO), as well as the corresponding lithium-doped PIL electrolytes [3]. The multifaceted experimental characterization of the molecular/atomic properties (multinuclear NMR, diffusion, relaxation and electrophoretic NMR) and the macroscopic behavior (density, viscosity, conductivity and thermal analyses) demonstrates the intimate correlation between properties and intermolecular interactions, and unveils the unique and unpredictable features of DBUH-IM14.

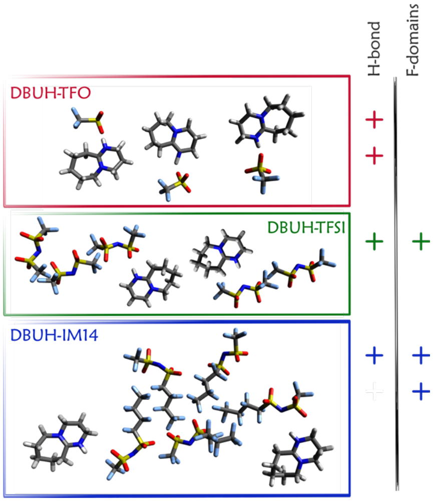

Figure 1. Sketch of the main intermolecular interactions in the studied PILs responsible for their peculiar behaviour.

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ILS8

Improving the thermal and electrochemicalstability of lithium-ion batteryelectrolytessafetyusing the ionicliquids and zwitterionic additives

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Lithium-ion batteries(LIBs) are becoming increasingly important for electrifying the modern transportation system and, thus, hold the promise to enable sustainable mobility in the future. However, their large-scale application is hindered by severe safety concerns when the cells are exposed to mechanical, thermal, or electrical abuse conditions. These safety issues are intrinsically related to their superior energy density, combined with the utilization of highly volatile and flammable organic-solvent-based electrolytes. Improving the thermal stability of electrolytes and the safety of LIBs is one of the imperatives of our investigations.

The challenges, which so far prevent the widespread replacement of organic carbonate-based electrolytes, start from rather "facile" electrolyte modifications by (partially) replacing the organic solvent and/or the addition of functional electrolyte additives, conceptually new electrolyte systems, including ionic liquids (ILs) are considered. Ionic liquid/organic solvent mixtures are investigated as optimal electrolytes for lithium-ion batteries that can combine low flammability, good thermal stability and high electrical conductivity. That approach provides a great chance of developing highly functionalized, new electrolyte systems, which may overcome the afore-mentioned safety concerns related to conventional electrolytes, also offering enhanced mechanical, superior thermal, electrochemical performance, and safety tolerance to both overcharge and thermal abuse. This investigation shows the addition of additive (1-butylsulfonate-3-methylimidazole, $C_2C_2imSO_3$) into ionic liquid-based electrolyte (used electrolyte is based on 0.5 $mol\cdot dm^{-3}$ lithium *bis*(trifluoromethylsulfonyl)imide, LiTFS, in ionic liquid 1,3-diethylimidazolium *bis*(trifluoromethyl-sulfonyl)imide, $C_2C_2imTFSI$) to improve Li-ion intercalate/deintercalate properties by electrochemical properties, without decomposition of the electrolyte, unlike the system without additive (Figure 1).

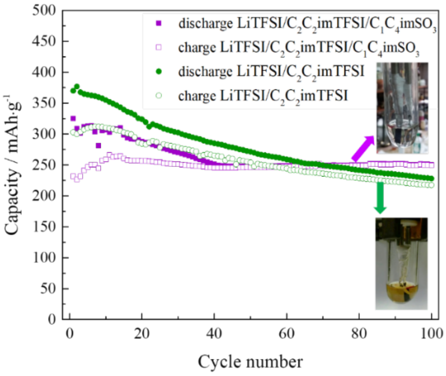

Figure 1. Galvanostatic discharge/charge performance of anatase TiO_2 nanotubes in different electrolytes

ILS9

A study of biological activity of bio-based ionic liquids

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Extensive research has been carried out on the possibility of the use of ionic liquids (ILs) for biological and medical applications. Due to their exceptional solvating ability, ILs dissolve bioactive compounds of various natures, retaining their specific properties for a long time. ILscandissolve poorly soluble drugs, enhancing the penetration of drugs through physiological barriers to increase therapeutic efficacy and exhibit antimicrobial, antifungal, and antiviral activity [1,2].

Much attention is paid to the possibility of using ILs as components of drugs and delivery systems based on them. A biologically active molecule can be attached to one of the IL ions via a covalent bond with the preservation of its activity, or introduced into the composition of the IL as one of its components (cation or anion). It is also possible to combine several biologically active molecules in one molecule, which are administered in different ways, thus obtaining dual-use drugs [3].

The ability to change the properties of ILs using various combinations of anions and cations makes it possible to obtain compounds with specified individual characteristics, for example, with agents that potentially increase cell permeability(e.g. amino acids), with various counterions [4]. A careful selection of suitable ions, synthetic approaches, and accurate study of their biological activity are important steps for their further wide practical application.

The different bio-ILs on the basis of structural frameworks of well-known imidazolium, pyridinium, and cholinium ILs in combination with salicylic, cinnamic acids and bio-derived platform chemicals (5 HMF) were synthesized, and their biological activity and physicochemical properties were studied [3-6]. Bactericidal activity of some ILs against Gram-negative and Gram-positive bacteria was tested. Depending on the position of the bio-fragment (anion, cation) and the substituents in the cationic core, the biological properties of final ILs vary significantly.

Acknowledgements: The part of the work was supported by the Russian Science Foundation (RSF Project № 21-73-10262).

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ILS10

Extraction of metals from waste by ionic liquids, DESs and organophosphorous-based acids

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Extraction efficiencies of metal ions extraction from model aqueous solutions, from "black mass"(BM) of waste Zn-MnO_2 alkaline batteries, from spent Ni-Cd batteries, spent Li-ion batteries and from electronic waste materials is presented. The extraction of Co(II) and Zn(II) from the model aqueous phase with new ionic liquids (ILs) was compared to well-known Aliquat 336, CyphosIL 101 and[$P_{6,6,6,14}$][BTMPP]. Extraction was provided with pure ILs and with the addition of complexion agents, such as: 18-crown-6, 24-crown-8, alkanes $C_{24}H_{50}$, $C_{27}H_{56}$, Triton TM X-100 and L-histidine. It was shown that quick and efficient extraction, where more than 90% of Co(II) and Zn(II) using some pure IL, or with additives, using synergistic effects of mixture of two ILs, or using ILs in Aqueous Biphasic Systems (ABS) method with NaCl at low temperature T = 303 K may be obtained. The best results were obtained with [$P_{6,6,6,14}$][SCN] for both metal ions.

A flow chart for zinc and manganese recovery from the BM of waste Zn-MnO_2 batteries is presented. The extraction process confirmed the high efficiency and distribution ratio using mixture of (Cyanex272 + diethyl phosphite (DPh)) for Zn(II) extraction. High extraction with 100% zinc and manganese recovery may be obtained using DESs (cholinum chloride: lactic acid 1:2) and (cholinum chloride:malonic acid 1:1) [1]. New methods of metal extraction from BM of spent Li-ion batteries, is presented with ILs ([$N_{8,8,8,1}$][Cl], Aliquat 336, [$P_{6,6,6,14}$][Cl],[$P_{6,6,6,14}$][SCN], [Benzet][TCM], with 8 DESs, withCyanex 272 and D2EHPA. It was shown that fast and efficient extraction, with 90–100 wt% recovery of Co(II), may be obtained using DESs. The high extraction efficiency of lithium (41–92 wt%) and nickel (37–52 wt%) using (Cyanex 272 +DPh) was obtained. A complete flow chart for the selective recovery of Co(II),Li(I) and Ni(II) from BM is presented [2]. The solid-liquid-liquid extraction of heavy metals from the BM of waste Ni-Cd batteries. The extraction efficiency of DESs (choline chloride + lactic acid and choline chloride + malonic acid), contrary to ILs ([$P_{6,6,6,14}$][Cl] and [$P_{6,6,6,14}$][SCN]) is at the level of 30 wt% for Ni(II) and 100 wt% for Cd(II) [3].

The extraction of metals from e-waste (WPCBs) with ILs, DESs and Cyanex 272 is presented. The new method of extraction of metals from the leachate and from the solid phase with, or without the leaching process was developed. Solvent extraction from the liquid leachate phase has been studied with ILs, using ABS method Aliquat 336, Cyanex 272 and two DESs [4].

The UltraWAVE digestion system combined with the AAnalyst 800 atomic absorption spectrometer (FAAS) was used for determination of metals content in the solid BM. The metal ions content in the aqueous and stripped organic solutions was determined by the ICP-OES method.

The proposed extraction methods may compete or be alternative to hydrometallurgical processes of metal recovery from secondary sources.

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ILS11

Pluronic-based biocompatible ternary systems for extraction of parthenolide

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Cancer is a major public health challenge and the second leading cause of death globally. Three-quarters of all anticancer agents used in medicine are natural products or products related to them. Feverfew (*Tanacetum parthenium*L. Bip.) is a perennial medicinal herb and a rich source of many therapeutic compounds with the parthenolide (PAR) as the main sesquiterpene lactone. In vitro studies have confirmed the highly selective cytotoxic activity of PAR against cancer cells, and the roots of feverfew have shown to increase the sensitivity of cancerous cells to chemotherapy and radiotherapy[1].

We will focus our research on developing a greener extraction method for parthenolide using an aqueous biphasic system formed by copolymers and ionic liquid, IL (choline lactate [Ch][Lac]) or natural deep eutectic solvent, NADES (choline chloride and lactic acid (ChCl:LA)) to avoid the widely used volatile organic solvents for parthenolide extraction [2]. Pluronic 10R5 and Pluronic 17R4 will be effectively used for this purpose for the first time, and their capacity to make ABS will be contrasted with the well-researched PPG400. Additionally, the impact of the IL and NADES on the production of ABS and the effectiveness of parthenolide extraction will be examined and addressed.

A quantitative analysis of PAR was assessed by HPLC with a DAD detector at 210 nm. The partition of PAR in studied ABS systems was expressed through extraction efficiency and partition coefficient (Figure 1). The pattern indicated that the preferential partitioning of this active pharmaceutical ingredient into the polymer-rich phase generating micelles is caused by PAR's hydrophobicity. Because of this, using polymer-based micelles as drug delivery systems is a viable method for making hydrophobic medicines more effective. These findings might lead to the development of a new technique for the extraction of the desired active pharmaceutical ingredient using possible drug delivery systems based on green chemical principles.

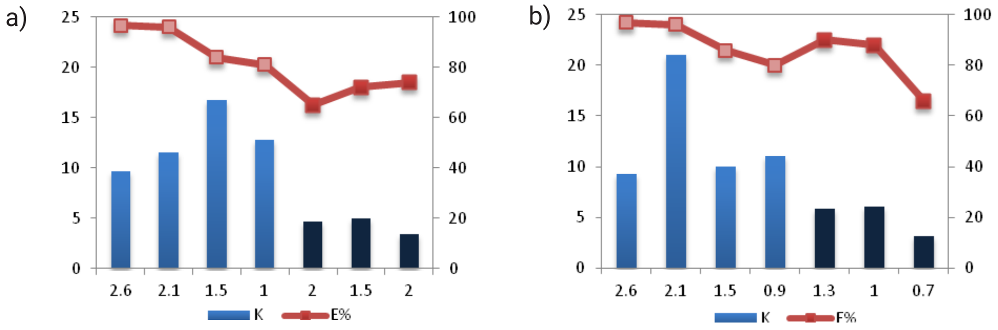

Figure 1. Partition coefficients (K) and extraction efficiency (E) of parthenolide in the studied ABS at 296.15 K and atmospheric pressure: a) {PL + ChCl:LA + H_2O}; b) ABS{PL + [Ch][Lac]+ H_2O}. Legend: PL17R4 (lightred or light blue); PL10R5 (darkred or dark blue).

Acknowledgements: This work was supported by the Ministry of Science and Technological Development of the Republic of Serbia (contract numbers: 451-03-47/2023-01/200017)

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ILS12

Separation of components of rare-earth magnets using phosphonium based ionic liquids

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In recent years, the recovery of rare earth elements (REEs) from secondary sources attracts research attention due to the limited primary rare-earth ore deposits [1]. The availability of raw materials is fundamental for current and future technologies needed for achieving the goals defined for sustainable development as described by the UN 2030 Agenda. Essential high-value products and devices, such as electronic components, batteries, motors for electric vehicles and turbines, fuel cells, are complex assemblies of parts made up of a variety of materials needed for their manufacturing and optimized to the required performances. Many of these materials are obtained starting from chemical elements which are often supplied from mining activity as primary source [2]. Secondary solid wastes such as permanent magnet waste, waste metallurgical slag, spent batteries, waste phosphors lamps etc. are the potential resources of REEs and other valuable metals. Among these secondary solid wastes, the neodymium magnets have been crucially significant sustainable materials rich in REEs like Nd, Pr and Dy [3].

Current hydrometallurgical processes for the recovery of the Nd^{3+} ions from aqueous solutions have some interesting advantages (low energy consumption, process flexibility, higher purity), but require the use of significant amounts of toxic volatile organic compounds (VOCs) in the solvent extraction stages and of multiple extracting ligands to separate the different metals present in the leachates [4]. Ionic liquids (ILs) have many potential applications. They are powerful solvents with many advantages such as negligible vapor pressure, non-toxicity, reusability, and high thermal stability [5]. In comparison to the nitrogen-based ILs, phosphonium-based ILs possess higher thermal stability and are more stable in strong basic media due to the absence of acidic proton [6].

In this work, we assess the performance of phosphonium based ILs ($[P_{66614}][Dec]$, and $[P_{66614}][Cl]$) (Figure 1) for separation of Nd^{3+} from Fe^{3+}. The versatility of more environmentally friendly IL with decanoate anion at different pH was studied. In the acid leaching step, the effects of acid concentration and leaching time with the leaching percentage were investigated. To complete the recovery process, further separation was proposed using two phosphonium based ILs. It was found that Fe^{3+} ion is extracted from highly acidic media, while Nd^{3+} prefers neutral pH in both ILs. Acid concentration in water media and timing for extraction was tested. After extraction, the water phase was measured by ICP-OES to quantitatively determine metal concentrations and magnet composition.

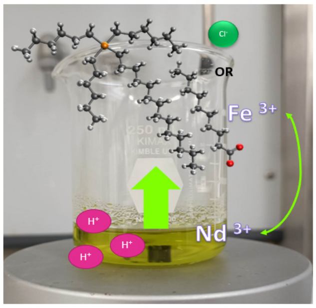

Figure 1. Graphical representation of selective extraction of metals by $[P_{66614}]$ [Dec] from acidic media.

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ILS13
Properties of deep eutectic solvents

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Deep eutectic solvents (DESs) has gain tremendous progress in the past few years [1]. The physicochemical properties of DESs are a prerequisite for the applications of DESs. Herein, we will report our work on the properties of DESs.

At first, the phase behaviors of both bulk and confined DESs in controlled pore glasses were first investigated. Glass transition, cold crystallization and melting behaviors alter significantly in the nanopores due to the size effect and interfacial interactions. Kinetic analysis of the crystallization reveals increased effective activation energies and pre-exponential factors under nanoconfinement [2]. Then, we report the calorimetric effect and thermokinetics in the formation process of a model DES, ChCl:urea. Mixing of a 1-to-2 molar ratio of choline chloride and urea shows a rapid endothermic process under stirring. Low activation energy and activation parameters demonstrate that the formation of this DES is a rapid process [3]. After that, we concluded that High-resolution TGA (HR-TGA) is required for evaluating the thermal stability of DESs. It could provide a better resolution than both the slow heating rate and the fast heating rate. By optimizing the resolution of the stability analysis and its influence on the kinetic parameters, the performance of HR-TGA is visibly better than that of the traditional TGA. HR-TGA–MS experiments were further performed for obtaining decomposition mechanism information [4].

Furthermore, we collected 107 DESs with 994 experimental values of viscosity from published works. The Morgan fingerprint was first employed as a feature to describe the chemical environment of DESs. And four machine learning algorithms were used to train models: support vector regression (SVR), random forest (RF), neural network (NN), and extreme gradient boosting (XGBoost), and XGBoost showed the best predictive performance. In combination with the powerful interpretation method SHapley Additive exPlanation (SHAP), we further revealed the positive or negative effect of features on viscosity [5]. We further developed two promising approaches to identify and characterize both Lewis and Brønsted acidities by applying acetonitrile as an infrared probe and trimethylphosphine oxide (TMPO) as a nuclear magnetic resonance (NMR) probe [6].

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ILS14

Machine learning-boosted functional liquids design and experimental verification: an example for CO_2 absorption liquid

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Efficient CO_2 capture is indispensable for achieving a carbon-neutral society while maintaining a high quality of life. Since the discovery that ionic liquids (ILs; room-temperature molten salts) can absorb CO_2, various solvents composed of molecular ions have been studied. However, it is challenging to observe the properties of each isolated ion component to control the function of ILs as they are mixtures of ions. Finding the optimal cation–anion combination for the CO_2 absorbent from their enormous chemical space had been impossible in a practical sense. This study applied electronic structure informatics to explore ILs with high CO_2 solubility from 402,114 IL candidates. The feature variables were determined by a set of cheap quantum chemistry calculations for isolated small-ion fragments, and the importance of molecular geometries and electronic states governing molecular interactions was identified via the wrapper method. As a result, it was clearly shown that the electronic states of ionic species must have essential roles in the CO_2 physisorption capacity of ILs. Considering synthetic easiness for the candidates narrowed by the machine learning model, trihexyl(tetradecyl) phosphonium perfluorooctanesulfonate was synthesized. Using a magnetic suspension balance, it was experimentally confirmed that this IL has higher CO_2 solubility than trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)amide, which is the previous best IL for CO_2 absorption [1].

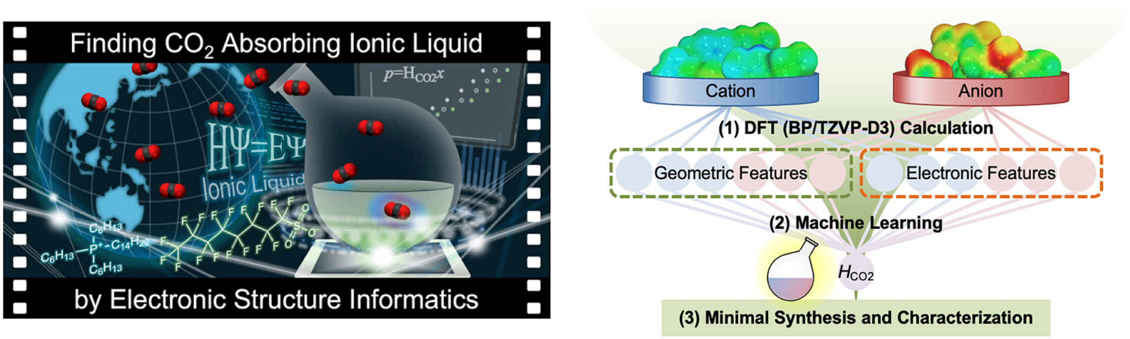

Figure 1. Proposed approach. By performing machine learning, synthesis, and precision measurement, ILs with excellent CO_2 solubilities were developed in a short period.

Acknowledgements: N.K. acknowledges support from the JST ACT-I and ACT-X projects of the Japan Science and Technology Agency (grant nos. JPMJPR16UB and JPMJAX20A9). HM acknowledges support from JSPS KAKENHI (grant no. 21H01894). DK acknowledges support from JSPS KAKENHI (grant no. 19K05130). The calculations were performed using supercomputer resources provided by the Research Center for Computational Science (RCCS) at the Okazaki Research Facilities of the National Institutes of Natural Sciences (NINS), Japan (project no. 22-IMS-C015).

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ILS15

Synthesis, characterization and the use of tin-ascorbate complex as precursor for tin sulfide nanoparticles

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The odd synthesis of tin sulfide films was used for deposition directly from abundant and biodegradable precursors via a simple SILAR method. Energy consumption is an urgent issue for the economic and social development of the world [1]. This consumption of fossil fuels spreads harmful greenhouse gases that cause global warming and a series of environmental damages [2]. In order to reduce the consumption of fossil fuels, it is very necessary to use more renewable energy sources. Therefore, energy storage technologies must also be developed. One of the most effective methods for the storage and conversion of renewable energy is based on electrochemical technologies, and one of the examples is supercapacitors. Supercapacitors as a type of electrochemical capacitors are one of the most promising energy storage devices due to a lot of advantages, such as high power density, long cycle life, low cost and fast charge-discharge processes [3]. In recent decades, tests have been performed to enhance the specific capacitance values by the use of nanoscience and nanotechnology fields. Nevertheless, tin-based chalcogenides (such as SnS, SnS_2, SnSe and etc.) have received more attention for application as supercapacitor materials. These layered structure materials were also explored as light absorbers, photodetectors, etc. Deposition of thin films based on cheap and relatively simple processes using materials of high abundance is one of the most difficult challenges. It is very important to find inexpensive, environmentally friendly products that have the possibility of deposition in a large area and that adhere well to the substrate method. The aim of the work was to form environmentally friendly thin tin sulfide films by applying the safety and inexpensive SILAR method and using eco-friendly precursors, aqueous solutions, low deposition temperature, and environmental safety complexing agent. For the preparation of the tin-ascorbate complex biodegradable L-ascorbic acid was used as well as a reducing and capping agent for the synthesis. Structural, optical and electrical properties of the deposited thin tin sulfide films were investigated. In addition, these films were characterised for supercapacitor application. Tin sulfide nanocrystals grow and adhere to the substrate well by van der Waals forces, forming thin films. As-deposited films had an average size of thickness of 535-850 nm, while after annealing the thickness decreased and lies in the range of 230-280 nm, depending on the amount of L-ascorbic acid and the number of SILAR cycles. Results of the XRD analysis of annealed films show the typically reported structure of herzenbergite (JCPDS card number 39-0354). Raman analysis together with XRD confirms the growth of single-phase SnS. The annealing of the deposited films improves the morphology and compactness of the films. SEM analysis clearly shows that annealing has a significant effect on grain size and surface roughness. Annealing affects not only compositional, optical and morphological properties, but also significantly increased energetic parameters, as well. Electrochemical evaluation of capacitive behaviour revealed that thermal treatment increases the specific capacitance by up to 6 times. These results clearly indicate that obtained thin tin sulfide films are suitable for supercapacitor application.

In this paper, a simple, eco-friendly method for the fabrication of nanoscaled tin sulfide particles as a complexing agent using ascorbic acid is reported. From the data obtained it could be seen that there is a strong impact of annealing in all areas – compactness and thickness of the films, clearly expressed XRD peaks and improved supercapacitive characteristics of all obtained thin films of tin sulfide. These conditions allowed the obtainment of mechanically stable and electrochemically active tin sulfide films that could find the application in supercapacitors.

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ILS16

Thermodynamic studies of micellization of surface active ionic liquids

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In our work, we synthesized 13 surface active ionic liquids (SAILs) and examined how their structural changes influence their micellization properties using isothermal titration calorimetry (ITC). The structural changes we studied were: modifying the structure and length of the hydrophobic cation tail, changing the cation aromatic ring and changing the counterion structure. The improved mass-action model [1] was used to interpret the data, which considers micellization as an equilibrium between micelles and monomers with a constant aggregation number. In order to confirm the experimentally obtained results, molecular dynamics simulations were performed for all the systems.

From thermodynamic measurements, we observed that the investigated systems behave mainly like common ionic surfactants and previously investigated SAILs. We found that the micellization process of the investigated systems is entropically driven at low temperatures (due to hydrophobic effect), while at high temperatures the enthalpy contribution becomes equally important (due to counterion binding). Moreover, we confirmed that counterion isomerism influences the micellization process the most, followed by the prolongation of the alkyl chain length on N3 position of the imidazolium ring and isomerism of cation. The molecular dynamics simulations that were performed revealed that, besides the interaction of water molecules with the compounds and the ion-ion interactions, steric hindrance plays a very important role in the process of self-aggregation [2-4].

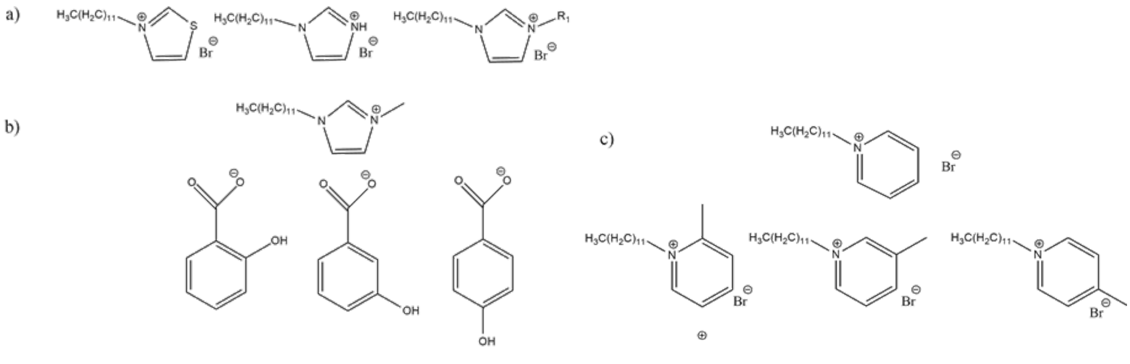

Figure 1. Structures of studied systems: a) imidazolium based SAILs with different alkyl chains at the N3 position; b) imidazolium-based SAILs with the changed counterion; c) pyridinium-based SAILs.

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COL1

The effect of glycine buffer on the β-lactoglobulin amyloid fibrillization tendency

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The understanding of amyloid protein aggregates characterized by their well-known cross-β structure and good mechanical properties is of great importance because of their appearance in patients with several untreatable diseases, such as Alzheimer's, Parkinson's, type II diabetes mellitus, and other amyloidosis. Even though amyloid aggregates were discovered several years ago, the mechanism of their formation and their connection to disease is still not fully understood. β-lactoglobulin (BLG) is often used as a model protein to study fibrillization because of its low cost and good availability. The mechanism of fibril formation by heating BLG solutions in water at low pH and ionic strength is well known; it consists of several steps, from denaturation, hydrolysis, disulphide-scrambling, self-association to solutions colloidal stability. Each of these steps can be influenced by different co-solutes in a unique way [1,2].

The most common co-solutes that we find in almost all protein formulations are buffers. The concentration of [H^+] ions is a major factor in fibrillization not just because of its ability to define molecular charge, but because it also affects the acid hydrolysis kinetics and protonation state of free sulfhydryl groups.

In the last years, many studies are showing that buffers can also have a key effect on the chemical, colloidal and conformational stability of proteins as well as having an influence on how they interact with interfaces [1-3].

In our recent study, we showed that by incubating BLG in pH 2 glycine solution the fibrillization path changes from peptide to spheroid oligomer fibril self-assembly, compared to the same process in the absence of glycine buffer molecules. Here we are presenting an insight into the possible mechanism, as suggested by molecular dynamics computer simulations. During the simulation, we studied the interaction between glycine buffer components with different amino-acid residues on the BLG protein surface and rank-ordered them accordingly. The simulation results show that glycinium cation molecular species have a high tendency to reside near the vicinity of the outer BLG disulphide bond CYS66-CYS160. This is in line with our hypothesis emerging from experimental observations that the positive charge on glycinium cation influences the disulphide scrambling reaction equilibrium and completely changes the fibrillization pathway. The new fibrillization pathway then leads to a new type of amyloid aggregates that were not yet detected in a BLG aggregation process. The newly found BLG amyloid fibrils don't just enrich the fibrilization field but open options to create new food structures or alternative hydrogels to make new drug delivery systems [4].

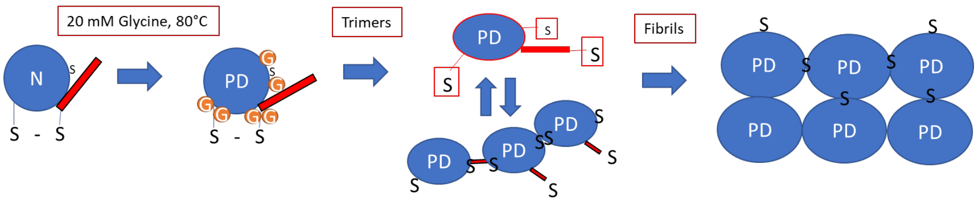

Figure 1. A model for a new fibrillization mechanism of BLG in pH 2 glycine solutions.

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COL2

Effect of the surface properties on the stability and activity of catalase-latex composites

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Besides the numerous advantages, the use of native forms of antioxidant enzymes in industrial and biomedical processes is impractical because of the lack of long-term operational stability and difficulty in recovering and reusing these enzymes. Catalase (CAT) are enzymes present in plant and animal tissues and possess a high turnover number in the decomposition of hydrogen peroxide. To tackle the above mentioned disadvantages of using native enzymes, development of CAT containing composite materials is in the focus of several research groups. Although several methods were reported for the immobilization of the CAT, the industrial applications desire simple methods such as physical adsorption, which is driven by electrostatic interaction between the particle and the enzyme [1]. Polystyrene particles are widely used in enzyme immobilization due the their inert nature, monodisperse size distribution and simple preparation even with different functional groups [2]. However, the effects of the surface properties of the particles on the stability and function of the developed CAT containing composites were not studied systematically.

In this study, CAT enzyme was immobilized on polystyrene nanoparticles prepared with emulsifier free emulsion polymerization with positively charged amidine (AL) and negatively charged sulphate (SL) groups. Since the CAT possesses slightly negative charge at physiological pH, it was necessary to functionalize the like-charged SL particles with positively charged glycol chitosan (GC) polyelectrolyte to achieve strong enzyme attachment. The dose of the polyelectrolyte was optimized with systematic electrophoretic mobility measurements. Colloidal stability of the obtained dispersions was assessed with time resolved dynamic light scattering (DLS) measurements in the presence of polyelectrolytes and salts. The surface forces between the particles were described within the DLVO theory [3]. The CAT enzyme was immobilized on the surface of the bare AL particles and on the GC functionalized SL particles. The dose of the immobilized enzymes was optimized with electrophoretic mobility measurements. The irreversible adsorption of the enzymes was proven by biochemical tests. The enzymatic activity of the AL-CAT and SL-GC-CAT particles were measured by biochemical assays and compared with the native enzyme solution. No significant loss in the hydrogen peroxide decomposing activity was observed upon immobilization on either particle. However, SL-GC-CAT showed significantly higher colloidal stability than AL-CAT indicating better applicability in heterogeneous systems such as the ones present in industrial manufacturing processes.

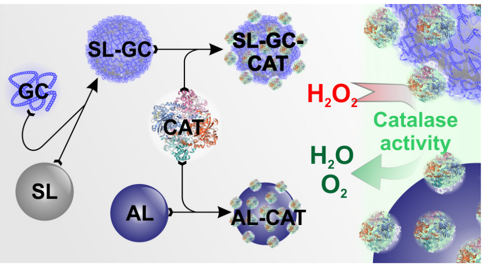

Figure 1. Schematic illustration of the preparation of the composite particles.

Acknowledgements: The research was financially supported by the Hungarian Academy of Sciences (Lendület LP2022-16/2022) and the National Research, Development and Innovation Office.

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COL3

Halloysite nanotube-based nanomaterials as efficient radical scavengers in colloidal dispersions

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Halloysite clay nanotubes (HNTs) are naturally occurring layered aluminosilicates ($Al_2Si_2O_5(OH)_4 \cdot nH_2O$) with hollow tubular structure. HNTs are of great potential in immobilization of biomolecules, owing to their advantageous surface features such a dual-charge nature, as well as wide-range accessibility and biocompatibility [1]. These beneficial properties make HNTs attractive for a variety of applications, such asimportant building blocks in composites used in biomedical, environmental, and catalytic processes. However, in many HNT applications, surface functionalization with polymeric compounds is required to enhance the adsorption of the quest molecules and to avoid unwanted aggregation processes.

Our research focused on the development of stable colloids of a nanocomposite consisting of self assembled biomacromolecules such as a protamine sulfate (PSP) polyelectrolyte and superoxide dismutase (SOD) enzyme on HNT surfaces. Remarkable structural and colloidal stability was confirmed by spectroscopic, scattering, and microscopic techniques. The superoxide radical anions scavenging activity was higher for HNT-PSP-SOD system than for native SOD indicating that the SOD enzyme kept its functional integrity upon immobilization. The obtained HNT-PSP-SOD composite dispersion can be considered as a highly active antioxidant with the advantages of the heterogenization process, such as easier separation from the reaction mixture.

In addition, the influence of bare and polyelectrolyte-functionalized HNT particles on the SOD-like activity of an enzyme-mimicking copper(II)-citrate complex was assessed. It was found that surface functionalization plays an important role in complex adsorption on the particles. These findings illustrate great opportunities toward the development of enzyme-mimicking nanoparticulate systems that are less sensitive to the environmental conditions than the native enzymes [2].

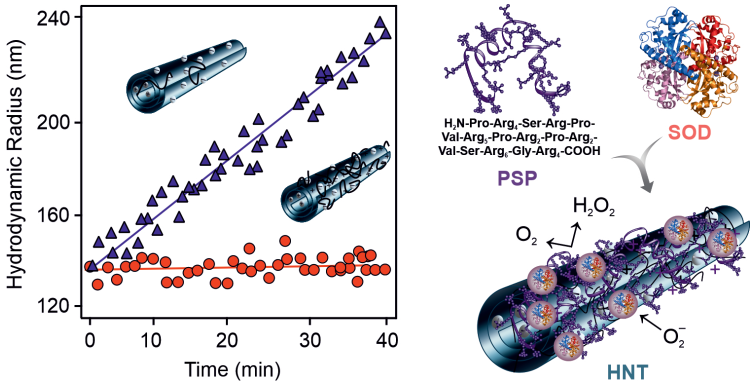

Figure 1. Schematic representation of the hydrodynamic radius of HNT particles versus time for different PSP doses measured by time-resolved DLS and illustration of the self-assembly of protamine biomacromolecule on HNTs for immobilization of SOD enzyme.

Acknowledgements: The research was financially supported by the Lendület program of the Hungarian Academy of Sciences (LP2022-16/2022) and the National Research, Development and Innovation office (TKP2021-NVA-19).

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COL4

Solubilization of aqueous-insoluble phenothiazine drug in TX-100 micellar solution and its interactions with cationic surfactants

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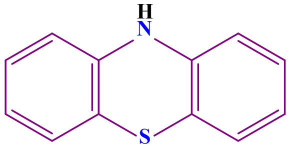
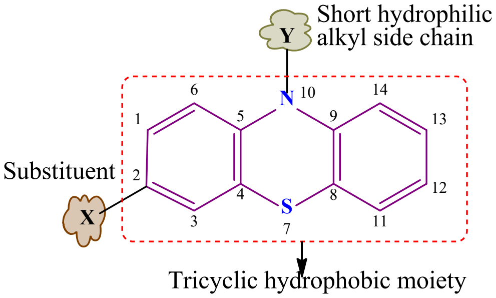
The solubilization of poorly soluble drug phenothiazine (PTZ) in triton X-100 (TX-100) micellar aqueous media at physiological pH and the interaction of cationic surfactants, viz., tetradecyltrimethylammonium bromide (TTAB), hexadecyltrimethylammonium bromide (CTAB), cetylpyridinium chloride (CPC) and cetylpyridinium bromide (CPB) in presence of drug PTZ in TX-100 are discussed. The interaction of surfactants in PTZ–TX-100 media has been studied using conductometric technique at three temperatures. The conductometric results reveal the sequence of critical micelle concentration (CMC) values of surfactants as TTAB > CPC > CPB > CTAB. UV-vis spectroscopy studies were used to learn the interactions of surfactants with the drug PTZ in TX-100 aqueous media (at 303.15 K and pH 7.4) which suggest the interactions are highly feasible (change of Gibbs energy; $\Delta G_b < 0$) and greatly improve beyond the CMC values of corresponding surfactants [1]. The estimated parameters using the Benesi–Hildebrand equation indicate higher binding constant (K_b) for cetylpyridinium surfactants and the drug–surfactant complex formations are found to be in 1:2 stoichiometric ratios. Fluorescence technique has also been employed to study the aggregation number of TTAB/CTAB in PTZ–TX-100 systems at 303.15 K.



(a) PTZ



(b) Derivative of phenothiazine drugs

Figure 1. Molecular structures of (a) phenothiazine drug (PTZ) and (b) schematic representation of phenothiazine drug derivative.

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COL5

On the colloidal stability of magnetic core@shell nanoparticles in ionic liquid-based solvents for thermoelectric applications

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Thermoelectric material shave been considered a promising tool in the context of the sustainable and alternative energies since it allows the direct conversion of heat energy, which is otherwise lost, into useful electricity. Recent research has shown that complex liquids composed of charged magnetic nanoparticles dispersed in ionic liquids-based solvents present promising results for thermoelectric applications. Nevertheless, many parameters may affect the colloidal stability of these nanofluids, which limits their applications, and the literature is scarce in this field.

The present survey focuses on the evaluation of the influence of the particle size and surface charge density on the colloidal stability of nanofluids composed of core@shell cobalt ferrite magnetic nanoparticles ($CoFe_2O_4@\gamma$-Fe_2O_3) dispersed in the ionic liquid 1-ethyl-3-methylimidazolium bistriflimide (EMIM/TFSI) or its mixtures with propylene carbonate. Three ferrofluid samples with different nanoparticle sizes were synthesized by coprecipitation in alkaline medium [1]. X-ray diffraction, transmission electron microscopy, flame atomic absorption spectroscopy, and magnetic characterization assays were performed to characterize the synthesized aqueous ferrofluids. The surface charge density was tuned in the ferrofluid dispersed in water before the transfer of the nanoparticles toward the ionic liquid [2]. A multiscale analysis incorporating dynamic light scattering and small angle X-ray measurements was performed to study the colloidal dispersions up to 200°C.

In general, the size and the surface charge density have a significant influence on the interparticle interaction regimes and the limits of colloidal stability. The obtained results considerably contribute to the elucidation of the optimum stable condition of the proposed nanofluids for energy recovery applications.

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COL6

Experimental and theoretical studies of the influence of crossinteraction effects on the structure, CMC, and mobility of SDS and TTAB micelles in aqueous mixtures

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Structural, thermodynamic, and transport properties of Sodium dodecyl sulfate (SDS) and Tetradecyltrimethylammonium bromide (TTAB) in aqueous solutions have each been the subject of several experimental and theoretical works. SDS (or TTAB) micelles are formed above their corresponding critical micellar concentration (CMC_{SDS} or CMC_{TTAB}), resulting from the spherical association of a fraction of the monomers (DS^- or TTA^+) proportional to their corresponding degree of micellization (1-β). In addition, micelles are partially neutralized by the condensation of their respective counterions ($X \equiv Na^+$ or Br^-), so that the apparent charge number of each micelle is equal to: $Z_{app} = Z_S(\alpha - \beta)/(1 - \beta)$ [1], where Z_S is the structural charge number (equal to the aggregation number), and (1- α) is the degree of the ionic condensation. Exact experimental determination of α, β and of the equivalent conductivities λ_i of the differently charged species "i" in solution are obtained by adjusting experimental conductivities with the results of the theoretical calculations based on the Onsager-Kim-MSA-Zwanzig's approaches [1-3] and the statistical model of the two states, by taking into account all the (Monomer – Micelle – X – H_2O) interactions [1]. In particular, λ_{SDS} allows checking the size R and the solvation state of the micelles.

Now, the main objective of our work is a tentative elucidation of what happens when the two monomers DS^- and TTA^+ are mixed in different proportions. In other terms: what is the influence of the cross-synergetic interaction (DS^- - TTA^+) on the structure, shape, CMC, aggregation number, counterion binding, apparent charge Z_{app}, and the mobilities of the formed micelles?

Indeed, the literature gives some empirical but non-exhaustive responses via systematic experimental studies concerning some micelle mixtures [4].

In this essay, we rather present a coherent deepening of the observed results according to different possible models.

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COL7

Heteroaggregation of microplastics with anionic clays in aquatic environment

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Microplastics (MPs) are an emerging class of pollutants of potential threat to the environment and human health [1]. Aggregation, including homo aggregation (MPs - MPs) and hetero aggregation (MPs - other particles), is a critical physicochemical process in the aquatic environments that determines the transport behavior and overall fate of MPs.Interfacial phenomena and related aggregation processes of MPs are influenced by several environmental factors, such as pH, ionic strength, electrolyte type, as well as the composition, charge and size of other particles present in aquatic compartments [1,2].

In this study, homo aggregation of polystyrene MPs (PS) and hetero aggregation of PS with anionic clay minerals, namely layered double hydroxide (LDH) under different hydrochemical conditions (NaCl, $CaCl_2$, Na_2SO_4) were systematically investigated using light scattering techniques. Accordingly, the salt type and ionic strength had significant effects on the stability of both PSand LDH particles individually and the results could be explained by the DLVO theory and Schulze-Hardy rule [3].

However, once mixing stable colloidal dispersions of individual particles hetero aggregation occurred between the oppositely charged PS and LDH particles, which was also confirmed with transmission electron microscopy images. Adsorption of the LDH particles led to charge neutralization and to overcharging of the PS at appropriate concentrations. Once the LDH adsorption neutralizes the negative charges of the PS spheres a rapid aggregation indicated by stability ratios close to one was observed, while stable suspensions formed at high and low LDH doses (Figure 1). The governing interparticle interactions included repulsive electrical double-layer forces as well as van der Waals and patch-charge attractions, whose strength depended on the interacting particle ratio and background water composition.

Our findings shed light on the colloidal behavior of PSs in a complex aquatic environment, and they are also useful in the development of LDH-based water remediation approaches to remove MPs contamination.

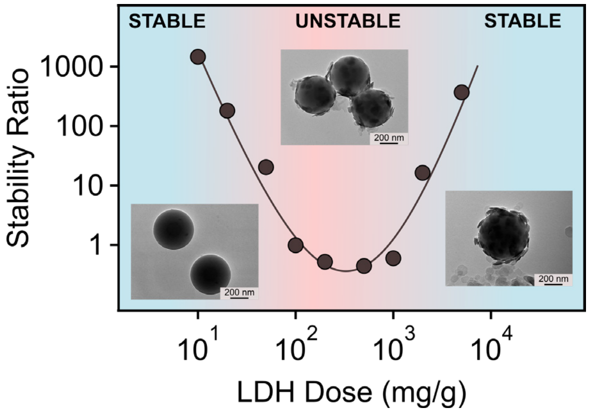

Figure 1. Stability ratio values of PS in the presence of LDH particles.

Acknowledgements: This research was financially supported by the Hungarian National Research, Development and Innovation Office (SNN142258). D. T was supported by the ÚNKP-22-3-SZTE-460 New National Excellence Program of the Ministry for Innovation and Technology from the source of National Research, Development and Innovation Fund.

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COL8

Calorimetric measurements of complexation and transfer of a europium salt in colloidal liquid-liquid extraction systems

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Liquid-liquid extraction used for metal separation is based on the transfer of several species (most importantly water, salts and acids) between two initial compositions of two different phases in pseudo-ternary phase diagrams. Since several different processes take place at an extraction step, it is difficult to decompose the enthalpy of the total extraction process into individual contributions associated with fundamental processes. Previous results obtained by calorimetry could not distinguish complexation enthalpy from enthalpy of transfer, since the phase diagram, the colloidal microstructures existing in both phases, and the equality of chemical potential of water and acid species co-extracted with the salts were generally not taken into account [1]. This was amended in the “ienaics” approach, which starts with the phase diagram and the microstructures, and breaks the free energy into individual well-defined contributions [1-4]. We show here that combining mixing calorimetry and isothermal titration calorimetry in several identified compositions in peculiar positions in the pseudo-ternary phase diagrams allows to distinguish the partial complexation enthalpy and the enthalpy of transfer for a lanthanide salt, water and co-extracted acids [4]. These quantities are of great importance in metal extraction or back-extraction experiments and could not be determined previously using global van’t Hoff methods, since the interfacial film and solvent reorganization enthalpy terms associated with the formation or modification of microstructures in the organic phase are by no means negligible. In addition, analysis of the ITC results using a microdroplet model of the oil phase allows to obtain estimates for the total enthalpy of the reversed micelles formed in the oil phase and the intermicellar interactions.

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COL9

Supramolecular assembly of polymers with calix[4]resorcin for design of drug delivery systems

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The non-covalent self-assembly of molecules underlies modern approaches of supramolecular chemistry and nanotechnologies, which make it possible to obtain ensembles with the required properties, controlled composition and morphology without the use of labor-intensive and time-consuming syntheses [1,2]. The supramolecular systems obtained can be used as nanocontainers with controlled drug binding capacity. Encapsulation of drugs in such nanocontainers increases their therapeutic efficacy by protecting against premature degradation, improving bioavailability, controlled release, and activation only in the required tissues.

In the present work, a supramolecular design of new functional aggregates based on viologen calix[4]resorcinol containing n-dodecyl fragments on the lower rim and different sodium salts of polymers was carried out for the subsequent incorporation of biologically active molecules into these aggregates. Using a wide range of physicochemical methods, the processes of joint self-assembly of calix[4]resorcinol and a polymer in an aqueous medium were characterized. The biosafety of the developed compositions, the selectivity of action against cancer cell lines, and the ability to penetrate into cells were determined.

Acknowledgements: This work was supported by Russian Science Foundation, grant no. 22-73-10050.

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GEN1

Advancements in the sustainable development of bio-based nanomaterials for wastewater treatment and desalination

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Water pollution is a common problem affecting the lives of people throughout the globe. It is considered one of the primary risk factors for illness and diseases and contributes to reducing available clean drinking. The current situation of wastewater treatments and desalination looks promising; however, certain barriers must be overcome for commercialising the processes. Many treatments and technologies like reverse osmosis (RO), ultrafiltration, nanofiltration, activated sludge and membrane bioreactor are already employed for water purification [1]. Some of these technologies have claimed to have achieved an efficiency of 99% or more but only under ideal operating conditions of pH, temperature and contaminant concentration. Under industrial conditions, the efficiency drops down [1,2]. Moreover, techniques like ion exchange resins only target one pollutant at a time, making the process time-consuming and impractical in situations where multiple contaminants are to be screened daily [2]. Finally, some of these techniques are highly expensive, and the affordable ones create secondary waste. Due to these reasons, wastewater purification and water desalination remain challenging, so much so that some developing countries have reached irreversible damage with the availability of clean drinking water.

Currently, nanotechnology plays a vital role in water purification and desalination.[3] Owing to their small size, large surface area, change in properties when exposed to different stimuli like pH and temperature, improved catalysis, high reactivity and adsorption properties, nanoparticles (NPs) have been a subject of active research in the field of water remediation. However, NPs can be toxic when released into the environment without proper precautions, and most of the synthesis methods of NPs can be expensive and not green [4]. This problem of cost, sustainability and pollution can be reduced by using biomass as the source to create NPs. Bio-based nanomaterials derived from biomass are interested in water purification owing to their cost-effectiveness, biocompatibility and biodegradability. Multiple studies have been done to create NPs from biomass effectively used in wastewater treatments. Materials like Zinc Oxide NPs, phytogenic magnetic NPs, biopolymer-coated metal NPs, cellulose nanocrystals, and silver NPs, all biosynthesised, have been shown to improve the water purification process [4]. Applying greener NPs provides an alternative way to eliminate pollutants from the water more effectively and sustainably. This study discusses biowaste, its sources, and how it can be converted to NPs through a greener approach. It will also discuss the current state-of-the-art available wastewater and desalination technology and how NPs can be incorporated into these processes.

Acknowledgements: The authors acknowledge the support of Qatar University through grant number IRCC-2023-129. Soumya Gupta also thanks the "E2S UPPA" for the PhD Talent Grant for its support.

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GEN2

Membrane process using complexation properties used to enhance separation between chemical species

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Membrane separation of chemical species as a clean process becomes extensively employed, its action mechanism is mainly based on fundamentals principles of structural chemistry. Membrane is not only used as a porous material but its surface charge, hydrophilic/hydrophobic balance, texture and many others physical and chemical properties depending on the medium matrix play a real role as material directly implicated in the transport and separation phenomena of species. The emergence of membranes having specific selectivity imply adoption of a new concept of separation based on the formation of complexes within the membrane material during the process of transport by chelation, conferring on the membrane a highly selective character regarding particular species existing in a very heterogeneous environment.

Polymer inclusion membranes (PIM) allow using this phenomenon of chelation and transport by complexation-decomplexation between feed-and-receive interfaces in the direction of transference flow. Polyethyleneneimine (PEI) has been used in this type of membranes for its chelating properties in aqueous media. This polymer behaves as a polyelectrolyte in aqueous solution, its viscosity, protonation rate and conformation depend on pH and ionic strength of water. Maintaining the pH value around $pK_a = 8.8$ leads to a structure containing both amine groups and ammonium groups which thus leading to polarization of the membrane surface. Similarly, more basic pH allows the predominance of amine groups and non-binding doublets of nitrogen and the prevalence of complexation mechanism instead of ion exchange one. At more acidic pH, negatively charged metal-ligand complexes are transported by ion pair mechanism into the membrane bulk.

Our work, for more than two decades, has focused on the study of various aspects of acid-base and complexing behavior of PEI in aqueous solutions and inside membranes or ion exchange resins as a surface modifier and as facilitatorof ion transport by complexation (Figure 1). Copper has been widely studied, it forms a complex having a very intense blue coloration which absorbs in the visible and ultraviolet ranges at 630 and 280 nm respectively.

Other molecules have also been used to provide synergy with PEI or as alternatives such as polyvinylpyrrolidone (PVP) for cobalt, thiourea for the separation of copper and silver, D2EHPA for the transport of chromium, or the extraction of rare earths as well as other complexing agents [1-3].

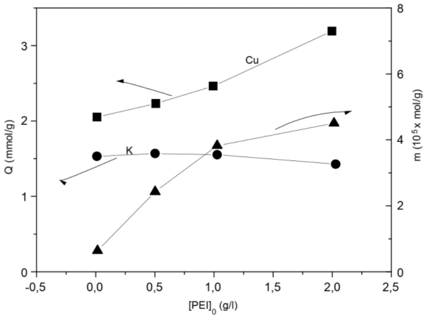

Figure 1. Improvement of copper/potassium separation by PEI complexation.

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GEN3

Analysis of Catalan hydrogen bond acceptor and donor parameters SB and SA using computational chemistry and comparison with corresponding Kamlet and Taft, Abraham and Gutmann parameters

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The use of linear solvation energy relationships, LSERs, is well established; thus one writes:

$$Y = Y^0 + \sum s_i P_i \tag{1}$$

where Y represents some chemical property, Y^0, is the value of Y in a hypothetical state where all s_iP_i terms are zero, the P_i are descriptors representing solute or solvent properties and the s_i the response of *Y* to those properties. Essentially, each s_iP_i represents a different type of solute–solvent interaction contributing to *Y*. The descriptors, P_i, are derived from experimental procedures that, ideally, capture only the property of interest.

Here, Catalan hydrogen bond acceptor and donor parameters, *SB* and *SA* [1,2], are analysed using molecular properties derived from computational chemistry. The approach assumes that the experimental parameters, P_i, vary linearly with calculated molecular properties; that is:

$$P = P^0 + \sum a_i Q_i \tag{2}$$

where Q_i are normalized descriptors reflecting: partial atomic charges, orbital energies, molecular polarizability, dipole moment or quadrupolar amplitude [3].

The results for *SB* and *SA* are compared with those for Kamlet and Taft's *β* and *α*, Abraham's *B* and *A* and Gutmann's donor number.

The solvent basicity parameters, *SB*, *β* and *DN* show remarkable consistency, correlating only with the partial charge on the most negative atom of the molecule and the energy of the donor orbital. Moreover, in all three cases the parameter values for alcohols show the same anomalous behaviour. In contrast Abraham's *B*, a measure of solute hydrogen bond basicity, correlates only with the negative partial charge and the values for alcohols show no anomaly.

The solvent (*SA* and *α*) and solute (*A*) hydrogen bond acidity parameters all show strong positive correlations with the partial charge on the most positive hydrogen atom of the molecule and show marked steric effects. However, *SA*, unlike *α* and *A*, also shows a strong negative correlation with the solvent polarizability.

Values of the coefficients of Eq. 2 and standard deviation between calculated and experimental parameter values

	Basicity Parameters[a]					Acidity Parameters[b]		
	SB	*β*	*DN*	*B*		*SA*	*α*	*A*
Intercept	−0.14	−0.27	−0.23	0.03	Intercept	−0.03	−0.58	−0.21
a_{q-}	0.51	0.64	0.59	0.65	a_{q+}	0.73	3.34	0.86
$a_{E(don)}$	0.46	0.57	0.60		a_{Pol}	−0.42		
σ	0.12	0.12	0.16	0.09	*σ*	0.06	0.25	0.12

[a] Values for *SB* unpublished, *β*,*DN*and *B* from [3] [b]Values for *SA* unpublished, *α* and *A* from [4]

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GEN4

Katoite synthesis from tricalcium aluminate *via* isomorphic substitution of silica

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Hydrogarnets belong to the series of $A_3B_2\{[TO_4]_{3-x}(OH)_{4x}\}$, where the x ranges between 0 and 3, with the end points of grossular (x = 0) and tricalcium-aluminate (x = 3) [1]. These compounds have a garnet structure in which partial or complete isomorphic substitution can occur, where corresponding to the formula $4(OH)^-$ may be substituted by one $(SiO_4)^{4-}$ and *vice versa*, which is referred to in the literature as *'hydrogarnet substitution'*. In the formula A and B represent di- and trivalent metal cations, respectively, and the T is a cation, most commonly silicon [2]. Theoretically this isomorphic substitution can occur continuously ($0 \leq x \leq 3$) and as a result a series of substituted substances could be formed. This category includes the group of katoites where the x ranges between 0 and 1.5 [3,4].

Silica containing katoites have been widely reported in the literature, however there is no example where a complete series of katoites were synthesized with the pre-set final composition. The aim of our work was therefore to find a synthesis method which can provide a series of katoites obtained by hydrogarnet substitution and a pathway for the tuning of the incorporated silica content. Our main approximation was to use tricalcium aluminate (TCA, $Ca_3Al_2(OH)_{12}$) (synthesized by us) as starting material and partially substitute the OH^- groups to $(SiO_4)^{4-}$ groups with the initial ratios from $Ca_3Al_2(SiO_4)_{0.1}(OH)_{11.6}$ to $Ca_3Al_2(SiO_4)(OH)_8$.

The synthesized products were characterized by powder X-ray diffractometry, scanning electron microscopy combined with energy-dispersive X-ray spectroscopy, thermogravimetry analysis, infrared, Raman and magic angle spinning (solid state) nuclear magnetic resonance spectroscopy. Our long-term goal is to investigate the catalytic activity of these materials, with a particular focus on the effect of $(SiO_4)^{4-}$ units in dialkyl carbonates and glycerol transesterification reactions.

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GEN5

Formation of heteronuclear complexes in the ternary Ca(II)–Nd(III)–gluconate system

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In the past decades, the storage of spent radioactive fuel has raised concerns due to its environmental hazards[1]. One of the key areas of radioactive waste's safety assessment is to construct thermodynamic models that are able to accurately predict the time evolution of actinides' solubility in alkaline pore waters surrounding the storage vessels[2]. The solubility can be increased by organic ligands (such as D-gluconate, $Gluc^-$) and alkaline earth metal ions present, through the formation of stable mixed-metal or heteronuclear complexes. Thus, quantifying the corresponding association equilibria is indispensable for a reliable model of these radioactive repositories.

To this end, we study the complexation between Nd(III), (a lanthanide ion considered to be an adequate model of actinides), Ca(II) and D-gluconate ($Gluc^-$) in strongly alkaline aqueous medium. Based on comparing experimental spectrophotometric and potentiometric data (Figure 1) with simulations assuming numerous chemical models, we find that ternary complexes incorporating both Nd(III) and Ca(II) areformedin concentrated solutions. Interestingly, the stoichiometric ratio of Ca(II):Nd(III) is 3:1 in all complexes dominating association equilibria, in agreement with the speciation inferred from recent solubility experiments [2]. The formation of heteronuclear species is supported by NMR and CD spectra as well.

Based on the proposed speciation model for binary Nd(III)–$Gluc^-$ and ternary Ca(II)–Nd(III)–$Gluc^-$ systems, our simulations for concentrations typical for waste repositories suggest the effect of $Gluc^-$ on the solubility of Nd(III) to be marginal.

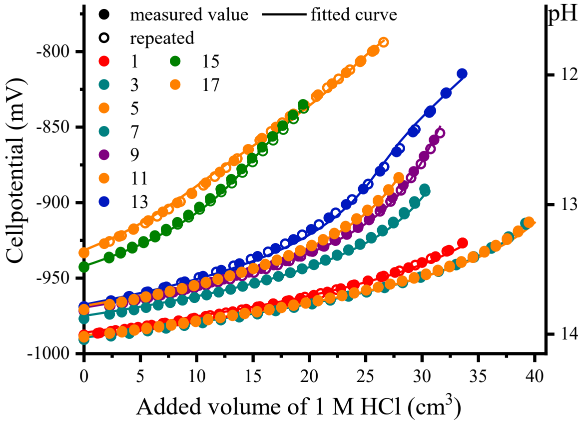

Figure 1. Reverse potentiometric titration curves of ternary samples containing Ca(II), Nd(III) and $Gluc^-$ (denoted by full and hollow circles) and data simulated employing the final model for the ternary system (continuous lines).

Acknowledgements: The authors acknowledge the financial support by the National Research Development and Innovation Office undergrant number NKFIH K 124265.

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SOL1

Effect of water addition on the formation of copper/zinc terephthalate MOFs

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The synthesis and study of metal-organic frameworks (MOFs) is one of the most extensively developed fields of modern coordination chemistry. Effect of pH, synthesis duration, temperature etc. on the formation and properties of MOFs is under consideration. Meanwhile far less attention is paid to a very important factor namely to the effect of solvent composition on the composition and structure of crystallizing compounds. To reveal this effect the study of solid phase formation in the systems $Cu(NO_3)_2$–1,4-BDC–amide–H_2O and $Zn(NO_3)_2$–1,4-BDC–amide–H_2O (amide–N,N-dimethylformamide, DMF or N,N-dimethylacetamide, DMA) was undertaken in the temperature range 90–180ºC. As a result, the crystallization fields of distinct MOFs were determined. In copper-terephthalate systems with low water content $Cu_2(BDC)_2(amide)_2$ MOFs are formed at temperature up to 130ºC, upon heating they gradually transform to $Cu(BDC)(NHMe_2)_2$. In water-rich solutions formation of copper basic terephthalate $(CuOH)_2(BDC)$ takes place.

In the zinc-terephthalate systems higher variety of compounds formed have been found that can be explained by high lability of complexes forming by ions with d^{10} configuration. Dimethylamide formed under acid-promoted hydrolysis of amide can both coordinate to zinc ion and serve as counter-ion in protonated $NH_2Me_2^+$ form.

The special attention will be paid to *anomal basicity of water* in DMF – H_2O systems effect that effect on both composition of MOFs and the conditions of their crystallization.

Acknowledgements: Authors acknowledge Saint-Petersburg University Research Park (Centre for X-Ray Diffraction Studies) for their assistance in experimental work.

SOL2

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.

SOL3

Hydrolytic and neutralization processes of hydroxysodalite

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Hydroxysodalite (HS, $Na_8[Al_6Si_6O_{24}](OH)_2$), which consists of aluminosilicate units organized in a cage-like framework [1], are generally thought to be insoluble and nonreactive solids in water. However, upon contact with water, HS yields suspension with pH > 11, which has been explained by an ion-exchange mechanism [2]. Since HS shares similar structural features with zeolites and is readily obtained in large quantities as by-product of alumina production [3], it could be used as a cheap, efficient adsorbent and catalyst [4]. Nevertheless, its efficient application requires a better understanding of its aqueous chemistry in a wide range of pH and electrolyte concentrations, in terms of both its equilibrium and kinetic chemistries. To this end, we studied the hydrolytic and neutralization processes as well as solid-state transformations of HS in both water and 1 M NaCl medium.

We synthesized HS by reacting kaolinite with concentrated $NaOH/NaAl(OH)_4$ solutions, and the thus obtained solid was characterized using X-ray diffraction, thermogravimetric, total organic carbon detection, infrared spectroscopic and inductively-coupled plasma mass spectrometric methods.

Subsequently, we monitored the temporal evolution of the hydrolysis of HS in water and 1 M NaCl solution. We found that mixing HS with water shifts the solution pH to the strongly alkaline regime, being ~11.5 for a suspension of $10\,g\cdot L^{-1}$. This suggests the dissolution of mobile NaOH from the sodalite framework, which is indeed suppressed by excess Na^+ ions in 1 M NaCl solutions. Nevertheless, the actual pH depends heavily on the solid:liquid mass ratio and for ratios of $\leq 1\,g\cdot L^{-1}$, the suspensions turn more acidic over time (with a decrease in pH by >1.5 units), suggesting solid transformation at least at the surface.

Upon addition of equivalent hydrochloric acid to HS, we find the pH to rapidly decrease to the slightly acidic / neutral region. This fast process is followed by a steady rise in pH, possibly due to the ion-exchange mechanism proposed recently [2]. Expectedly, the presence of NaCl does not to alter the reaction mechanism. Furthermore, we quantified the progression of the reaction via analysing the supernatants with ICP-MSand potentiometry as well as studied the concurrent solid-state transformations using XRD and IR methods.

Overall, we find sodalite to react with water in the neutral to alkaline pH regime, driven by the interplay between ion mobility and framework stability.

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SOL4

Salt-specific effects on the phase stability of BSA-PEG solutions below and at the isoionic point of BSA

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Studies on the influence of co-solutes on protein aggregation are important for life sciences and industry, and especially for the pharmaceutical industry, since formulations of biopharmaceuticals must be free of aggregates to ensure high potency and low solution viscosity [1-3]. Various salts, buffers, and uncharged polymers (often polyethylene glycol, PEG) are frequently components of protein formulations. Studies on the effect of PEG on liquid-liquid phase transition or solubility in protein solutions have focused mainly on salt-free systems (e.g., [4-6]), and only a limited number of cases involving protein PEG-salt solutions are known (e.g., [7-9]). There are no studies that systematically investigate the mutual effect of salts and PEG on the phase stability of protein solutions as a function of pH.

To learn more about protein aggregation and the effect of low molecular weight salts and PEG on phase stability, we measured the cloud point temperatures of bovine serum albumin (BSA)—PEG—salt solutions in acetate buffer at $\mathrm{pH} = 4.6$ (close to the isoionic point of BSA, i.e., $\mathrm{pH} \approx \mathrm{pI}$) and at $\mathrm{pH} = 4.0$(net charge of the protein is positive, $\mathrm{pH} < \mathrm{pI}$). We found that [10]:

(*i*) PEG promotes BSA aggregation in solutions with or without added salt. The influence of PEG is more pronounced at higher PEG molecular masses. As PEG concentration increases, the cloud point temperature increases and larger concentrations of PEG are required for phase separation at $\mathrm{pH} <\mathrm{pI}$. These observations are consistent with previous results on protein solutions and can be attributed to depletion forces.

(*ii*) Addition of salt (NaCl) to BSA-PEG solutions has qualitatively different effects at $\mathrm{pH} \approx \mathrm{pI}$ and $\mathrm{pH} < \mathrm{pI}$. At pH near the isoionic point, the addition of salt stabilizes the solution against phase separation, while salt decreases the stability of the solution at $\mathrm{pH} < \mathrm{pI}$.

(*iii*) Qualitatively different ion-specific trends were observed for $\mathrm{pH} \approx \mathrm{pI}$ and $\mathrm{pH} < \mathrm{pI}$. At $\mathrm{pH} \approx \mathrm{pI}$, the phase stability of the solution against phase separation increases from NaF (least stable) to NaI (most stable) and from LiCl to CsCl. Exactly the opposite trend is observed at $\mathrm{pH} < \mathrm{pI}$.

(*iv*) These observations correlate with the free energies of hydration of the added salt ions and with the effect of adsorption of salt ions on the protein surface on protein-protein interactions. Kosmotropic ions decrease the phase stability of BSA-PEG-salt solutions at $\mathrm{pH} < \mathrm{pI}$, while increasing it at $\mathrm{pH} \approx \mathrm{pI}$. Results can be rationalized by the Collins' concept of matching water affinities [11].

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SOL5
Neutralization of tricalcium aluminate hydrates with hydrochloric acid

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Red mud is the main by-product of the alumina industry, generated during the extraction of alumina from bauxite ore by the Bayer process. The global production is more than 150 million tons annually [1], and almost all waste is stored indefinitely in land-based disposal areas [2]. There are several studies and implementation ideas to utilize red mud as secondary raw material, their realization is hampered by the high alkalinity of red mud (pH ranges between 10–13, depending on the composition of the source ore, the production process and age of the residue). Based on various studies [3,4], one of the components of red mud giving rise to the alkalinity is tricalcium aluminate hydrate, TCA ($Ca_3Al_2(OH)_{12}$). The goal of our work is the determination of the neutralization mechanism of this solid, thereby gaining insights into the understanding of the dissolution and neutralization behaviour of red mud.

To this end, tricalcium aluminate hydrate was synthesized by a novel method, using so-called "green liquor" (supersaturated sodium aluminate solution). This synthesis pathway produces a solid product whose properties are close to the characteristics of the one obtained under industrial conditions. We compared this "Bayer" TCA with a TCA prepared via calcining a mixture of CaO and Al_2O_3 at 1300°C followed by hydration, which is a well-known method [5]. A multitude of structural characterization methods showed only minor differences between the two TCA samples.

The solubility and the neutralization mechanism of these solids were investigated, focusing on the reaction mechanism between TCA and hydrochloric acid. We find that after the dissolution of TCA, the solid instantaneously reacts with the acid forming a layered double hydroxide (LDH, $Ca_2Al(OH)_6Cl$) as a stable equilibrium product, with the chloride anion being incorporated between the layers to balance the positive charge of the $Ca_2(Al(OH)_6)^+$ units. Lowering the pH below 7, the LDH dissolves completely yielding calcium and aluminium chloride, as well as aluminium hydroxide as the predominant solid phase in acidic medium.

Our findings shed light on the complex mechanism of TCA neutralization, which helps us understand the intimate relationship between solid-liquid equilibria in aqueous red mud slurries better.

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SOL6

Modifying Macrocycle Stability and Supramolecular Chemistry in a Deep Eutectic Solvent

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Deep eutectic solvents (DESs) are unique solvents composed of at least two organic components that are usually solid at room temperature, which upon mixing form a liquid with remarkable solvation capabilities [1,2]. Although DESs and their applications for industrial use have spurred considerable interest, very little is known about their molecular mechanism of solvation.

Here we focus on reline, the DES formed from choline chloride and urea, and resolve the mechanism through which its constituents solubilize β-cyclodextrin, over an order of magnitude more than water [3]. Combining experiments and simulations, we determined that β-cyclodextrin solubility increases by a unique synergism between both urea and choline chloride [4]. We further show that β-cyclodextrin solubility grows remarkably when choline chloride is replaced by other salts, and that the attained solubility is much higher than expected from the summed urea-salt effect. Finally, we show how β-cyclodextrin solvated in reline maintains its supramolecular complexation capability with a guest dye molecule even in the complete absence of water. By resolving how multiple solutes act together to mediate both solubility and supramolecular assembly, we provide guiding principles to design future solvents that are tailored for specific needs.

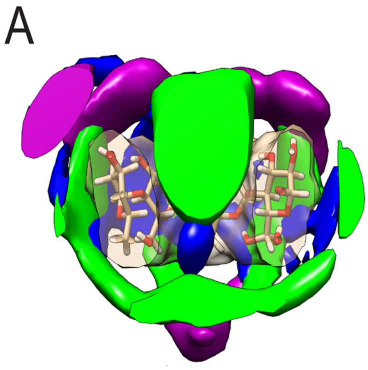

Figure 1. Spatial distribution of urea (green), choline cations (purple), and water (blue) around β-CD extracted from a molecular dynamics simulation of a 50 wt% reline solution.

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SOL7

The effect of methyl salicylate as an additive on the solubility and self-aggregation of caffeine - a thermodynamic and computational approach

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Caffeine, the most widely used psychoactive substance, belongs to the group of xanthine alkaloids. As an ingredient, caffeine can be found in coffee, black and green tea, soft and energy drinks [1]. Caffeine solubility in water is relatively low (approximately $16\,\mathrm{mg \cdot mL^{-1}}$ at room temperature), which is one of the crucial problems, especially in preparations consumed or stored at low temperatures, such as some drinks, and also for some supplements, pharmaceuticals and cosmetic industries [2]. Caffeine is considered limitedly soluble in water due to the self-association and aggregation of caffeine molecules by hydrophobic interactions [3]. Our research aims to determine caffeine solubility and the structural organisation of its molecules in solvents suitable for wide use in the previously mentioned industries. One of the molecules that meet both criteria is methyl salicylate. Usually, it is used as a fragrance and as a flavouring agent in mouthwash in low concentrations. But in higher concentrations, methyl salicylate is used as a topical analgesic for muscle pain.

The present study analysed experimental data from solubility, volumetric, viscosimetric measurements and computational simulations to understand caffeine aggregation properties in methyl salicylate. At lower temperatures, the solubility of caffeine in methyl salicylate is 69% higher than in water, while at higher temperatures, the solubility is 7% lower. The dissolution of caffeine in methyl salicylate occurs with heat absorption and an increase in the order of the system. The results noted in volumetric and viscosimetric measurements indicate that caffeine self-aggregation does not happen in the presence of methyl salicylate (Figure 1.). Molecules of methyl salicylate form a clathrate-like structure around the one caffeine molecule. According to the molecular dynamic simulations, interactions between caffeine and methyl salicylate molecules occur through hydroxyl groups of methyl salicylate and carbonyl caffeine groups. Based on obtained results, it is concluded that in the methyl salicylate solution caffeine is in a zwitterionic structure.

The presented study provides clear guidelines on how the biocompatible solvent methyl salicylate increases solubility and doesn't lead to caffeine self-aggregation. These measurements make the system suitable for topical and transdermal caffeine delivery in the pharmaceutical and cosmetic industries.

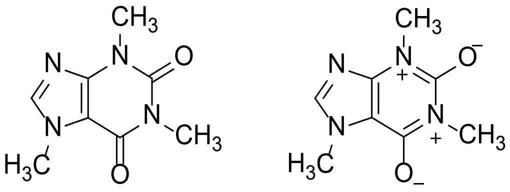

Figure 1. Representation of chemical structures for caffeine: neutral and zwitterionic form.

Acknowledgements: The acknowledgement for the support of the Cost Action CA18202 " NECTAR - the Network for Equilibria and Chemical Thermodynamics Advanced Research", and the Secretariat for Higher Education and Scientific Research of the Autonomous Province of Vojvodina, Serbia (Grant No. 142-451-2545/2021-01/2).

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IND1

Solution properties of scleroglucan: a promising biopolymer for enhanced oil recovery

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Polymer flooding is a popular technique among enhanced oil recovery methods and has been used for decades. It is well known that the performance of traditionally used synthetic polymers (e.g., HPAM) decreases in harsh conditions such as elevated salinity or temperature, while some biopolymers possess remarkable resistance to these impacts. Among them, scleroglucan (Figure 1) is a promising environmentally friendly substitute for HPAM.

In the present work, the physicochemical properties of scleroglucan were investigated using different techniques at different salt concentrations in the presence of monovalent and divalent salts.

The possible intermolecular interactions between the triple helical helix chains were explored using rheology in both rotational and oscillatory modes under different experimental conditions. The rheological properties of the biopolymer solutions were found to change significantly at a salinity level of 50 g/L in the presence of NaCl. Accordingly, the observed pseudoplastic behaviour indicates remarkable intermolecular interactions below this threshold, while trends in the parameters of the flow curves as well as in the storage and loss moduli clearly confirm the breakup of such a coherent (gel-like) structure above 50 g/L NaCl concentration. In contrast, the obtained data for divalent salts ($CaCl_2$ and $MgCl_2$) show that the macromolecular chains form a gel structure even at elevated salinity levels. These results clearly indicate a divalent ion enhanced intermolecular interaction. The rheological results were further supported by light scattering and electrokinetic measurements.

To avoid the loss of thickening ability at high NaCl concentrations, two types of ionic liquids were tested to stabilize coherent structures, namely, C2-mim and C4-mim have been studied. Our results indicate that salt level, which induces sol-gel transition can be shifted towards higher NaCl concentrations.

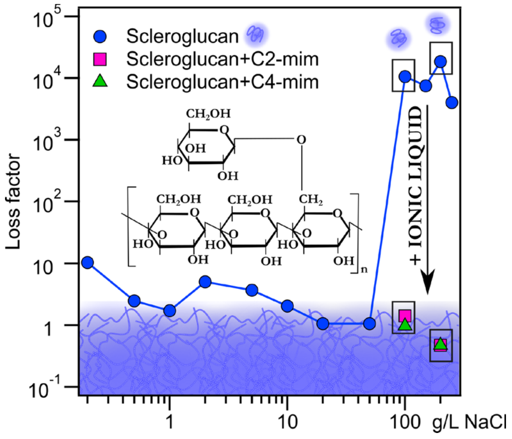

Figure 1. Loss factor data of scleroglucan solutions as a function of NaCl concentration (C2-mim: 1-ethyl-3-methylimidazolium chloride, C4-mim: 1-butyl-3-methylimidazolium chloride). The data close to unity indicate a coherent structure.

Acknowledgements: Financial support from the NRDI office (SNN142258) is gratefully acknowledged.

STR1

On the electroactive species in rechargeable Mg battery electrolytes: a vibrational study on solution chemistry

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The divalent redox change of Mg is responsible for the design of batteries with volumetric capacity and energy density higher than the conventional lithium-ion ones. Furthermore, its larger Earth abundance, environment aspects and deposition/stripping kinetics without dendrite formation make promising its use in energy storage devices [1]. Recent advances in the development of unexpensive and high electrochemical performance electrolytes have increased our expectations about the next technological stages towards commercialization of rechargeable Mg batteries. Since the discovery of magnesium aluminum chloride complex (MACC) electrolytes in 2014 [2], attempts have been done to characterize the most likely active species at the electrode-electrolyte interface and establish a relationship with their electrochemical activities. In this context, our research group has effectively contributed by using experimental and theoretical vibrational spectroscopy.

The significantly improved electrochemical performance of the 2:1 MACC-tetrahydrofuran (THF) electrolyte as compared to the 1:1 MACC-THF system seems to be due to the presence of $[MgCl_2(THF)_4]$ and appreciable amounts of $[(\mu\text{-}Cl)_3Mg_2(THF)_6]^+$, as revealed by the respective Raman bands at 212 and 240 cm^{-1} [3]. The latter electrolyte was characterized by the majority existence of $[Mg(THF)_6]^{2+}$ and $[MgCl(THF)_5]^+$, whose the average numbers of ether molecules around Mg(II) were determined from quantitative Raman analyses. Tiny quantities of $[(\mu\text{-}Cl)_3Mg_2(THF)_6]^+$, which is believed to be an electrochemically active species, have been also detected, in contrast to the spectra recorded in dimethoxyethane (DME). Actually, $[(\mu\text{-}Cl)_2Mg_2(DME)_4]^{2+}$, which is another electroactive complex and characterized by a Raman band at 222 cm^{-1}, is the major component at the 1:1 MACC-DME electrolyte, as demonstrated from experimental and theoretical data [4].

It is known that MACC electrolytes need electrolytic conditioning to get good reversibility and such a limitation has led to the development of conditioning-free methods, in which the addition of Mg powder to the MACC-ether system, named MMAC, has provided unprecedent electrochemical performance results. Recently, the 1.45:1 MMAC-DME electrolyte has been studied by vibrational spectroscopy and the solution data pointed out to the presence of $MgCl_2(DME)_2$, $[(\mu\text{-}Cl)_2Mg_2(DME)_4]^{2+}$ and $[(\mu\text{-}Cl)_4Mg_3(DME)_5]^{2+}$, where the latter is formed by the combination of precursor with the dimer bridged by two chlorine atoms and identified by a Raman band at 236 cm^{-1} [5]. On the other hand, the 2.39:1 MMAC-THF and 1:1.22 MMAC-diethylene glycol dimethyl ether (G2) systems revealed the presence of the same soluble Mg(II) complexes detected for the respective 2:1 and 3:5 stoichiometries [6,7]. The full conversion of $AlCl_3$ to $[AlCl_4]^-$, as revealed by the disappearance of the 330 cm^{-1} band, elucidates the Coulombic Efficiency of 100% determined for the THF-based electrolyte, in contrast to the G2-containing system, in which appreciable amounts of the Lewis acid are responsible for the lower activity. For the DME-based ternary system, the tiny $AlCl_3$ quantity allied to the presence of the trimer, observed for the first time in solution, may be related to the high electrochemical performance.

Acknowledgements: Fundação de Amparo à Pesquisa do Estado de Minas Gerais/FAPEMIG

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STR2

Structure of complete hydration shells of metal ions in aqueous solution

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Hydrated metal ions in aqueous solution bind different number of water molecules depending on its size and charge. The number water molecules close to the metal ion with different physico-chemical parameters than bulk water molecules, can be regarded as the hydration number. The reported hydration numbers of metal ions in aqueous solution reported in the literature vary a lot depending method applied. In this presentation the structures of the hydrated metal ion aqueous solution determined by large angle X-ray scattering (LAXS) will be reported. LAXS is more or less the only experimental method able to determine long distances, as to second and third hydration shells, in aqueous solution [1]. Furthermore, hydration shells outside the first one have not for any metal ion been reported in solid state. Therefore, the determination of hydration shells outside the first one must be performed in aqueous solution. Double difference infrared (DDIR) spectroscopy can be used to determine whether a hydrating water molecule in a hydration shell is stronger or weaker bound than in bulk water [2]. This can be used to determine whether a metal ion has structure making or breaking properties.

For the alkali metal ions, except lithium, and thallium(I) only a single hydration shell has been detected, while lithium, silver and the divalent metal ions have two well-defined hydration shells, and tri- and tetravalent metal ions may also have at least traces of a third hydration shell. The distances to the first and second hydration spheres and between the oxygens in the first and second hydration spheres gives the $M\text{-}O_I\cdots O_{II}$ angle, and thereby the polarization of the oxygen in the water molecules in the first hydration sphere. Metal ions forming mainly electrostatic interactions give $M\text{-}O_I\cdots O_{II}$ angles close to 120º, while for metal ions forming strong covalent interactions this angle is close to 109.5º. The structure of the complete hydration shell of a large number of metal ions in aqueous solution from newly determined LAXS data will presented and discussed.

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STR3

Solution structures of a lithium-containing electrolyte system

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Lithium-ion batteries and lithium batteries are important power suppliers of notebook computers, mobile phones, and many other electronic devices. Developing higher quality and more efficient batteries is the aim of many people working in the related industries and basic research laboratories. As an essential constituent of the batteries, lithium ion-containing electrolytes have attracted much attention. In spite of lots of efforts, a very basic question is still under debate: What are the solution structures of the Li^+-containing electrolytes? More specifically, what species and/or aggregates take part in the conduction of electricity?

To address the question, we selected the popular lithium bis(trifluoromethane)sulfoneimide (LiTFSI) as the salt and a neutral molecule propylene carbonate (PC) as the solvent to make a model electrolyte. Using the method of excess infrared spectroscopy, we identified experimentally the following species/complexes in the binary system: positively charged $Li^+(PC)_4$; negatively charged $TFSI^-$, $TFSI^-(PC)$, $TFSI^-(PC)_2$, and $Li(TFSI)_2$; ion pair and its solvated forms LiTFSI, LiTFSI(PC), $LiTFSI(PC)_2$, and $LiTFSI(PC)_3$, as well as PC monomer, dimer, and PC multimers. Among them, $Li^+(PC)_4$ is the only positively charged species. Quantum chemical calculations show a strong interaction between Li^+ and PC, suggesting that Li^+ would transport in the mode of solvation-carriage in the batteries. On the other hand, the interaction between $TFSI^-$ and PC is weak, implying the anions may transport in the mode of popping.

Generally, it is not an easy job to identify experimentally the complexing/associating/aggregating forms of molecules or ions in a solution. It is thus worthy to say a few words about the special method used in this work. The method is called excess spectroscopy [1-4]. It is based on the understanding that different complexing forms of a molecule will generate more or less different spectral signals such as absorption bands in the case of infrared spectroscopy. An observed spectrum is the weighted sum of all the existing complexes in the solution. By mixing the molecules with another component, the amounts of the complexes will change, most likely in a non-linear manner. Subtracting the spectrum of a mixture by the corresponding linear prediction, the so-called ideal spectrum, we get an excess spectrum. The next thing is to assign the positive and negative peaks of the excess spectra. Quantum chemical calculations are used to finalize the assignments based on the linear relation criterion of calculated versus experimental peak positions [5-8].

Acknowledgements: National Natural Science Foundation of China

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STR4

Speciation of aluminum ions in $AlCl_3$-Glyme solutions

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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. The electrodeposition of Alusing various non-aqueous solutions such as $AlCl_3$-based molten salts and organic solvents-based solutions have been reported. However, they have drawbacks such as reactivity with atmospheric water and high electrodeposition temperature [1,2]. Recently, Kitada and Murase *et al*. reported that in the electrochemical reaction of Al with glymes ($CH_3O(CH_2CH_2O)_n$ CH_3, 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 [3]. However, it is unclear the molecular insight into the Al^{3+}-Cl^- complex formation reaction and the Al dissolution/precipitation reaction in the $AlCl_3$-G2 solution. In this study, speciation analysis of Al ions in $AlCl_3$–glyme solutions was performed for the purpose of identifying reactive species and clarifying the reaction mechanism.

The ambitious three Raman bands from 200 to 600 cm^{-1} was observed for all $AlCl_3$-Gn(n = 2-4) solutions, which was assigned to the mono-and dimer-chloroaluminate according to results of theorical Raman bands. It is indicated that both chloroaluminates were existed in all systems. In the ^{27}Al NMR spectra for $AlCl_3$-Gn(n = 2-4) solutions, the peaks were observed around 104 and 25 ppm, which were assigned to tetrahedral- and octahedral coordination structures of Al^{3+}-Cl^- complex, respectively. The peak at 104 ppm shifted to the high magnetic field side with increase of $AlCl_3$ concentration, which indicates that chemical exchange of Al^{3+} was faster than NMR time scale, hence the averaged signals of Al were observed. Dielectric relaxation spectroscopy (DRS) is helpful method to be able to detect the chemical species with dipole. Figure 1 shows the DRS spectra of $AlCl_3$-Gn (n = 2-4) solutions. The relaxation of solvents around 10 GHz decreased and the new relaxation below 1 GHz was observed as the $AlCl_3$ salt concentration increased. The relaxation below 1 GHz was assigned to contact ion pair (CIP). It suggested that the $AlCl_3$ and $AlCl_2^-$ complex with dipole was formed in the solutions. We performed the curve-fitting for the DRS spectra based on Debye equation and the DRS spectra can be explained by four Debye relaxation modes. In the four Debye relaxations, the lowest relaxation was attributed to the CIP and appeared at lower frequency with increasing the length of the ethylene oxide chain. It was consistent with the viscosity of the neat glymes, hence it associated to the increase in solution viscosity. The intensity of the lowest relaxation in the G2 system was larger than that in others. The dipole moment was also discussed by means of the molecular orbital calculation.

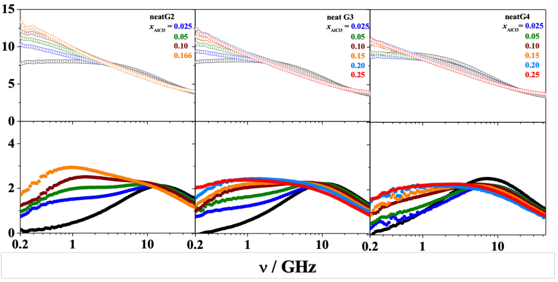

Figure 1. Dielectric relaxation spectra of $AlCl_3$-G*n*(*n* = 2-4) solutions.

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STR5

Ion pairs in the sodium-ion aqueous solution by IR ratio spectra and Raman excess spectra

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Sodium salts in aqueous solution are important for many fields. For example, sodium ions are most abundant in the ocean, and they are essential for humans. The molecular interactions in these sodium salt aqueous solutions are very complex but important to understand the physical properties of these solutions. In this presentation, I will demonstrate some novel vibrational spectral analysis methods, such as IR ratio spectra and Raman excess spectra. Using these methods, the ion pairs in some sodium ion aqueous solutions can be observed. Through the IR ratio spectra in the O-H stretching region of sodium ion aqueous solutions, the hydration number of the anions Cl^-, Br^-, I^-, NO_3^-, ClO_4^- can be recorded. It is observed that the hydration number of anions decreases with increasing the concentration of sodium salts, which directly shows that the concentration of ion pairs increases with increasing the concentration of sodium solutions. Through the Raman excess spectra of the sodium salts with NO_3^- and ClO_4^-, two new spectra peaks of the anions stretching bands are observed directly, which can be assigned to be solvent-shared ion pairs and direct contacted ion pairs. The concentration of such ion pairs can be recorded through the Raman excess spectra. These data can be used to understand some physical properties of the sodium ion aqueous solutions.

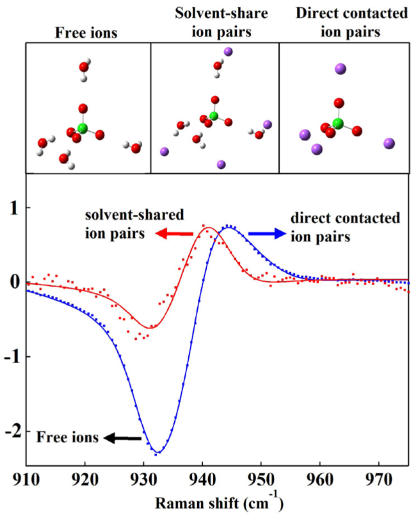

Figure 1. Raman excess spectra of $NaClO_4$ in aqueous solutions and the schematic diagram of the free ion, solvent-shared ion pairs and direct contacted ion pairs.

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STR6

Xenon NMR spectroscopy: structure and dynamics of simple liquids, ionic and porous liquids

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^{129}Xe NMR spectroscopy is commonly used to investigate the structure and dynamics of many different materials such as pure liquids [1], ionic liquids(ILs) [2], and porous solids [3]. This is because xenon NMR parameters such as chemical shift, relaxation times and diffusion coefficient allow the probing of the physical properties of the host material over different scales (from a few angstroms to microns). Xenon gas, soluble in several liquids, can travel through the material and explore the size and shape of the accessible volumes such as pores, dynamic cages, layers and nano-domains.

Here we report the recent results on the peculiar structure of different liquid systems, starting from simple solvents such as dihalomethanes (CH_2X_2, X=Cl, Br, I), ionic liquids based on 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [$C_nC_1$im][TFSI] (with $n = 2–10$) and more complex type II porous liquids(PLs). The type II PLs are prepared using Noria-OEt (a derivative of the paddlewheel-like molecular host Noria - Figure 1) as an empty molecular host dissolved in 15-crown-5 solvent at different concentrations [4]. Experimental ^{129}Xe NMR data, combined with molecular dynamics simulations, indicate that in simple liquids xenon is preferentially solvated by the halogen atoms with respect to the hydrogens of the dihalomethanes. In more complex ILs, xenon diffusion motion reveals the presence of alternating polar/hydrophobic domains that become looser with changing the ILs anion.

Finally, xenon traveling in type II porous liquids detects, through its chemical shift variation, the presence of multiple sites formed by the ri-arrangement of the host cavities within the porous 15-crown-5 solvent.

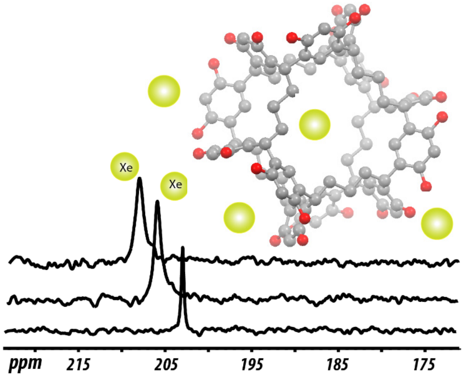

Figure 1. ^{129}Xe spectra of Type II porous liquid with increasing Noria-OEt concentration. Molecular structure of Noria.

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STR7

Two dimensional Raman and dielectric relaxation correlation analysis for $LiCF_3SO_3$ – propylene carbonate solutions

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In the development of next-generation lithium-ion batteries (LIBs), higher energy density by increasing electromotive force and capacity is being considered, and a high ionic conductivity electrolyte is essential for capacity increase. On the other hand, super-concentrated lithium salt solution has been reported to have a specific lithium ion conduction mechanism with high lithium ion transference number and conductivity, and is expected to be a next-generation LIB electrolyte. However, the lithium ion conduction mechanism in super-concentrated lithium salt solutions has not been clarified, and the relationship with the lithium ion local structure in the solution is also unknown. In this study, in order to clarify the specific lithium ion conduction in $LiCF_3SO_3$ - PC (PC: propylene carbonate) solutions at the molecular level, the rotational motion, which probably play a key role in lithium ion conduction, was investigated as dipole reorientation dynamics with the dielectric relaxation spectroscopy (DRS), and Raman spectroscopy The speciation was also elucidated with the Raman spectra.

In the DRS spectra of polar liquids such as PC, reorientational relaxation of the solvent dipole is generally observed in the frequency band around/above 10 GHz. The intensity of this relaxation decreased and shifted to the low frequency side by dissolving the lithium salt. In addition, a new relaxation around 1 GHz was observed with increasing the lithium salt concentration probably be due to dipole reorientation of solvent-ion-pair (SIP) and/or contact-ion-pair (CIP). Furthermore, when measurements were performed down to the lower frequency range, a new relaxation appeared in a quite low frequency range around 20-50 MHz for highly concentrated solutions of the lithium salt, and the relaxation intensity increased with increasing lithium salt concentration. This relaxation of quite low frequency has not been reported in most cases so far, and it is difficult to attribute this relaxation. Therefore, 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 $LiCF_3SO_3$ - PC solutions shown in Figure 1, the relaxation that appears at the lowest frequency at the higher lithium salt composition can be attributed to CIP or aggregates (AGG).

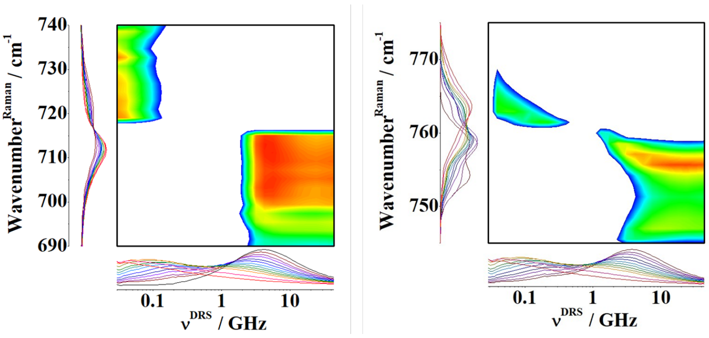

Figure 1. 2D-RDCA for the LiCF$_3$SO$_3$ – PC solutions. The fingerprint region of Raman bands for PC and CF$_2$SO$_3$ are shown in the left and right panel, respectively.

STR8

The effect of added ions on hydration and ion binding of aqueous glutamate

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The physiological activity of a small biomolecule is governed by the delicate balance of its simultaneous interactions with its receptor, water, and other compounds, particularly ions, present in the carrying intra- or extra-cellular fluid. Whilst recent decades have brought tremendous progress in our understanding of biomolecule-receptor interactions, the role of water is still debated [1] and the effect of ions puzzling [2].

A typical example for such a compound is the glutamate (Glu^-) ion. This amino acid (anion) is not only a prominent constituent of proteins and used as flavour enhancer in food industry but also acts as an excitatory neurotransmitter. As such, Glu^- is essential to fast and efficient signal transmission in the nervous system and linked to brain dysfunctions and various diseases. Although intensively studied, the interaction of Glu^- with its receptors, which is evidently connected to its hydration and ion-binding properties, is still not completely understood [3].

A recent investigation of aqueous sodium glutamate (NaGlu) solutions, combining broad-band dielectric relaxation spectroscopy (DRS) and statistical mechanics, revealed significant Glu^- hydration that decreased with increasing solute concentration [4]. At ~0.4 M NaGlu one water molecule is strongly bound (“frozen”; $Z_{ib} \approx 1$) and $Z_s \approx 10$ H_2O are moderately bound (“slow H_2O”) by Glu^-. Counterion binding appeared to be negligible.

In this contribution we report on the effect of up to 0.8 M LiCl, NaCl, $MgCl_2$ and $CaCl_2$ added to 0.4 M aqueous NaGlu solutions. Whilst LiCl and NaCl addition did not affect Z_{ib}, the amount of moderately bound H_2O molecules strongly increased. On the other hand, addition of $MgCl_2$ and $CaCl_2$ did not affect Z_s but induced negative Z_{ib} values. Additionally, the effective dipole moment of Glu^- decreased significantly upon addition of LiCl, $MgCl_2$ and $CaCl_2$. In combination, these results suggest the formation of $[M{\cdots}OOC(CH_2)_2NH_3COO]^+$ (M = Mg, Ca) contact ion pairs and of $[Li{\cdots}H_2O{\cdots}Cl{\cdots}OOC(CH_2)_2NH_3COO]^-$ complexes. Corresponding binding constants ($\log K_A^\circ \approx 1\text{-}1.5$) will be reported. We argue that similar to LiCl also NaCl weakly binds as an ion pair to Glu^- but that the lifetime of these complexes is comparable to the reorientation time of glutamate and thus not reflected in the effective dipole moment.

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STR9
Hydration of Hofmeister ions

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Water dissolves salt into ions and then hydrates the ions in an aqueous solution. Hydration of ions deforms the hydrogen bonding network and triggers the solution with what the pure water never shows such as conductivity, molecular diffusivity, thermal stability, surface stress, solubility, and viscosity, having an enormous impact to many branches in biochemistry, chemistry, physics, and energy and environmental industry sectors [1-3]. However, regulations for the solute-solute-solvent interactions are still open for exploration. From the perspective of the screened ionic polarization and O:H-O bond relaxation, this work features the recent progress and a perspective in understanding the hydration dynamics of Hofmeister ions in the typical YI, NaX, ZX_2, and NaT salt solutions (Y = Li, Na, K, Rb, Cs; X = F, Cl, Br, I; Z = Mg, Ca, Ba, Sr; T = ClO_4, NO_3, HSO_4, SCN). Phonon spectrometric analysis turned out the f(C) fraction of bond transition from the mode of deionized water to the hydrating. The linear $f(C) \propto C$ form features the invariant hydration volume of small cations that are fully-screened by their hydration H_2O dipoles. The nonlinear $f(C) \propto C^{1/2}$ form describes that the number insufficiency of the ordered hydrating H_2O diploes partially screens the anions. Molecular anions show a stronger yet shorter electric field of dipoles. The screened ionic polarization, inter-solute interaction, and O:H-O bond transition unify the solution conductivity, surface stress, viscosity, and critical energies for phase transition.

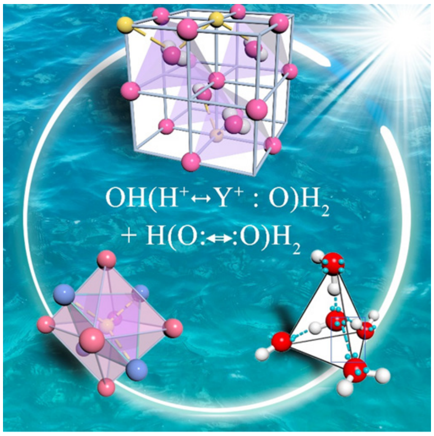

Figure 1. Model of Y^+ cationic occupancy in a $(2a)^3$ cube and a tetrahedral unit and OH^- occupancy.

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STR10

A multidisciplinary approach to unveil the structural arrangement of deep eutectic solvents: from local order to nanoscale organization

Matteo Busato, Valerio Di Lisio, Alessandra Del Giudice, Alessandro Tofoni, Giorgia Mannucci, Francesco Tavani, Valentina Migliorati, Andrea Martinelli, Mauro Giustini, Alessandra Gentili and Paola D’Angelo

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Deep eutectic solvents (DESs) deal with mixtures of two or more compounds which, for well-defined compositions, show a melting point depression that is deeper than the ideally predicted one, allowing the achievement of a liquid phase even from solid starting materials. This behavior relies on the extensive interplay among the components, so that DESs are high-entropic systems with tens of punctual interactions ruling the overall chemical-physical properties. This complexity makes the achievement of a clear picture about the structural arrangement of these materials a fundamental knowledge to understand their macroscopic behavior and ultimately promote their applications.

In this contribution, we demonstrate how a multidisciplinary approach combining X-ray absorption spectroscopy (XAS), small- and wide-angle X-ray scattering (SWAXS), UV-Vis, attenuated total reflection Fourier transform infrared (FTIR), and near-infra-red (NIR) spectroscopies with molecular dynamics (MD) simulations is a powerful strategy to unveil the structural arrangement of DESs and their mixtures with co-solvents (*i.e.*, water, methanol) ranging from short- to intermediate-scale levels. We focused on the eutectic formed by choline chloride (ChCl) and sesamol at a 1:3 molar ratio and on the metal-based deep eutectic solvent (MDES) formed by $NiCl_2 \cdot 6H_2O$ and urea at 1:3.5 molar ratio. In the former system, the employed techniques were able to detect a nano-phase segregation between water pools confining most of the ChCl and sesamol-rich domains (Figure 1a.), which is formed for high water contents [1], differently from methanol addition [2]. In the $NiCl_2 \cdot 6H_2O$: urea 1:3.5 MDES, we observed a close packing of Ni^{2+} ion clusters forming oligomeric agglomerates thanks to the mediation of bridging chloride anions and water molecules [3]. Conversely, urea acts as a sort of “inner solvent” owing to the formation of nanostructures intercalating the Ni-rich regions (Figure 1b.). This arrangement is disrupted upon the introduction of additional water, diluting the system up to an aqueous solution of the MDES constituents. Our digression from shorter to larger lengths allowed the achievement of an all-round picture able to clarify the structural arrangement of these inherently complex systems.

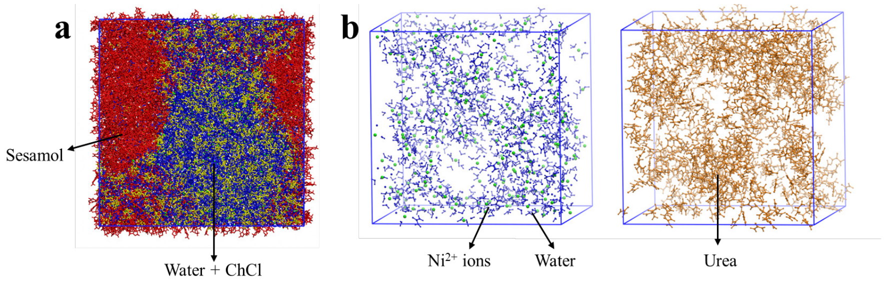

Figure 1. Nano-scale structures formed in the ChCl: sesamol 1:3 (a) and $NiCl_2 \cdot 6H_2O$: urea 1:3.5 (b) DESs.

[1] M. Busato, V. Di Lisio, A. Del Giudice, P. Tomai, V. Migliorati, L. Galantini, A. Gentili, A. Martinelli and P. D’Angelo, *J. Mol. Liq.*, 2021, **331**, 115747.

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STR11

Improved data analysis for molecular dynamics in liquid benzene

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To measure the collective dynamics of molecular liquids with different intermolecular interactions, we have carried out a series of inelastic x-ray scattering (IXS) experiments at BL35XU of the SPring-8, such as liquid acetone with dipole interaction [1], liquid CCl_4 with a van der Waals one [2], and liquid benzene with π-π stacking one [3]. The obtained IXS spectra were analyzed by using a generalized Langevin formalism (GLF) with a memory function including thermal and two viscoelastic damping [4]. The left panel of Figure 1 shows the $S(Q,\omega)$ spectra of liquid benzene (circle: data, solid curves: GLF fits), and the right one is the dispersion relation. The dashed line is the hydrodynamic prediction with the sound velocity of 1,299 m/s, and the IXS excitation energies in the low Q region exceed it by more than 50%. Note that such a very fast sound is observed in any of molecular liquids [1-3] independent of the intermolecular interactions, and much larger than those of monatomic liquid metals of about 15%. Since the parameters in the GLF fits interfere with each other and the obtained microscopic elastic properties are physically meaningless [3], we recently improve the analysis by including a simple sparse modelling idea and found that the fast and slow viscoelastic relaxation times correspond to the vibrational and rotational relaxations of the molecule, respectively [1-2], by which the terahertz sounds require the extra energies for the propagations. In this study, the improved GLF analysis with a sparse modelling is applied to the $S(Q,\omega)$ spectra of liquid benzene for clarifying the viscoelastic origin of the fast sounds by comparing with other molecular liquids with different vibrational and rotational relaxation times [1-2].

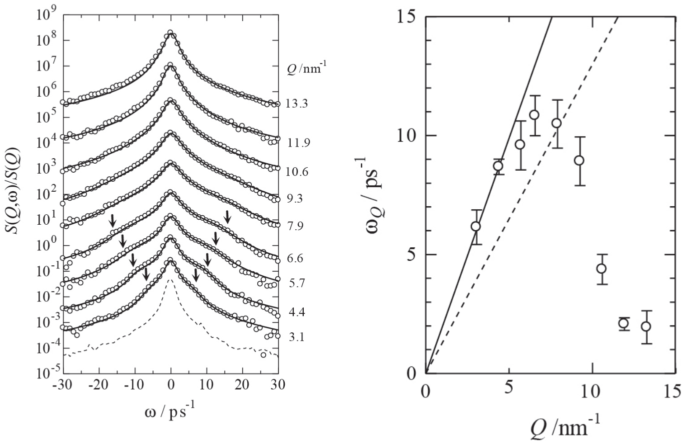

Figure 1.(Left) Logarithmic plots of $S(Q,\omega)$ spectra of liquid benzene. (Right) Dispersion relation. The dashed line indicates the hydrodynamic value with the sound velocity of 1,299m/s. Taken from Referen. [3].

Acknowledgements: This work was supported by JSPS Grant-in-Aid for Transformative Research Areas (A) ‘Hyper-Ordered Structures Science’ (No. 21H05569) and the JST CREST (No. JPMJCR1861).

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STR12

The Complex Story Behind a Deep Eutectic Solvent Formation as Revealed by L-Menthol Mixtures with Butylated Hydroxytoluene Derivatives

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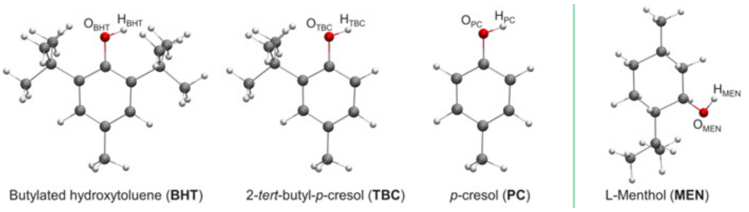
Deep eutectic solvents (DESs) are currently ruling the research topic about advanced processing media as a more sustainable alternative to traditional solvents. Along with this, the scientific debate about the fundamental definition of these systems is still going on. Strictly speaking, DESs are defined as mixtures of two or more compounds showing a melting point depression that is deeper than the ideally predicted one for a defined composition. This unusual thermal behavior seems to rely on the diffuse hydrogen-bond (H-bond) network between the parent compounds, so that this has become a common way to identify DESs.

In this contribution, we present an in-depth study about the eutectic mixtures formed by L-menthol (MEN) with the butylated hydroxytoluene (BHT), 2-*tert*-butyl-*p*-cresol (TBC), and *p*-cresol (PC) compounds. The idea for the present work traces back to the observation that the BHT molecule carries a high steric encumbrance provided by two *tert*-butyl substituents close to the hydroxyl group, which in principle should be responsible for the H-bond formation. Nevertheless, a liquid phase at room temperature can be obtained when BHT is mixed with MEN at 1:3 molar ratio [1]. For these reasons, we synthetized new eutectic mixtures with the TBC and PC components, which are analogues to the BHT one but with a different degree of steric hindrance around the hydroxyl group. The thermal characterization of these systems obtained by means of differential scanning calorimetry (DSC) and polarized optical microscopy (POM) allowed to classify the BHT/MEN system as an ideal eutectic, while the TBC/MEN and PC/MEN ones behave as hydrophobic DESs (HDESs). The rationale for this thermal behavior was achieved by proton (1H) nuclear magnetic resonance (NMR) and Raman spectroscopy measurements aided by *ab initio* and classical molecular dynamics (MD) simulations. The experimental and theoretical outcomes agree in finding that almost no H-bonds are played by the BHT compound and that apolar-apolar attractions between the BHT and MEN components is the driving force for the eutectic formation. On the other hand, TBC addition to MEN provokes the replacement of the H-bonded network among MEN molecules with the more favorable TBC-MEN donor-receptor H-bond due to the exasperated H-bond donor nature of TBC because of a concurrence of steric and electrostatic factors. Finally, the PC species can establish the favorable PC-MEN interaction through intercalation into the H-bonded network due to the absence of steric hindrance around its hydroxyl group. The obtained results, along with the peculiarity of the inspected systems, provided an archetypal study having the potentiality of challenging and possibly pushing a little bit further the fundamental definition of these complex systems.



Butylated hydroxytoluene (**BHT**) 2-*tert*-butyl-*p*-cresol (**TBC**) *p*-cresol (**PC**) L-Menthol (**MEN**)

Figure 1. Molecular structures of the eutectic components MEN, BHT, TBC and PC

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STR13

Molecular insight on the properties of ionic liquid + water mixtures: from experiment to modelling

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Chemical process design need, for the sake of quality of investment, operation and safety, accurate values of the thermophysical (and toxicological) properties of liquids. Ionic liquids as possible replacements of currently chemicals for which European and International agencies have mandatory requirements, in actual and future chemical processes, generate a plethora of mixtures, that need an effort to devise reliable prediction and estimation methods, in the impossibility of measuring all properties of all systems known [1,2].

Water, as the main chemical engineering fluid, is a natural choice, but its use alone is not sufficient. In our laboratory a systematic study of the properties of [C_2mim][X] ionic liquids mixtures with water, by measuring properties that can give a molecular insight on the structure of the mixtures, combined with molecular simulation and spectroscopic information.

It is the purpose of this contribution to report our findings, for ionic liquids where X = CH_3COO^-, $CH_3SO_3^-$ and $N(CN)_2^-$, for properties like density, speed of sound, viscosity, electric conductivity, thermal conductivity, infinite dilution diffusion coefficients and refraction index [3-5] and discuss the possible structure of their aqueous systems, in all range of compositions, schematically presented in Figure 1 for the [C_2mim][CH_3SO_3] + water mixture [4], extended to all systems.

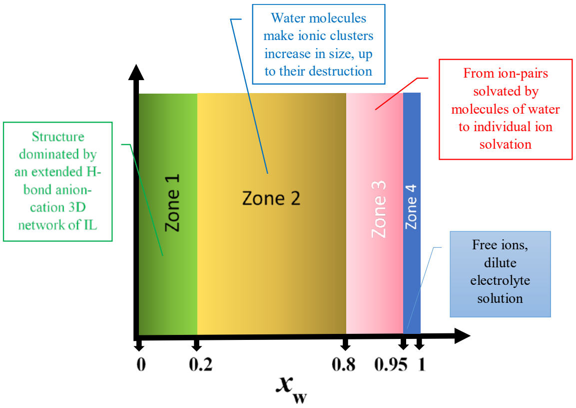

Figure 1. Schematic representation for the different structural zones of the [C_2mim][CH_3SO_3] + water mixture. Scale in mole fraction is not proportional.

Acknowledgements: This work was partially supported by Centro de QuímicaEstrutural - UID/QUI/00100/2013, UID/QUI/00100/2019, and UIDB/00100/2020, funded by FCT – Fundação para a Ciência e Tecnologia, Portugal. The author thanks all his collaborators contribution to the related publications.

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COM1

New treatment of hydrated protein complexes in silico

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Hydration and selective binding of proteins are fundamental processes to the functioning of living organisms and underlie most cellular functions. The protein-water and protein-ligand interactions play crucial role for the structure, dynamics, folding, and functionality of proteins. Therefore, a characterization of hydrated protein complexes is important for understanding of the running of many vital processes. However, in many cases a determination of the parameters of biomolecule hydration and complex formation by the experimental methods presents a significant problem, not only technical but also the financial one.

In this contribution we present two new ideas for calculations of biomolecular hydration and binding parameters. We consider them under the theory of liquids in the framework of the 3D-reference interaction site model (3D-RISM) method and MD simulations. The first idea is directed on correct determining the thickness of the hydration layer. As a result of application of this straightforward but effective procedure, now we are able to obtain the total hydration number of biomolecules properly. The second idea is pointed by calculating the parameters of complex formation of biomolecules in a limited region of their hydration shell to increase the speed of calculations.

The application of these *in silico* approaches are considered on the examples of proteins bovine pancreatic trypsin inhibitor (BPTI) and tyrosine phosphatase 1B (PTP1B) as well as a set of drug compounds for which protein 1B (PTP1B) is a target. The results are also presented for a complex involving the receptor-binding domain (RBD) of the SARS-CoV-2 spike (S) protein and the human cellular membrane receptor angiotensin-converting enzyme 2 (hACE2).

Acknowledgements: This work was supported by the Russian Science Foundation (project No. 22-23-00184, https://rscf.ru/en/project/22-23-00184/).

COM2

The hydration of Li^+ and Mg^{2+} in subnano carbon nanotubes by multiscale theoretical approach

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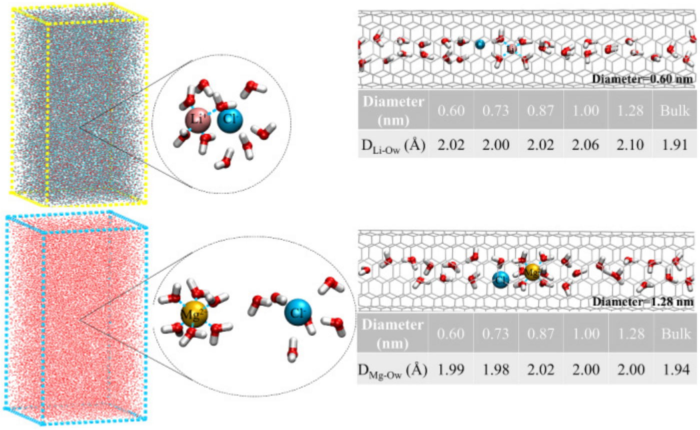
The separation of brines and seawater with high Mg/Li mass ratios still faces huge challenges. To provide a theoretical basis for the design of precise separation materials, the hydration of Li^+ and Mg^{2+} in confinement using carbon nanotubes (CNTs) as the 1-D nanopore model was investigated by a multiscale theoretical approach. According to the statistics and analysis of the first coordination layer of the cations, we find that the coordination shell of two cations exists inside CNTs, and the second coordination shells of the cations are unstable. Moreover, the results of the structure analysis indicate that the hydration layer of Li^+ is not complete in the CNTs with diameters of 0.73, 0.87 and 1.00 nm, yet this case does not occur in the 0.60 nm CNT, which is explained by the formation of contact ion pairs (CIP) between Li^+ and Cl^-, going through a solvent-shared ion-pair $[Li(H_2O)_4]^+$, which is studied by an additional 400 ns in the 0.60 nm CNT. However, the hydration layer of Mg^{2+} is complete and not sensitive to the diameter of CNTs by molecular dynamics simulation and ab-initio molecular dynamics (AIMD). Furthermore, the results of the Li^+ and Mg^{2+} orientation distribution indicate that the water molecules around Mg^{2+} are more ordered than those around Li^+ in the CNTs and are more analogous to the bulk solution. We concluded that it is energetically unfavorable for confining Li^+ inside the CNT with a diameter of 0.60 nm, and is favorable for confining Li^+ inside the other four CNTs and Mg^{2+} in all CNTs, which is driven by the strong electrostatic interaction between cations and Cl^-. In addition, the interaction between cations and water molecules in the five CNTs is also analyzed from the Noncovalent Interaction (NCI) perspective by AIMD.



Diameter (nm)	0.60	0.73	0.87	1.00	1.28	Bulk
$D_{Li\text{-}Ow}$ (Å)	2.02	2.00	2.02	2.06	2.10	1.91

Diameter (nm)	0.60	0.73	0.87	1.00	1.28	Bulk
$D_{Mg\text{-}Ow}$ (Å)	1.99	1.98	2.02	2.00	2.00	1.94

Figure 1. The hydration structure of ions and the average bond lengths of cations and water molecules, Li^+ and Cl^- in bulk solution and the five CNTs.

Acknowledgements: This work was financially supported by the National Natural Science Foundation (21973106) and the Nature Science Foundation of Qinghai Province (2022-ZJ-T03).

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COM3

Are there water-free solvents in general: the “sudden” behaviour of tautomeric switching systems in organic solvents

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The effect of the solvent is crucial for the equilibrium state of tautomeric systems and the dynamics of proton transfer [1]. This effect is not only a consequence of the simple polarity of the solvent, but a result of complex solute-solvent and solvent-solvent interactions, where the solvent molecules can stabilize given tautomeric form or even transfer the proton over long distances.

There are serious problems in describing the solvent complexity both experimentally and theoretically. No doubt, the Linear Solvation Energy Relationships theory and its variations are a good tool to describe the macroscopic solvent behaviour in the tautomeric molecules [2]. However, such a description is difficult to reproduce experimentally. The situation is even more complicated – are we absolutely sure that the organic solvents are absolutely water-free? And, can the traces (so low to be neglected in a normal understanding) affect the tautomeric proton transfer?

In the current presentation, the classical description of the solvent effects in some tautomeric systems will be considered along with the difficulties arising from the attempts to describe the complexity of the solvent effect by means of theoretical chemistry. Special attention will be given to the well-known water-assisted long-range proton transfer in 7-hydroxy quinoline and 7-hydroxy coumarin, and to the “sudden” switching behaviour of rotary switches [3] and proton cranes [4], caused by traces of water in organic solvents. The systems to be discussed are shown in Figure 1.

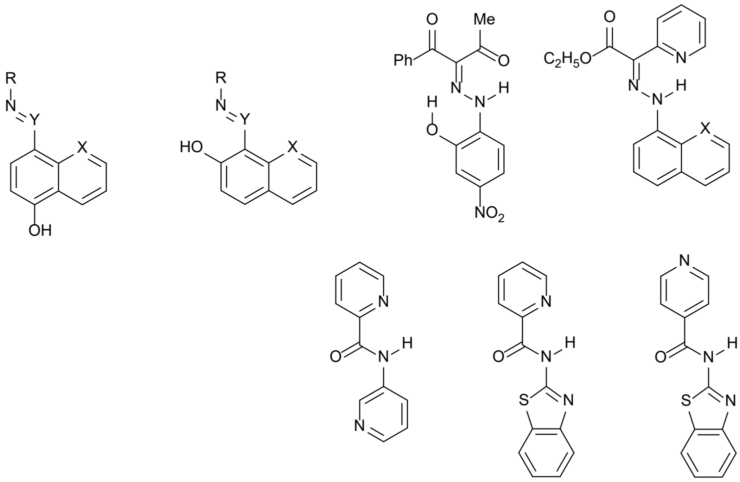

Figure 1. Tautomeric switching systems to be discussed (X and Y can be N or CH).

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COM4

Solvent topology in bond decomposition analysis: The path to natural intrinsic acidity

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Solvents are used as an effective means for experimental evaluation of acidity. It was known that solvents can stabilize interacting species, regardless of their reactive nature. Moreover, recent experimental practice has demonstrated a phenomenon in which different solvents can act differently on similar reactive species and/or reactive sites in specific topologies. By evaluating the monomeric molecular topologies of different solvents using an efficient bond decomposition analysis (BDA) within the framework of the natural bonding orbital (NBO) formalism, one will be able to understand the deeper quantum mechanical results of solvents in different stabilization interactions with different reactive sites. Due to its broad scope, this method is expected to reveal a comparative aspect of the reactivity of monomeric solvent molecules as a function of their critical binding components - partial atomic contributions in terms of their orbital interaction probability. Their representation (natural intrinsic acidity, NIA) is compared with the unique autoionization constants of selected solvents to formulate a new type of linear-free energy relation that adequately accounts for both NIA and BDA accuracy.

Acknowledgement: We gratefully acknowledge financial support from the Slovenian Research Agency (Research Core Funding Grant P1-0230).

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TER1

New, simple and highly effective models for predicting thermodynamic and transport properties for binary and multicomponent solutions

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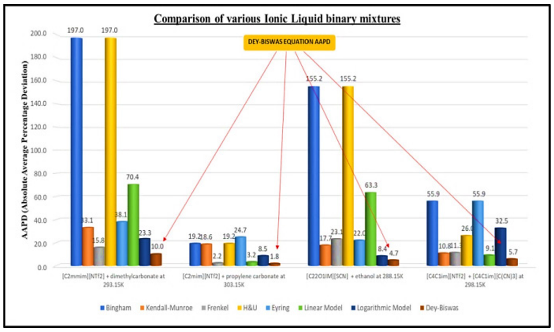
Density, viscosity and ultrasonic velocity are key thermophysical properties integral to solution thermodynamics which can be used to optimize the mass and energy exchange processes. These properties are helpful in understanding the nature and strength of molecular interactions between constituent components. Measurements and analysis of thermophysical properties for pure, binary and higher-order liquid mixtures play a vital role in solution thermodynamics and have been utilized in designing and optimizing various chemical processes. Prediction of thermophysical properties has gained appreciable significance during the global shutdown of experimental research labs due to the COVID-19 pandemic.

There remains a strong demand for accurate and robust predictive approaches, especially for viscosity, the most important transport property since it does not exhibit a linear trend with the change in concentration and is highly susceptible to temperature variations. Thus, it is very challenging to develop a model for predicting viscosity for binary and higher-order liquid mixtures. Dey et al [1–5] have developed new models exhibiting an appreciable amount of success which are working well for Ionic Liquid (IL) mixtures too. The Dey Biswas model [4] has now been tested on around 500 binary and a good number of multicomponent mixtures including ionic liquids [1,6], Deep Eutectic Solvents [7] and is showing great promise [1,4,6].

Ultrasonic velocity (*u*) is one of the most important thermodynamic properties. Recently, an approach has been developed by us for predicting ultrasonic velocity and tested on 100 binary systems. Findings exhibit very good results outclassing existing well-established approaches (Table1).

Table 1. Comparative %APD values of Ultrasonic velocity of 100 Binary systems by various models.

Grand % APD of 100 Binary systems	Nomoto	Van Dael	Danusso	Junjjie	CFT	**Proposed Model**
	1.36	5.65	2.58	2.35	1.90	**0.52**



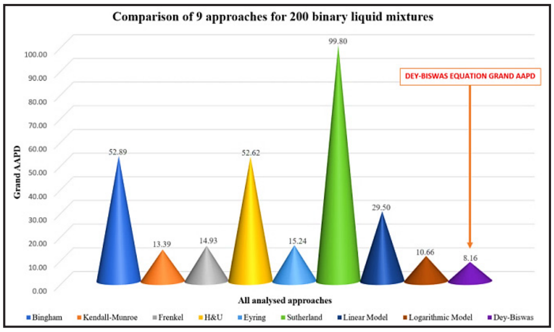


Figure 1. Comparative %APD values of Viscosity of ILs Binary system using various models

Figure 2. Comparison of grand %APD of 200 Binary system using various models

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TER2

About the use of the compressibility equation from Kirkwood-Buff theory to the study of electrolyte solutions with a concentration dependent dielectric constant (Adelman's theory)

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The compressibility equation from the Kirkwood-Buff theory of solutions [1,2] at the McMillan-Mayer (MM) level, when only the solute particles are considered, is applied to the study of electrolyte solutions. The models considered include a solute concentration-dependent dielectric constant as shown by the Adelman's theory of solutions [3], which does not assume the additivity of the potentials among the solute particles. In this approach, the non-additivity effects (NAE) are formally included in the treatment.

By using experimental data for the dielectric constant of alkali halides in water at 298.15 K and several models for the pair correlation functions, some information can be extracted about the influence on the short-range forces among the ions due to the non-additivity of the "effective potentials" employed. Finally, a comparison with equivalent results obtained using the osmotic pressure equation for the same pair correlation function models [4] will be given and discussed.

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TER3

Coupling an equation of state and the entropy scaling concept to correlatethe transport properties of pure fluids

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Transport properties are required for the design of process equipment and for the optimization of chemical or energy processes. In 1977, in his pioneering paper on the entropy scaling concept, Rosenfeld pointed out that there was a univariate dependence of transport properties on residual entropy if the transport property was made dimensionless after its division by a suitable *reference expression*. The entropy scaling concept was born and opened the door to the development of models for estimating transport properties from an equation of state. The latter can indeed straightforwardly be used to not only estimate the residual entropy of any given fluid at specified temperature and pressure but also the reference expression. In this study, two well-established equations of state (EoS): PC-SAFT and *tc*-PR (*translated-consistent* Peng-Robinson) were used to correlate the three transport properties (shear viscosities, thermal conductivities and self-diffusion coefficients). It was concluded that six component-dependent parameters were enough to correlate the dimensionless transport property with residual entropy.

The shear viscosities (η) were correlated as:

$$\left\{\begin{aligned} &\ln\left(\frac{\eta}{\eta_{ref}}\right)_{calc} = \left[\left(\frac{a_1 + a_2\tilde{s}_{Tv-res}}{1+e^{cX_{ES}}}\right) + \left(\frac{b_1 + b_2\tilde{s}_{Tv-res}}{1+e^{-cX_{ES}}}\right)\right] X_{ES} + \frac{d}{\tilde{s}^{c}_{Tv-res}} \\ &\text{with: } \eta_{ref} = \rho_N^{2/3}\sqrt{m_0 k_b T} \text{ and } X_{ES} = -\left(\frac{s_{Tv-res}}{s^{c}_{Tv-res}}\right) - \ln\left(\frac{s_{Tv-res}}{s^{c}_{Tv-res}}\right) \end{aligned}\right.$$

a_1, a_2, b_1, b_2, c and d are 6 component-dependent (and equation of state-dependent) parameters that have to be fitted over experimental data. $\tilde{s}_{\mathrm{Tv-res}}$ is the residual entropy divided by the gas constant in order to make it dimensionless. The reference viscosity is similar to the one proposed by Rosenfeld and involves the molecular density (ρ_N), the molecular mass (m_0), the Boltzmann constant k_b and the temperature. In this study, following Van der Waals' idea for reducing EoS variables when he proposed the corresponding-states theorem, it has been decided to scale the residual entropy using the corresponding critical value ($\tilde{s}^{\mathrm{c}}_{\mathrm{Tv-res}}$). It was thus possible to reduce dramatically the difference between quantitative predictions of Tv-residual entropy from one EoS to another but also from one component to another. The proposed equation is able to predict the viscosities in the whole fluid region (liquid, gas and supercritical states), which is a great advantage in comparison to most of the correlations available in the open literature that are specific to a physical state. Model parameters were fitted over a large database containing more than 100 000 pure-fluid experimental data associated with 142 chemical species. Whatever the equation of state (SAFT or cubic) an average deviation lower than 4% was obtained although many components were self-associating and polar.

The self-diffusion coefficients (D) were correlated with a similar approach. Once again, six component-dependent parameters were fitted on experimental data. 2400 experimental self-diffusion coefficients for 72 pure species (from dense liquid to supercritical gas) were found in the open literature. Similar accuracies in the correlation of such self-diffusion coefficients were obtained using either the PC-SAFT EoS (MAPE on D_{self} = 7.5%) or the *tc*-PR EoS (MAPE = 7.9%), with a slight advantage for the PC-SAFT model. The success of this approach is patent; indeed, the complex and difficult to model self-diffusion coefficients of water could be correlated with a deviation of 7% although the 2 equations of state did not embed an association term.

A similar strategy was applied to the thermal conductivities (λ). The approach was validated against a large experimental database and made it possible to conclude that using component-dependent parameters, the thermal conductivities of pure fluids could be accurately correlated with an average deviation of only 3% which is really promising.

TER4

Thermodynamics of the association of KCOSAN in different solvents

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The metallacarboranes, including the [cobalt(III) bis(1,2- dicarbollide)](1-) anion, which is called COSAN (Cobalt SANdwich) are a peculiar class of nanoions with an uneven structure and charge distribution (Figure 1) [1]. In this work, the association properties of potassium salts (KCOSAN) in methanol (MeOH), acetonitrile (MeCN) and dimethylsulfoxide (DMSO)were investigatedby molecular dynamicssimulations (MD) and electrical conductivity measurements at different temperatures. To corroborate the results of the simulations and conductivity measurements, we also measured the enthalpies of dilutionusing isothermal titration calorimetry (ITC).

MD simulations of COSAN and solvent molecules were performed using the GROMACS simulation package [2]. Using force field parameters and partial charges of COSAN atoms taken from the literature [3], all atom simulations were carried out at different concentrations of COSAN molecules and temperatures, providing the values of association constant(K_A). From the temperature-dependent Gibbs energy of ion-pair formation, the entropy, and the enthalpy of the association process are available.

The experimental values of the molar conductivities of KCOSAN solutions of dilute solutions were analysedusing theFuoss-Justice equation for associated electrolytes based on the low concentration chemical model [4] of electrolyte solutions yielding the limiting conductivities and K_A. All thermodynamic parameters were derived from the temperature dependence of K_A.

The enthalpies of dilution of solutions of KCOSAN in the above solvents were measured using the TAM IV calorimeter by titrating a concentrated solution of KCOSAN in a selected solvent into a cell containing the same solvent.

From MD simulations it was found thatthe K_A values of COSAN increase with the increasing temperature and in the order DMSO>MeOH>MeCN. The same trends were found for K_A and values obtained from experiment (Figure 1). The comparison between the thermodynamic data of ion-pair formation of KCOSAN in the studied solvents as obtained from MD, conductivity measurements and heat of dilution measurementswill be presented in detail to shed light on the interactions between KCOSAN and solvent molecules.

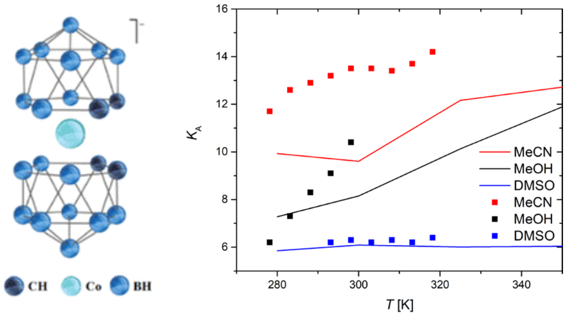

Figure 1. Temperature dependence of the associationconstant (K_A) of KCOSAN in different solvents. Linesrepresent resultsof MD simulations and symbols from experiments.

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TER5

Thermodynamic study of binary mixtures of aliphatic nitriles (acetonitrile, propionitrile, butyronitrile and acrylonitrile) with dimethylsulfoxide (or diethylsulfoxide)

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he study of thermodynamic properties such as volumetric and rheological properties, liquid-vapor phase equilibrium of solutions of nitrile group containing compounds (acetonitrile (AcN), propionitrile (PN), butyronitrile (BN) and acrylonitrile (AN)) with dimethyl- (DMSO) and diethylsulfoxide (DESO) is of great interest due to the fact that the components of these systems are capable to form both homo- and heteromolecular associates.

The volumetric, rheological and liquid-vapor phase equilibrium properties for nitrile-sulfoxide binary mixtures have been investigated by density, viscosity and saturated vapor pressure measurements at temperatures from (298.15 to 323.15) K [1,2].

Excess and partial molar thermodynamic quantities such as excess, V_m^E, and partial, $\overline{V}_i$, molar volumes, viscosity deviation, η^E, and excess molar Gibbs energies, ΔG^E, were calculated and described by the Redlich–Kister equation. Correlation parameters and standard deviations were calculated as well.

The obtained negative values of excess molar thermodynamic parameters (volumes (Figure 1), viscosities (Figure 2) and Gibbs energies) testify that very strong molecular interactions take place in mentioned binary systems mainly by dipole-dipole interaction between –S=O group of DMSO and –C≡N group of nitriles. Deviation of the behavior of these solutions from ideal is explained by the presence of competing homo- and hetero-molecular interactions, and by the effect of the length of the hydrocarbon chain of sulfoxides on the values of volumetric parameters.

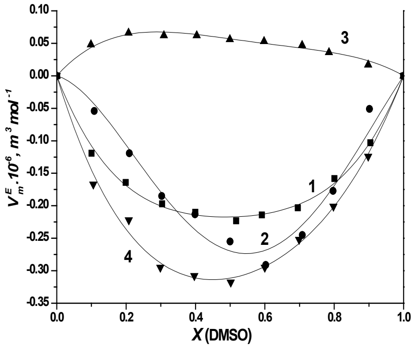

Figure 1. Excess molar volumes of (*1*) AcN–DMSO, (*2*) PN–DMSO, (*3*) BN–DMSO, and (*4*) AN–DMSO binary mixtures at 298.15 K.

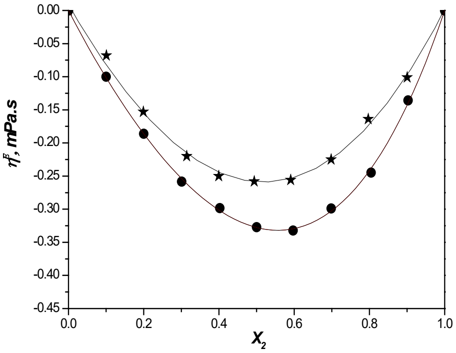

Figure 2. Viscosity deviations, η^E, of AcN(*1*)–DMSO(*2*) (●), and AcN(*1*)–DESO(*2*) (★) binary mixtures at 298.15 K.

Acknowledgements: This work was supported by the RA MES State Committee of Science, in the frames ofthe “Physical chemistry” research project.

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TER6

Physicochemical properties of aggressive acid solutions at elevated temperatures

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Aqueous solutions of chemically aggressive reagents such as sulfuric and nitric acids are among the most widely used anthropogenic chemicals on the planet. As might be expected due to their vast range of applications, the physicochemical properties of such strong acid solutions have received considerable attention. It is therefore quite surprising to discover that many of the key properties of these solutions, such as density and heat capacity, are virtually unknown above 100°C. Of the few available data, the most reliable source is the *International Critical Tables*, published almost 100 years ago in 1928. Of course, reliable measurements of such properties at elevated temperatures are a significant materials challenge. The purpose-built high-temperature vibrating-tube densimeter at Murdoch University employs all-Pt or Pt/Rh tubing, which is inert to acid attack under most conditions. More recently, we have fitted purpose-built tantalum cells and tubing to a commercial differential scanning calorimeter (SetaramC80) to enable us to measure the heat capacities of acid solutions. This talk will present and discuss our recent volumetric and heat capacity measurements on the aqueous solutions of sulfuric and nitric acids up to high concentrations at temperatures up to 200°C.

TER7

Volumetric properties of ionic aminated resorcin[4]arenes

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The volumetric properties of two ionic resorcinarenes, C-methylresorcin[4]arenetetramino-ethylated hydrochloride (TAE) and C-ethylresorcin[4] are tetraminomethylated hydrochloride (ETAM), have been determined in aqueous solutions and in DMSO. Density and speed of sound have been measured in a concentration range of 0.005 – 0.08 mol/kg for both compounds. The standard molar properties have been obtained at different temperatures (273.15 - 308.15 K) and the results are discussed in terms of solute-solvent and solute-solute interactions. The effect of substitution on the ionic moieties is studied and the results are compared with anionic resorcinarenes.

TER8

Atypical micellization of *closo*-dodecaborate-based dianionic surfactants in water

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Anionic boron cluster compounds, such as boranes, carboranes, and metallacarboranes, are unique class of inorganic nanoions with 3D cage-like structure, delocalized charge, and peculiar type of non-covalent interactions, in which they are involved [1]. Solution behavior of *closo*-dodecaborate dianion, typical example of charged borane clusters, is also complex, but it shares similarities with weakly hydrated bulky ions. It is very water soluble, however, micellization is improbable and only ion pairing is anticipated at elevated concentrations [2].

Based on the current knowledge about anionic boron cluster compounds, we designed a true amphiphilic compound soluble in water and showing classical head-and-tail structure by attachment of hydrophobic alkyl tails to *closo*-dodecaborate dianionic head. Our aim was to inspect the micellization behavior of novel surfactants with weakly hydrated "superchaotropic" head as well as impact of counterions on their self-assembly. The alkoxy tails were connected to *closo*-dodecaborate dianionic head via short di(oxyethylene) linker in the form of disodium salts (abbreviated B12-EO2-R).

From the experimental data, namely, surface tension measurements, isothermal titration calorimetry (ITC), dynamic light scattering (DLS), ^{1}H DOSY NMR and T_1 relaxation ^{23}Na NMR spectroscopy supported by all-atom MD simulations, we observed an atypical process of micellization of the novel surfactants in water. Despite introducing a relatively long non-polar alkyl chain these surfactants self-assemble in water to form relatively small micelles. Furthermore, the aggregation number is decreasing with the surfactant concentration as binding of sodium counterions increases. The extensive counterion binding is a key characteristic of the B12-EO2-Rmicelles (Figure 1). The concept of step-like micellization with singular critical micelle concentration was found inappropriate for these types of micelles.

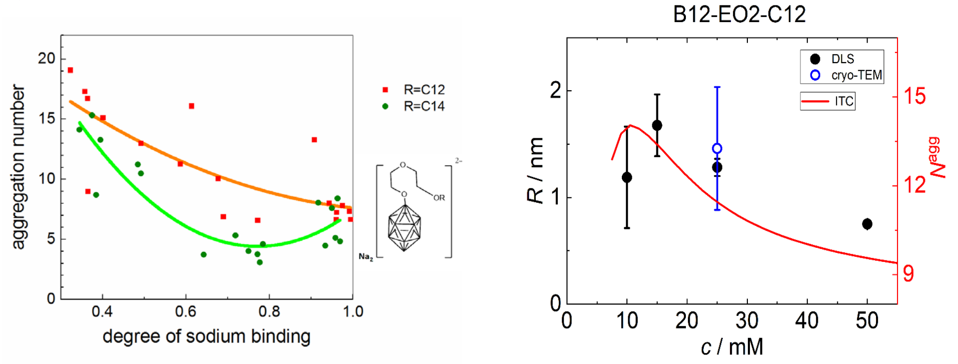

Figure 1. Interplay between aggregation number and degree of sodium binding as obtained by the applied model to the ITC experimental data and comparison of the obtained micelle size dependencies on concentration for B12-EO2-C12 by different methods.

Acknowledgements: The authors would like to acknowledge LA CEUS bilateral grant of the Czech Science Foundation 21-20008K and ARRS N1-0186.

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TER9

Activity coefficients of the system $\{y\mathrm{NaCl}+(1-y)\mathrm{NaH_2PO_4}\}$ (aq) at $T = 298.15$ K

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Zero-current cell-potential measurements were used to determine the solution activity coefficient in a ternary system $\{y\mathrm{NaCl} + (1-y)\mathrm{NaH_2PO_4}\}$(aq) at a temperature $T = 298.15$ K, in the total ionic strength range $I = (0.1-1.0)\ \mathrm{mol \cdot kg^{-1}}$. The Na–ISE | NaCl($m_{\mathrm{NaCl}}$), $\mathrm{Na_2HPO_4}$($m_{\mathrm{NaH_2PO_4}}$) | Ag | AgCl, cell was used where m_{NaCl} and $m_{\mathrm{NaH_2PO_4}}$ are the stoichiometric molalities of the NaCl and $\mathrm{NaH_2PO_4}$ electrolytes in the mixture. The ionic strength fraction of NaCl in the total ionic strength of the mixed solution was y=(0.199;0.310; 0.4101; 0.5051; 0.6090; 0.7776; 0.9037). The standard electrode potential of the electrode pair is $E°= 23.22737$ mV. The values of the mean ionic coefficients of NaCl in the mixed electrolyte solution, $\gamma_{\pm\mathrm{NaCl}}$, were estimated using Nerst equation (1):

$$E_{\mathrm{m}} = E° + k\ln\left[\gamma^2_{\pm\mathrm{NaCl}}\, m_{\mathrm{NaCl}}\,(m_{\mathrm{NaCl}} + m_{\mathrm{NaH_2PO_4}}) + K^{\mathrm{pot}}\gamma^2_{\pm\mathrm{NaH_2PO_4}}\, m_{\mathrm{NaH_2PO_4}}\,(m_{\mathrm{NaCl}} + m_{\mathrm{NaH_2PO_4}})\right] \tag{1}$$

where E_{m} is the electrode potential of the cell, $\gamma_{\pm\mathrm{NaH_2PO_4}}$ is mean ionic activity coefficient of $\mathrm{NaH_2PO_4}$ in the mixture and K^{pot} is selectivity coefficient having values less than $K^{\mathrm{pot}} < 10^{-4}$ and therefore, was neglected.

The ionic strength of the solution is $I = m_{\mathrm{NaCl}} + m_{\mathrm{NaH_2PO_4}}$ where as the ionic strength fraction of NaCl is: $y = m_{\mathrm{NaCl}}/I$. To generate a set of parameters for the system $\{y\mathrm{NaCl} + (1-y)\mathrm{NaH_2PO_4}\}$ (aq) that can be applied in the investigated range of mixed solution ionic strengths, Pitzer models [1] were used to fit the experimental data, represented in Figure 1. Parameter values for the pure electrolyte solutions of the second and third virial coefficients, B_{NaCl}, $B_{\mathrm{NaH_2PO_4}}$, $C^{\mathrm{T}}_{\mathrm{NaCl}}$, $C^{\mathrm{T}}_{\mathrm{NaH_2PO_4}}$, respectively, that aremixture components, were taken from literature [2,3]. The treatment of experimental data using Pitzer's model yieldedthe following values of the mixing parameters $\Theta_{\mathrm{Cl,H_2PO_4}} = -\ 0.710$and $\Psi_{\mathrm{Na,Cl,H_2PO_4}} = 0.1269$.The experimental and calculated values of the thermodynamic properties of the studied system were in excellent agreement, with standard deviation s.d. ($\gamma_\pm$NaCl) = 0.0041.

Pitzer's model is giving the following relation for the mean ionic activity coefficient of NaCl in the aqueous mixture $\{y\mathrm{NaCl} + (1-y)\mathrm{NaH_2PO_4}\}$ (aq):

$$\begin{aligned}\ln\ \gamma_{\pm\mathrm{NaCl}} &= F + I(1+y)\,B_{\mathrm{NaCl}} + I(1-y)\,B_{\mathrm{NaH_2PO_4}} + 0.5I\,(y + y^2 + 1 + yI)\,C^{\mathrm{T}}_{\mathrm{NaCl}} + 0.5I\,(1-y)\,(1+2I)\,C^{\mathrm{T}}_{\mathrm{NaH_2PO_4}}\\ &+ I(1-y)\,\Theta_{\mathrm{Cl,H_2PO_4}} + 0.5I^2\,(1-y^2)\,\Psi_{\mathrm{Na,Cl,H_2PO_4}} \end{aligned} \tag{2}$$

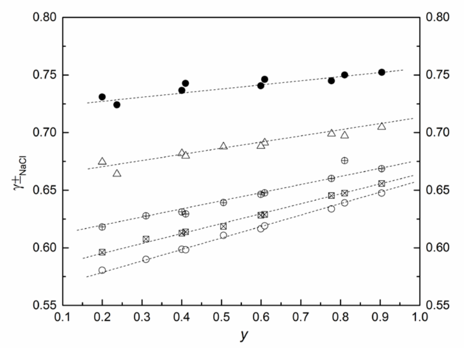

Figure 1. Experimental data on the mean ionic activity coefficient of NaCl, $\gamma_{\pm NaCl}$, vs ionic strength fraction of NaCl, y, in the system {yNaCl + (1−y) NaH_2PO_4} (aq) at T = 298.15 K for the following values of the ionic strength of the solution (mol · kg^{-1}): ○ – I ≈ 0.9; ☒ – I ≈ 0.7; ⊕ – I ≈ 0.5; Δ – I ≈ 0.3; ● – I ≈ 0.1.

Acknowledgements: The work was supported by the Ministry of Education, Science and Technical Development of the Republic of Serbia (Contract No. 451-03-68/2022-14/200287, 451-03-68/2022-14/200135, 451-03-68/2022-14/200053)

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TER10

Study of interaction between sulfonated resorcin[4]arenes and bovine serum albumin

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The sulfonated resorcin[4]arenes are macrocyclic compounds of great relevance in supramolecular chemistry because of their host-guest properties. The interaction between C-tetra (ethyl) sodium resorcin[4]arene sulfonate (Na_4EtRA) and C-tetra (propyl) sodium resorcin[4]arene sulfonate (Na_4PrRA) (Figure 1.) with bovine serum albumin (BSA) in aqueous solutions was studied at 298.15 K. The interaction between BSA and the ionic resorcin[4]arenes have been studied by means of spectroscopic, and calorimetric techniques. In addition, the effect of the macrocycles in the aggregation properties of BSA have been studied. The results were discussed considering the aggregation concentration (Cagg), excess surface concentration (Γ) and the Gibbs energy of aggregation and adsorption.

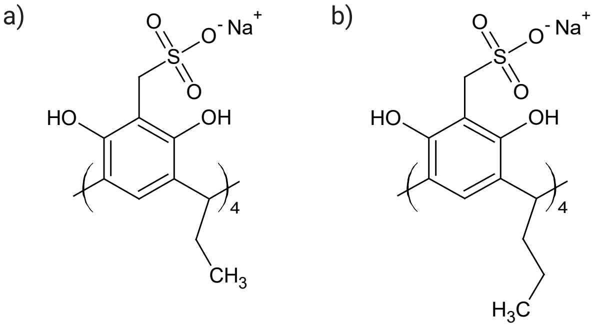

Figure 1. Structure of two ionic resorcinarenes, C-tetra (ethyl) sodium resorcin[4]arene sulfonate (Na_4EtRA) b) C-tetra (propyl) sodium resorcin[4]arene sulfonate (Na_4PrRA).

FLU1

The inhomogeneous locale structure of water at ambient and supercritical conditions: Voronoi polyhedral and density-based spatial clustering analysis

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Supercritical water has several applications in various fields, including: energy generation, Environment, Materials and Food processing, nanotechnology and biotechnology. Therefore the supercritical water was investigated using an array of spectroscopic technics (X-Ray [1], Neutrons scattering, vibration spectroscopy and NMR) and molecular dynamics simulation [2]. The responses to questions such as whether the locale structure is homogeneous or inhomogeneous or to which extent the hydrogen bond tetrahedral locale distribution of water is distorted are still controversial [3]. The purpose of this contribution is to quantify the structural changes occurring in the locale structure of water along the coexistence curves at different isobars. For this purpose statistical distributions of observables, such as the nearest neighbors radial and their corresponding interactions energies, the trigonal, tetrahedral and pentagonal distributions of water as well as the Voronoir polyhedra [4] and the density-based spatial clustering distributions [5], were calculated and their dependence on the thermodynamical conditions were investigated.

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FLU2

Verificationof the structure-making/breaking concept of ion solvation from the structure of aqueous MCl (M = Li, Na, K, Rb, and Cs) solutions in the gigapascal pressure range

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Ion solvation and association and water structure under pressure at the molecular level are essential issues in fundamental science of ion solvation and various applied sciences, such as the geological processes in the Earth's upper mantle, pressure-induced protein denaturation in chemical biology and biotechnology, and salty ice formation in planetary science. For example, in the Earth's upper mantle in the gigapascal (GPa) pressure range, the water interacts with rocks to form fluids enriched in dissolved salts, which reduces the frictions between continental plates to induce the earthquake and develops the magmatic systems to the eruption of a volcano. However, information on ion solvation and water structure in the GPa pressure range at the molecular level is minimal because of experimental difficulties in obtaining reliable diffraction data at higher pressures.

We have succeeded in measuring water and various electrolyte solutions in the GPa pressure range by x-ray and neutron diffraction experiments at synchrotron x-ray facilitySPring-8and thepulsed neutron source J-PARC MLF, respectively. Both X-ray and neutron interference functions are subjected to an empirical potential structure refinement modeling to extract partial pair correlation functions, coordination number distributions, angle distribution (orientational correlation), and spatial density functions (3D structure).

For a series of alkaline chloride solutions from LiCl to CsCl, the solvation behavior of structure making ions (Li^+ and Na^+ [1,2]) and structure breaking ions (Rb^+ [3] and Cl^- [1-3]) shows a marked contrast in the GPa pressure range. The solvation structures of Li^+ and Na^+ are retained in the GPa pressure range as those under ambient condition, although the solvation structure is more distorted. On the contrary, the solvation shells of the structure breaking ions, such as K^+, Rb^+, Cs^+, and Cl^- evolve and extendin the GPa pressure range. This apparent change of the solvation shell in the solutions with structure breaking ions are caused by a drastic change of water structure from a tetrahedral network under ambient condition to random closed packing in a simple liquid, such as liquid Ne. It is interesting to note that the intermolecular O-H hydrogen bonds never be broken down even at 4 GPa and 523 K, although they are weakened and distorted.

Acknowledgements: The works were partially supported by KAKENHI (No. 23550028, 26288073, 19K05551). The X-ray experiments were performed under the Shared Facility Use Program of Japan Atomic Energy Agency with the approval of the Japan Synchrotron Radiation Research (No. 2012B3623, 2013A3614). The neutron experiments were performed under a user program (No. 2014A0119, 2017B0179, 2018B0248, 2019B0277).

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P1

The effect of pH value on the partitioning of technology-critical elements in aqueous biphasic systems based on a deep eutectic solvent

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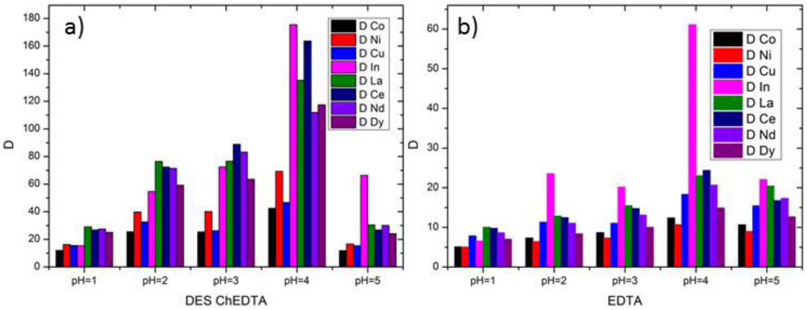
Technology-critical elements (TCEs) are crucial to the growth of emerging technologies, including renewable energy, electronics, aerospace, etc. TCEs are increasingly being released into the environment, necessitating a better understanding of their mobility, reactivity, and chemical transformations. This study aims to investigate partitioning of the targeted TCEs in aqueous biphasyc systems based on either ethylenediaminetetraacetic acid (EDTA) or choline chloride EDTA deep eutectic solvent (2ChCl : EDTA) and polymer (PPG400). The effect of the initial sollution pH on the partitioning of the TCEs is presented in Fig. 1. Significantly higher partitionig of TCE s was obatined using ABS {$(ChCl)_2$: EDTA + PPG400 + H_2O} comparing of ABS based on EDTA. The influence of pH was also more pronaunced in ABS based on DES. The highest partioning (D > 160) was obtaned for In and Ce at pH = 4.0. Additionally, the results show the good ability of proposed green extraction methods for separation of some TCEs e.g. separation factor between In and Co at pH = 4 is 5.



Figures 1a and 1b. Partitioning coefficients (D) of the studied TCEs in ABSs (a) {2ChCl : EDTA + PPG400 + H_2O}, and (b) {EDTA + PPG400 + H_2O} at 296.16 K and atmospheric pressure at different pH values.

Acknowledgements: This work was supported by the Ministry of Science and Technological Development of the Republic of Serbia (contract numbers: 451-03-47/2023-01/200017).

P2

Description of ionic liquids with simple models

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We developed (coarse-grained) models to study system of ionic liquids and water. Core-softened discs have been used for water and screened electrostatic potential was used to describe interactions between ions. To represent characteristic large cations we combined multiple discs into one particle. The study was done with Monte Carlo computer simulation in NpT ensemble. We observed internal energy, density, structure and heat capacity of systems.

Since only Lennard-Jones potential is used to describe ion – water interactions the ions do not get hydrated. Consequently, system is not homogeneous and we get density anomalies. With larger single disc same charge ions Lennard-Jones attraction can exceed screened electrostatic repulsion, thus some interaction parameters have to be modified.

P3

Partitioning of metals by green aqueous biphasic systems based on functionalized ionic liquid and deep eutectic solvent

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Electronic waste (e-waste) is one of the fastest-growing waste streams in the world due to the rapid development of electronic devices, their successive obsolescence, and disposal. Depending on the size of the electronic device, the value of the metals in waste devices can range from 80% of the total value and that is why it is important to find environmentally friendly solutions for recycling those metals. An aqueous biphasic system (ABS) is a green extraction method that combines water-soluble substances in a specified concentration range to form two immiscible phases. Ionic liquids (ILs) and deep eutectic solvents (DES) are superior green solvents used in ABS as phase-forming chemicals. In this study as salting-out agents for building ABS have been used: IL choline DTPA ($[Ch]_3[DTPA]$, DES ($(ChCl)_3$:DTPA) and DTPA are compared to separate metals from ABSs. ABSs were created by combining IL/DES/DTPA and polypropylene glycol 400 (PPG400). The targeted ABSs have been applied for the extraction of metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, In^{3+}, La^{3+}, Ce^{3+}, Nd^{3+} and Dy^{3+}). Metal complexes are formed with DTPA. The choline chloride from DES and cation from the IL, on the other hand, are responsible for ABS formation and complex separation. The ICP-OES method was used to measure the concentrations of all metals. Distribution coefficients (D) higher than 1, indicate that the targeted metals preferentially migrate into the IL or DES-rich phases than in the PEG-rich phase.

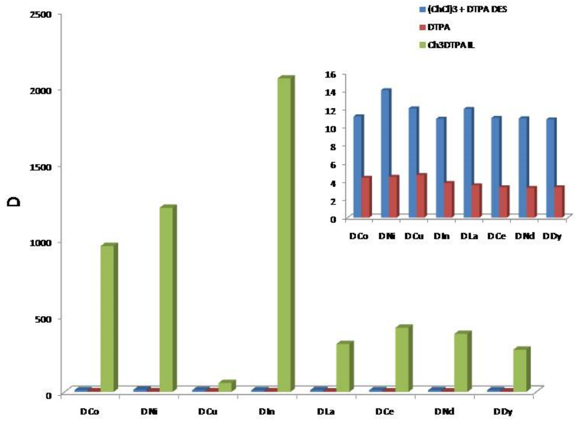

Figure 1. Distribution coefficients of the targeted elements in ABS-s based on IL/ DES/ DTPA and PPG 400 at 296.16 K and atmospheric pressure. Mixture composition: 20% IL/DES/DTPA and 30% PPG 400.

The highest D (D_{In} = 2058) was obtained for In^{3+} in ABS based on IL. Generally, significantly lower D was obtained by applying ABS based on DES and DTPA compared to ABS based on IL. Namely, D_{In} in the case of ABS based on DES and DTPA are 200 and 500 times lower compared to D_{In} obtained with ABS based on IL. The highest extraction selectivity value was achieved between indium and copper where the selectivity value is S = 35. The obtained results show the significant superiority of IL-based ABS for the extraction of In^{3+}, Co^{2+} and Ni^{2+} compared to other tested metals and ABS systems.

Acknowledgements: This work was supported by the Ministry of Science and Technological Development of the Republic of Serbia (contract numbers: 451-03-47/2023-01/200017).

P4

Thermal and electrochemical properties of ionic liquids bearing allyl group with sulfonate-based anions

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Ionic liquids (ILs) consist of cations and anions, have generally melting temperature below 100°C and remain liquid at wide temperature range. Their attractiveness to the ever-expanding research areas is dictated by low volatility of those compounds, non-flammability, high chemical inertness, low vapor pressure, high ionic conductivity and thermal stability [1]. Compounds having an unsaturated group in their structure are a special group of ionic liquids. The introduction of a group with terminal double bond, e.g., allyl [2], 4-vinylbenzyl [3] makes them multifunctional ILs, with the possibility of further transformations. For a special group of anions, we can consider sulfonate-based anions, such as methylsulfate ($MeSO_4$), methanesulfonate ($MeSO_3$), triflate (OTf) and tosylate (OTs). In our previous work, we demonstrated simple and extremely effective method of synthesis of ILs with abovementioned anions [4]. The main advantage of the proposed metathesis reaction is ability to obtain ionic liquids with very high purities, with non or negligible halide impurities. Furthermore, described method allows to obtain compounds with no restrictions to the cation structure in comparison to the widely used synthetic route, where the tertiary amine undergoes quaternization reaction with methylated ester of sulfonate-based acid. Moreover, ionic liquids have been found to be a new wave of hardeners for epoxy resin polymerization. the mixture of ionic liquid/epoxy resin can be stored at room temperature for a long time because the polymerization process starts only at elevated temperature. Additionally, the quantity of IL needed for successful hardening process is much lower than abovementioned compounds, at around 5% weight (or in many cases even less).

Sulfonate-based ionic liquids with allyl-containing cations have been previously obtained by us, however the present study aims to investigate the thermal, electrochemical and curing properties of these ILs. To determine the temperature range, in which ionic liquid maintains liquid state, thermal properties must be examined using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Melting, cold crystallization and glass transition temperatures have been discussed, as well as decomposition temperatures for imidazolium and pyridinium-based ionic liquids. The conductivity and electrochemical stability ranges have been studied to investigate their potential applicability as electrolytes. Finally, the potential of triflate-based ILs as polymerization initiators for epoxy resins has been proved [5].

Acknowledgements: This work was supported by the National Science Centre (Poland), project OPUS 18 grant number 2019/35/B/ST8/03736 and project SONATA BIS 7 grant number 2017/26/E/ST8/01059.

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P5

Synergism in solvent extraction and separation of 4f-elements in ionic liquids: acidic-basic ligands couple

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Study of the liquid-liquid extraction of Eu(III) ion with a series of chelating ligands by the well-known method of slope analysis and determination of the process parameters are presented employing three ionic liquids, ($[C_1C_n\text{im}^+]/[C_1C_4\text{pyr}^+][Tf_2N^-]$, n = 4, 10) and $CHCl_3$ as diluents. Study of the liquid-liquid extraction with a chelating compound, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (HP), 4-benzoyl-3-phenyl-5-isoxazolone (HPBI) as well as by the β-diketone 2-thenoyltrifluoroacetone (HTTA) alone and in combination with two synergistic agents d,l-hexamethylpropyleneamine oxime (HM-PAO) and its bis-imine precursor (pre-HM-PAO) and determination of the process parameters are presented. The term synergism in solvent extraction describes the co-operative effect of two extractants where the distribution ratio for the combination is greater than the sum of individual *D* ratios (measured under comparable conditions) [1,2]. The enhancement in the synergistic solvent extraction of metallic species may depends on the nature and strength of the possible interaction between the two ligands. The prediction of the extraction systems properties remains a difficult task due to a lack of knowledge about the behaviour of the acidic/neutral or acidic/cationic couples [3]. The interaction between the two extractants (acidic/neutral) in deuterochloroform has been studied by ^1H, ^{13}C, ^{19}F spectra and ^1H-^1H NOESY experiments. Several conclusions are given highlighting the role of the ionic diluent in complexation processes and selectivity with an employment of the chelating agent HL for various metal s-, p-, d- and f-cations in periodic table. The objective is to optimize a synergistic system for RE extraction, based on the HM-PAO and β-diketone/isoxazolone/pyrazolone partnership. As detailed above, enhancements of extraction efficiencies have been obtained either by use of basic synergistic agents, such as HM-PAO and/or by use of pre-HM-PAO. The competitive solvent extraction test of almost 25 metal ions as well as nearly 18 f-ions by the chelating ligand HL diluted in ILs and $CHCl^3$ has also been conducted in order to evaluate the switchable hydrophilic diluent, ethylene glycol as a more polar liquid phase.

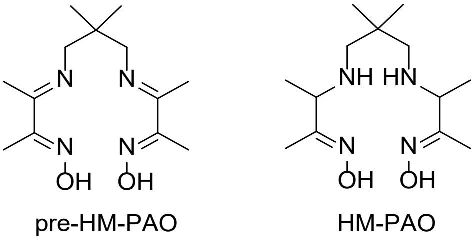

Figure 1. Structural formula.

Acknowledgements: The research leading to those results received funding from the Bulgarian National Science Fund: Grant Agreement № КП-06-Н69/5(2022), “Green twist to synergistic solvent extraction and separation of rare earth metals”.

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P6

Optical fiber grating-prism fabrication by imprint patterning of ionic-liquid-based resist

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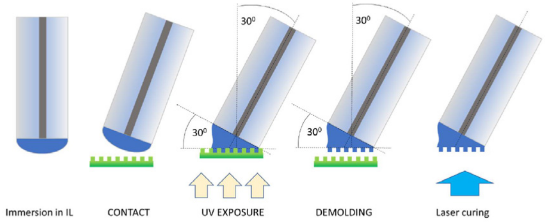
Ionic liquids (ILs) have always been of keen interest in the scientific community. Recently, they became interesting materials for electron beam patterning and optical components fabrication. Since ILs possess unique properties, valuable for applications mentioned above, such as low vapor pressure, they are the main focus of presented research. They can also be implemented in the applications without the need of organic solvents, which is a great advantage over any other materials used for optical components [1,2]. Nanoimprint lithography (NIL) is one of the best methods for obtaining fine structures at low cost.

Herein we would like to present the method of microstructure fabrication on the tip of the optical fiber using a UV soft-imprint process of polymerizable ionic liquid-based optical resist [3]. Designed and synthesized specific ionic liquid, bearing two UV-sensitive vinylbenzylconstituted resist base material. The fabrication process itself was solvent-less, except of cases where organic salt was solid under experiment conditions. In those cases non-toxic propylene glycol was used as an auxiliary. The impact of propylene glycol amount and exposure dose on optical and mechanical properties was investigated.

The final procedure of the UV imprint on the optical fiber tip was developed, including the moldpreparation, setup building, UV exposure and post-laser cure. As the IL-containing vinylbenzylgroups can also be polymerized by the radical reaction of double bonds by thermal treatment [4], the influence of BHT polymerization inhibitor was verified. As a result, we present the fabricated diffraction gratings and the optical fiber spectrometer component – GRISM (grating-prism), which allows to obtain a dispersion spectrum at the output of an optical in line with the optical fiber long axis, as the main component in an optical fiber spectrometer. The process is very simple due to the fact that its optimization already starts in the process of molecule design, which is part of the trend of sustainable technologies. The final material can be designed by the tailoring of the anion and/or cation of a monomeric ionic liquid, which in turn can lead to a more efficient fabrication procedure and additional functionalities of the final structure.



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P7

New ionic derivatives of benzotiadiazole with biostimulation activity

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In view of the ever-increasing demand for food and the limitation of the use of toxic pesticides, the search for new agents supporting plant development becomes a necessity. Biostimulants are one of the latest achievements of science in the field of plant cultivation. The European Union, recognizing the potential of biostimulants, introduced a new Regulation on fertilizing products, which also regulates issues related to biostimulants. It expands the definition of fertilising products to include new categories, including biostimulants. The purpose of this regulation is, inter alia, to make available on the market products that until now have not been covered by uniform rules. This applies to biostimulants.

The vast majority of biostimulants are obtained from natural raw materials with significant environmental safety for their use, but not always well-defined and confirmed biological activity. On the other hand, there are also biostimulants of chemical origin.

Typically in agrochemistry, the neutral form of a pure active substance is selected for agricultural tests. However, such a neutral form often suffers from toxicity, low solubility and a variety of factors which affect bioavailability. The use of substances in ionic form has many advantages, such as higher solubility, thermal and pH stability, lower toxicity and tunable biological activity [1].

The results show the possibilities of using new and designed chemicals in agriculture, which are derivatives of benzothiadiazole acid. Our research shows that such substances have activity related to the biostimulation of wheat growth and development. Additionally, these active substances have been tested for their possible influence on selected environmental aspects [2].

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P8

Hexamethylenetetramine-based ionic liquids as an active ingredient in latent curing formulations with ethylene glycol for DGEBA

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Ionic liquids (ILs) are chemical compounds with an ionic structure, consisting of a cation and an anion and having several specific properties. The cation of the ionic liquid is usually of organic origin and has a varied structure. On the other hand, anions of ionic liquids can be both organic and inorganic, and their nature significantly affects the properties of the entire compound [1]. The most important feature of this group of compounds is undoubtedly an extremely wide range of applications, in which the following should be distinguished: (i) dissolution and processing of biomass [2], (ii) catalytic reactions [3], (iii) active ingredients in pharmaceutical preparations [4] or (iv) design of polymerizable monomers intended for modern material solutions5.

The aim of this work was to provide new solution in the field of multifunctional initiating systems for the polymerization of epoxy resins. Here we present the preparation of new ionic liquids based on hexamethylenetetramine (HMTA) with bis(trifluoromethanesulfonyl)imide and dicyanamide anion (Fig. 1), which were characterized in detail in terms of their purity (Ion Chromatography) and thermal properties (Differential Scanning Calorimetry), as well as stability. The obtained substances were used to develop curing systems with ethylene glycol, which were successfully tested for their application with bisphenol A diglycidyl ether molecule (DGEBA) [1].

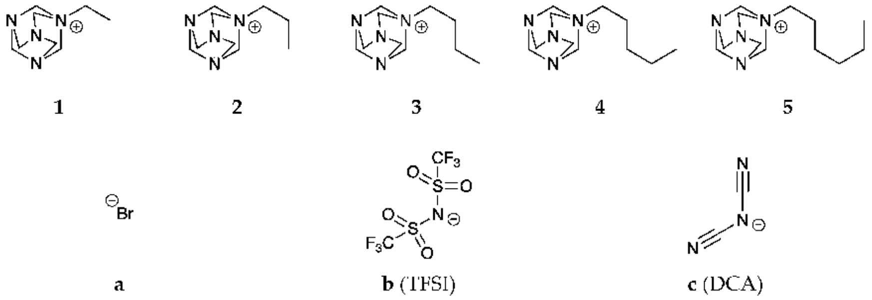

Figure 1. Chemical strucutres of synthesised HMTA-based ionic liquids.

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P9

Coexistence of ordered and disorderedphases in phosphonium-based ionic liquids

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When a liquid is rapidly cooled faster as compared with its crystallization rate, the molecular arrangement remains disordered while molecular motion freezes, to be an amorphous state. Few molecular liquids such as water and triphenyl phosphite(TPP) have different amorphous states, or liquid-liquid transitions, that appear depending on the thermal history before cooling [1,2].The coexistence of microcrystals and liquidis always observed on TPP when such a liquid-liquid phase transition is observed. Several studies on trihexyltetradecylphosphonium-based ionic liquids recently implied the liquid-liquid phase transition [3]. However, the coexistence of liquid and crystal has not even been considered. In this study, we study the alkyltributyllphosphoniumbromide ([P444,*n*][Br] (*n* = 6, 8, 12)) of phosphonium-based ionic liquids by DTA and XRD to investigate if they showany coexistence ofliquid and crystal depending on the thermal history.

The samples used were [P444, *n*] [Br] (*n* = 6, 8, 12) (Tokyo Chemical Industry, with purities of 98.8%, 100.7%, and 98.7%, respectively) as shown in Figure. 1. The samples were dried under vacuum for at least 48 hours at room temperature to remove any moisture and then sealed in a glass cell with helium for measurement. Karl-Fischer titration determined the water contents to be 1.3645%, 1.6757%, and 0.6686%, which are relatively higher than the typical hydrophobic ionic liquid because of their high hydrophilicity.

[Results and Discussion] During the cooling process of [P444.6][Br], an exothermic effect was observed at 242 K, indicating a crystallization or an ordering to amesophase from the liquid state (Figure 2). On further cooling, a baseline shift was observed at 198 K due to a glass transition. Despite the ordering at 242 K, the glass transition implies that the ordered phaseincludes a kind of molecular disorder to undergo a freezing-in process. In other words, [P444,6][Br] is in the partially ordered phase. Considering the previous studies on similar systems such as [C_8mim][BF_4] or [C_8mim][AzoO] [4], a phase coexistence of liquid and ordered phase at the lower temperature. In addition, an endothermic peak was simultaneously observed accompanied by the glass transition phenomenon at 198 K while nopeak was observed if the sample was annealed at 218 K. This endothermic effect might stem from a structural change in the partially ordered phase or the disordered phase. In the case of [P444,8][Br], no order is observed upon cooling and the order appears upon heating. Notably, a mesophase is induced by annealing for [P444,8][Br].In the case of [P444,12][Br], which has the longest alkyl chain in this study, ordering occurs without a disordered phase. The results of phase behavior with and without annealing are also shown in Table 1. The effect of chain length is not simply understood. Combining the results of XRD, we will discuss the possible structure in the coexistence state.

Table 1. Phase behavior of [P444, *n*][Br].

Sample	No annealing	With annealing
P444.6	Cry-Amorphous (With Tg peak)	Cry-Amorphous (No Tg peak)
P444.8	Amorphous	Cry-meso
P444.12	Ordered phase	-----

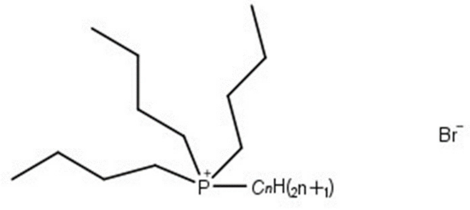

Figure 1. The structures of [P444.*n*][Br] (*n* = 6,8,12)

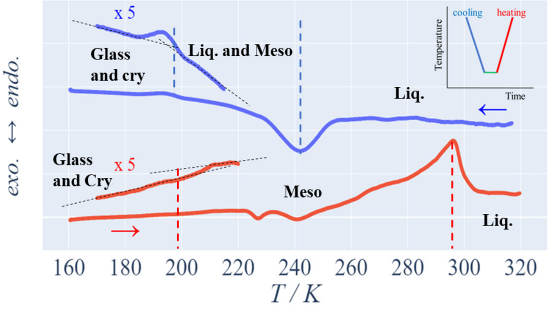

Figure 2. DTA curves of [P444.6][Br] at the scanning rate of 3 K min^{-1}.

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P10

Application of pyridinium-based ionic liquids as carbon paste electrode modifiers for trace-level voltammetric determination of benzophenone-3

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Recently, ionic liquids (ILs) have been extensively used in the design of electrochemical sensors. The properties of ILs can be easily adjusted for specific applications by changing the diverse cations and anions. Their specific features including possible catalytic activity, low toxicity, electrochemical stability and excellent conductivity make them suitable for electrochemical applications. Various electrochemical sensors based on ILs have been successfully fabricated, where ILs are used as electrolytes or electrode modifiers [1,2]. One type of working electrode that can be easily modified by ILs is the carbon paste electrode (CPE). Generally, CPE is made of conductive carbon (graphite) powder and a non-conductive liquid binder (e.g. paraffin oil). In order to decrease the detection limit, enhance the signal intensity and improve the analytical performance, CPEs are chemically modified by adding appropriate components either to the bulk or to the electrode surface, and liquid modifiers as ILs are very popular in this field [2-5].

In this work, CPE was bulk-modified with previously synthesized pyridinium-based ILs (1-butyl-3-methylpyridinium chloride ([N-C_4-$3C_1$Py]Cl) or 1-ethoxyethyl-3-methylpyridinium chloride ([N-C_2OC_2-$3C_1$Py]Cl) to prepare sensitive and reliable working electrode for trace-level voltammetric determination of organic UV filter benzophenone-3 (BP-3). [N-C_4-$3C_1$Py]Cl-CPE showed more favorable interactions with the target analyte. BP-3 redox behavior at [N-C_4-$3C_1$Py]Cl-CPE was studied by cyclic voltammetry indicating that the redox reaction is irreversible and adsorption controlled. After optimization steps concerning the selection of working electrode, pH of supporting electrolyte and amount of CPE modifier, the [N-C_4-$3C_1$Py]Cl-CPE in combination with square-wave adsorptive stripping voltammetry (SW-AdSV) was used for anodic BP-3 determination. At pH 3.0, a linear response for BP-3 was obtained in the concentration range of 0.05 to 0.89 μg mL^{-1}, the relative standard deviation did not exceed 1.5%, while achieved detection limit in the model solution was 0.015 μg mL^{-1}. The developed SW-AdSV method was successfully applied for the determination of BP-3 in swimming pool water sample, with good repeatability and recovery. The obtained results demonstrate an excellent potential of the IL-CPEs, especially of the [N-C_4-$3C_1$Py]Cl-CPE, for determining selected UV filter in various real samples.

Acknowledgements: The authors gratefully acknowledge the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-47/2023-01/200125) and the Provincial Secretariat for Higher Education and Scientific Research (Grant No. 142-451-3167/2020-03).

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P11

Behavior of water in 1-methyl-3-alkylimidazolium carboxylate RTIL-water systems

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Water is a unique and ubiquitous solvent which occurs in various solutions, mixtures, and materials. Its behavior is highly dependent on conditions and its environment, mainly due to its strong orientation-dependent hydrogen bonding and intermolecular interactions. Its interactions with ions have been studied extensively in a wide range of concentrations [1], however low water concentrations are of particular interest (water – in - salt). In this context, room-temperature ionic liquids (RTILs) provide an excellent opportunity to study in detail the interactions of water in this concentration range.

Various simulations and experimental studies have indicated that the interactions of RTILs with molecular solvents show a great deal of complexity, including the contributions of long-range electrostatic interactions in pure RTILs, hydrogen bonding with the molecular solvent, as well as within the cation-anion pair itself, which all appear to affect the miscibility with the solvent of interest [2]. The choice of anion thus appears to be of significant importance when considering interactions with molecular solvents, such as water [2,3].

Imidazolium-based RTILs were synthesized from 1-methylimidazole in a three-step procedure using a 1-haloalkane with the appropriate chain length (x = 2,4), ion exchange resin (AMBERLITE IRN78) and carboxylic acids (y =2,4,6,8) to prepare 6 compounds of the type $[C_xMIm][C_{y-1}H_{2y-1}COO]$, allowing comparison between different alkyl chain lengths in the anion and cation. Water was titrated in small aliquots into the prepared RTILs in the TAM IV calorimeter (TA Instruments, New Castle, USA) where the heat flow was measured and integrated to obtain the partial excess molar enthalpy the mixture as a function of composition in the titration cell.

The experimental results were then fitted to Redlich-Kister polynomials to allow the calculation of the enthalpies of mixing for a given system [4]. A model for the behavior of water in a confined space of ions in imidazolium-based RTILs will be proposed based on the experimental results[2,5].

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P12

Scanning transitiometry as a tool to measure the energies of intrusion and extrusion of liquids into/from porous materials

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Scanning transitiometry is an innovation built upon *PVT* high-pressure calorimetry, which was constructed to measure the heat effects associated with variations of the state variables (pressure, volume, temperature). The addition of a simultaneous recording of the mechanical variable with the thermal variable permitsthe creation of this new technique: *scanning transitiometry* [1].

That technique allows a user to measure, during one experiment, the two contributions - thermal and mechanical as related to the thermodynamic potential change during a transition, performed under precisely defined and controlled thermodynamic conditions. An important advantage of this type of instrument is the possibility to record the changes occurring in the investigated sample as a result of changes in pressure. Then by making use of the respective Maxwell relations, one readily obtains the main thermophysical properties of investigated substances under elevated pressure [2].

The aim of the poster is to present the technique and the recent contributions it has made to current and future projects in energy storage in high-pressure and high-temperature conditions with simple and complex systems. It has been demonstrated that hydrophobic nanoporousmaterials can be used for thermal-to-mechanical energy conversion when coupled with water. In the process where a non-wetting liquid, for example water, is forced to enter a porous material by applying hydrostatic pressure intrusion pressure P_{int} at which non-wetting liquid wets the pore and corresponding volume reduction ΔV of the system (which is defined by the volume of the pores V_{pore}) define the accumulated mechanical energy $W_{int} = P \cdot \Delta V = P_{int} \cdot V_{pore}$. Upon decompression, “drying” of the pore may occur at certain extrusion pressure and the system recovers its initial volume due to non-wetting liquid expulsion (extrusion) from the pore releasing the mechanical energy as a work of extrusion $W_{ext} = P_{ext} \cdot V_{pore}$. We will demonstrate the usefulness of *PV* isotherms and heat effects recorded by the scanning transitiometer for research on the forced intrusion of a nonwetting liquids into nanopores can be used for energy storage (molecular springs) or dissipation (shock absorbers/bumpers).

In addition, through the combination of the scanning transistiometry and MD computer simulations we have shown the role of the topology of the pore system on the intrusion/extrusion of water into/from porous materials. This secondary subnanometer porosity promotes the wetting/drying of the materials, as shown in the examples of zeolites and MOFs [3,4].

Acknowledgements: We are grateful for the financial support based on Decision No.2018/31/B/ST8/00599 from the National Science Centre (Poland).

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P13

Interaction of poly(α-alkyl carboxylic acids) with titanium dioxide nanoparticles in aqueous suspension

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Titanium dioxide (TiO_2) nanoparticles are amongst the most widely used metal oxide nanoparticles, with application in many fields of industry. In aqueous solution, nanoparticles tend to aggregate, which is why dispersants are often added to suspension to ensure its stability [1]. Understanding the interaction of dispersants with nanoparticle surface is important for tailoring suspension properties for different applications.

Poly(α-alkyl carboxylic acids) are a family of synthetic weak polyelectrolytes that are known to stabilize nanoparticle suspension through adsorption to nanoparticle surface [2]. With elongation of the alkyl group bonded to the α-carbon in the repeating unit, hydrophobicity of the chain and the pK_a of its COOH groups is increased, affecting solubility and conformational properties [3]. In addition to that, the stereochemistry of the chain also has an important role in solution behaviour [4].

In this study we employed a combined experimental and *in silico* approach. We conducted zeta potential and dynamic light scattering measurements of TiO_2 suspensions with added poly(α-alkyl carboxylic acids). We complemented that with molecular dynamics (MD) and Monte Carlo (MC) computer simulations of interaction between nanoparticle surface and polyacids. We used poly(acrylic) (aPAA), poly(methacrylic) (aPMA) and poly(ethacrylic) (aPEA) acid in atactic variety, as well as PMA in isotactic variety (iPMA). Results show that hydrophobicity of the polyacid plays an important role in suspension stabilization, which is most notable in the shift of isoelectric point (IEP) with addition of polyacid in regard to plain nanoparticles (Figure 1). More hydrophobic polyacids cause a smaller shift in IEP. Role of stereochemistry is less noticeable, except at low pH values, where iPMA is not soluble and greatly destabilizes the suspension.

With the use of MD simulations we found that the length of the alkyl group in the repeating units affects the ability of the polyacid to form hydrogen bonds with nanoparticle surface, making more hydrophobic polyacids less likely to adsorb. MC simulations showed pK_a values of COOH groups also play an important role in adsorption.

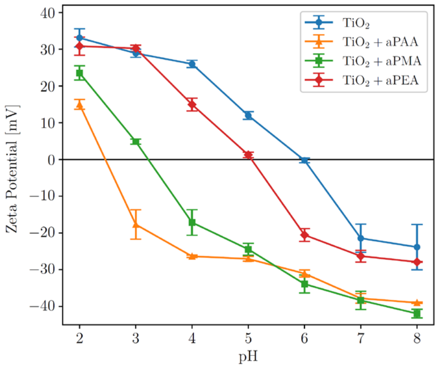

Figure 1. Dependence of zeta potential on the pH value of nanoparticle suspensions with and without added poly(α-alkyl carboxylic acids).

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P14

Supramolecular system based on sodium carboxymethyl cellulose and viologen calixarene for facile loading of hydrophobic food bioactive compounds

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The knowledge of colloidal and supramolecular chemistry can be combined to design non-covalent complexes between hydrophilic and hydrophobic components, which are called supramolecular amphiphiles or supra-amphiphiles [1]. Supra-amphiphilic systems are attracting great attention due to the possibility of fabricating various colloidal nanostructures through the spontaneous self-assembly of hydrophilic and hydrophobic building blocks involving both components. In addition, the non-covalent nature of the formation of supramolecular interactions in these systems ensures their effective response to various stimuli and triggers. These unique characteristics could make supra-amphiphiles promising smart systems for the encapsulation of biologically active compounds.The use of biologically active compounds is often limited due to their poor aqueous solubility, which generally reduces their bioavailability and useful efficacy. In this regard, a wide search is currently underway for colloidal systems capable of encapsulating these compounds. In the creation of colloidal systems, long-chain molecules of surfactants and polymers are mainly used, which in an individual state do not always aggregate into homogeneous and stable nanoparticles.

In the present work, three-dimensional calixarene was used for the first time to order polymeric molecules of the sodium salt of carboxymethyl cellulose. A set of physicochemical methods demonstrated the spontaneous formation of spherical nanoparticles by non-covalent self-assembly between these macrocycle and polymer, and the formed nanoparticles were able to encapsulate hydrophobic quercetin and oleic acid. Interestingly, in the case of using quercetin as a solubilisate, a significantly greater amount of this flavonoid binds in a mixed system with a slight excess of one of the components than in pure solutions of macrocycle and polymer. Such a synergistic effect in the binding of lipophilic bioactive substances was first revealed for aggregates based on supramolecular amphiphiles. The data obtained demonstrated the versatility of these aggregates as a delivery vehicle for lipophilic biologically active molecules; and these particles and component size optimization have the potential for a wide range of therapeutic applications.

Acknowledgements: This work was supported by Russian Science Foundation, grant no. 22-73-10050.

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P15

Self-assembly of supramolecular amphiphiles based on oppositely charged protein and calix[4]resorcinol

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Biopolymers play a significant role as components of drug delivery system due to their biocompatibility, biodegradability, and low immunogenicity. Casein is widely available and inexpensive milk protein. It is able to change its morphology depending on environmental conditions which allows it to act as a convenient carrier for biologically active substrates. A promising method for the functionalization and ordering of casein molecules is supramolecular self-assemblywith amphiphilic molecules.

In this work amphiphilic viologen calix[4]resorcinol (VR, Figure 1.) is used as a modifying component for sodium caseinate. The supramolecular interaction between VR and caseinate and the properties of formed supramolecular system are studied by a wide range of physicochemical methods. It was shown that electrostatic interactions between oppositely charged groups, together with the hydrophobic effect, contribute to the formation of VR–caseinate complex. The presence of VR in aqueous solutions of caseinate leads to aggregation at lower concentrations of polymer, and the diameter of mixed aggregates is 1.5-2 times greater than that of pure caseinate. Nevertheless, the size of mixed particles does not exceed 200 nm, which is optimal for drug delivery system. These nanoparticles exhibit a binding ability to both hydrophobic quercetin and oleic acid and hydrophilic doxorubicin. Encapsulation of doxorubicin increases its anticancer activity due to better permeability through the cell membrane and induction of apoptosis. In addition, a decrease of pH below the isoelectric point of the protein (pH 4.6) leads to recharge of caseinate and further to the decomposition of aggregates. The pH-controlled behavior, optimal size, and selectivity to cancer cells indicate the potential of VR–caseinate aggregates as an effective drug delivery system.

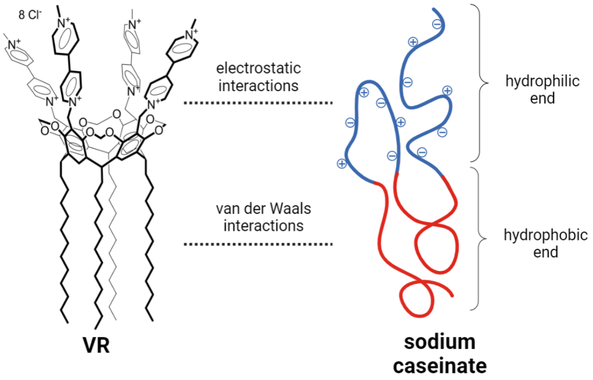

Figure 1. Structure of viologen calix[4]resorcinol and its interaction with caseinate fragments.

Acknowledgements: This research was funded by Russian Science Foundation, grant number 22-73-10050.

P16

Size determination of nanoparticles of vitamins B1 and B6 in DMSO-water mixtures by dynamic light scattering

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Vitamin B$_1$ (Thiamine HCl) and vitamin B$_6$ (Pyridoxine HCl) are important water-soluble vitamins and play biological roles in them etabolic processes of the carbohydrates in the human body. They reduce the damage by free radicals and aides in preventing degenerative disease [1].

Size determination (hydrodynamic diameter) of nanoparticles of vitamins B$_1$ and B$_6$ in DMSO-water mixtures was performed by dynamic light scattering (DLS) method using Anton Paar Litesizer 500 instrument [2].

Vitamin B$_1$ and B$_6$ solutions were prepared at optimal concentration in the wide range of binary solvent DMSO-deionized water compositions then filtered through a 220 nm pore-size filter (WhatmanAnotop 25) prior to measurement. All measurements were made at 25°C with 10 repetitions to verify the measurements' reproducibility (Figure 1.).The optimum measurement (90°C) angle was automatically selected by the instrument for each sample.

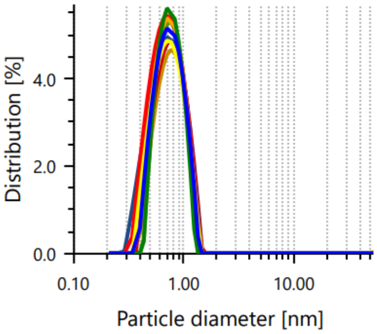

Figure 1. Particle size distribution by intensity of vitamin B$_1$ dissolved in deionized water.

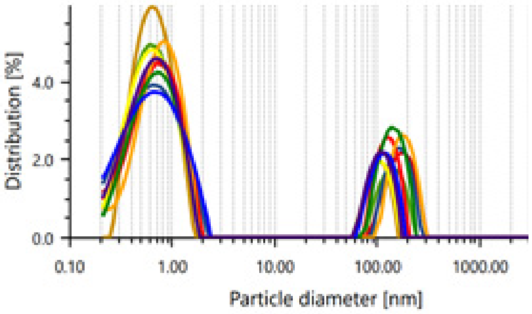

Figure 2. Particle size distribution by intensity of vitamin B$_6$ in DMSO-deionized water (4:1 v/v) mixture.

As it follows from the results obtained, with increasing of quantity of DMSO in mix solvent, the hydrodynamic diameters of nanoparticles of B$_1$ and B$_6$ vitamins increase. In addition, at high content of DMSO in mix solvent the two well-defined peaks were visible in the intensity-weighted size distribution curve (Figure 2.). The first peak corresponded to a mean particle size (0.7 ± 0.02) nm. The second peak had a mean size of about 200 nm. This suggested that some level of aggregation of vitamin particles had occurred.

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P17

Nitrate-induced photodegradation of nadolol in water solution

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Many scientific studies reported the presence of pharmaceuticals in surface and groundwater. The stability of pharmaceutical products in the environment mainly depends on susceptibility to hydrolysis, sorption, biodegradation, and photolysis. Direct and indirect photolysis, particularly in surface waters, are the main abiotic pathways for the degradation of hydrolysis-resistant pharmaceuticals [1].

Nitrates are present in the natural aquatic environment, ranging from 10^{-5} to 10^{-3} mol/dm^3. The variation in nitrate concentration is highly related to geographic location and human activity. Therefore, to elucidate the environmental stability of nadolol in water, different light sources and nitrate concentrations (0.3 and 3.0 mmol/dm^3) on the efficiency of nadolol photolysis were investigated (Figure 1.) to simulate environmental conditions. Degradation of the investigated compound was negligible under simulated solar (SS) irradiation, while 11.0% and 14.7% were degraded under UV-LED and UV irradiation. The addition of nitrates did not significantly increase the efficiency of the process, using 3.0 mmol/dm^3 nitrates 21.9% of nadolol was degraded under UV irradiation.

Moreover, a nitrate concentration of 0.3 mmol/dm^3 slowed the degradation process. Niu et al. [2] reported that nitrates could promote, suppress, or have a minor effect on the photolysis of organic pollutants. Namely, nitrates excited by light could form reactive nitrogen and oxygen species (ROS), which means nitrates can act as photosensitizers. The inhibitory role of nitrates could be explained by competitive nitrate photoabsorption or ROS quenching with the organic pollutant.

Photolysis of organic pollutants in the presence of hydrogen peroxide proved very efficient [3]. Therefore to improve nadolol degradation in the aquatic environment, the influence of lower nitrate concentration on the degradation efficiency of nadolol in the presence of 3.0 mmol/dm^3 hydrogen peroxide under SS, UV-LED, and UV radiation was investigated. The inhibitory role of nitrates in nadolol indirect photolysis was likely due to ROS quenching with nadolol.

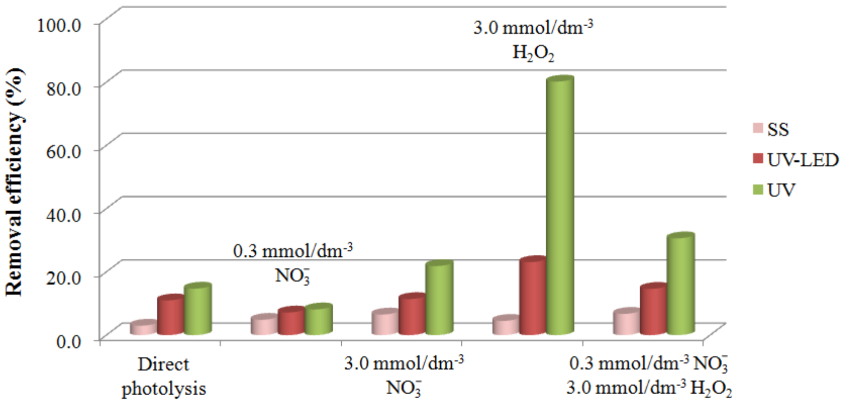

Figure 1. The removal efficiency of nadolol (0.05 mmol/dm^3) under different irradiation in the absence/presence of nitrates, hydrogen peroxide, and their mixture

Acknowledgements: This work is supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects: 451-03-47/2023-01/200125) and the Association for the International Development of Academic and Scientific Collaboration – AIDASCO

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P18

What actually happens in solution during DLLME procedure?

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We are currently witnessing strong development of instrumentation in general and of analytical instrumentation in particular. Nevertheless, the most laborious and time-consuming step of chemical analysis is the pre-treatment of a sample. In analytical chemistry, the requirements of green chemistry [1] are manifested mostly by using lesser amounts of chemicals, thus producing significantly less waste. The easiest way to achieve this goal seems to be through miniaturization and automation. Articles demonstrating the possibility of using a single drop for analytical purposes began to appear in the second half of the 1990s [2-7]. These pilot studies later led to the development and implementation of various solvent micro-extraction techniques. Since introducing of Dispersive liquid-liquid microextraction (DLLME) by Rezaee in 2006 [8], more than 3,000 research and review papers have been published on this topic, and different modalities of the original version of the method have been suggested.

Despite the relatively large number of research papers devoted to the development of DLLME procedures for determination of different analytes in a variety of samples, the number of articles devoted to a detailed understanding of the extraction process is limited [9]. Therefore, we decided to look deeper into exactly what happens in the sample solution after adding a mixture of the extraction and dispersive solvent: How do the extraction and dispersive solvent type, the volume of the extraction mixture (ratio of the aqueous sample to the extraction mixture) and the volume of the dispersive solvent (dispersive and extraction solvent ratio) affect the cloudy state quality? We will present our new results and considerations in this area.

Acknowledgements: Authors would like to express their thank to the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic (VEGA 1/0220/21) for financial support.

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P19

The effect of the solvent on the switching properties of 7-hydroxy quinoline azo and azomethine dyes

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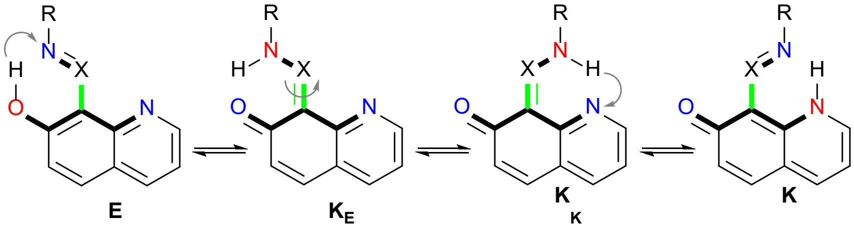
Four novel, 7-hydroxyquinoline based, Schiff bases and azodyes (**1**-**4**, Figure 1) have been synthesized and their spectral properties have been investigated by combined use of optical and NMR spectroscopy and theoretical DFT calculations [1,2]. The results indicate that phenyl substituted compounds (**1** and **3**) exist as a mixture of enol (**E**) and two keto (**K_E** and **K_K**) tautomers in solution, while pentarfluorophenyl substituted ones (**2** and **4**) are presented as a single enol form. Upon irradiation, through excited state intramolecular proton transfer mechanism, a rotation around the C_{quin}-CH or C_{quin}-N bond (indicated in green in Figure 1) occurs, showing that these compounds are suitable to be used as molecules switches.

The switching and tautomeric properties are substantially influenced by the solvent environment. While toluene and acetonitrile act mainly as polar media, leading to a stabilization based on the relative values of the individual tautomers, the use of use of chloroform causes stabilization though intermolecular hydrogen bonding.



1 X=CH, R=C_6H_5
2 X=CH, R=C_6F_5
3 X=N, R=C_6H_5
4 X=N, R=C_6F_5

Figure 1. Sketch of the long-range proton switching in **1**-**4**.

Acknowledgements: The financial support from Bulgarian National Science Fund within National Science Program VIHREN by project T-Motors (contracted as KP-06-DV-9/2019) is gratefully acknowledged.

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P20

Partitioning of L-tryptophan and vanillin in aqueous biphasic systems containing novel polymerized ionic liquids

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Aqueous biphasic systems (ABSs) based on ionic liquid (IL) and kosmotropic salt are considered as promising for the liquid-liquid extraction of biomolecules [1]. By chemical modification of ILs' ions it is possible to influence intermolecular interactions and, as a result, obtain ABSs with the required properties. For instance, ILs with amino acid anionsattract special attention because of their low toxicity [2] and likely biocompatibility. Another example of modified ILs is polymerized ILs (PILs), which have recently been considered as new promising candidates for the enhanced bioextraction [3].

Theaim of this work is to investigate the effect of chemical structure of PILs on liquid-liquid equilibrium (LLE) in ABSs (PIL-K_3PO_4-H_2O) and on the partitioning of model solutes (L-tryptophan, vanillin) between liquid phases. Our studies include poly-(diallyldimethylammonium) chloride (poly-[DADMA]Cl) and amino acid PILs based on poly-(diallyldimethylammonium) cation (poly-[DADMA]X, where X = [Leu] – L-Leucinate, [Val] – L-Valinate, [Lys] – L-Lysinate) that have been synthesized for the first time.

In the selected ABSs, we obtained data on LLE and on the partition coefficients of L-tryptophan and vanillin (Figure 1). The partition coefficients in ABSs with amino acid PILs are higher than in the systems with poly-[DADMA]Cl. Similar partitioning of L-tryptophan was observed in ABSs based on 1-butyl-3-methylimidazolium ILs [4]. We found specific interactions (hydrogen-bonding) between vanillin and amino acid anions, which explain the high extractive capacity observed for ABSs with amino acid PILs.

We conclude that ABSs with amino acid PILs are promising for the extraction of small hydrophobic biomolecules. Our results help in understanding the driving forces of phase separation and partitioning of the solutes and may be of use in developing methods of extraction that belong to the field of "green chemistry".

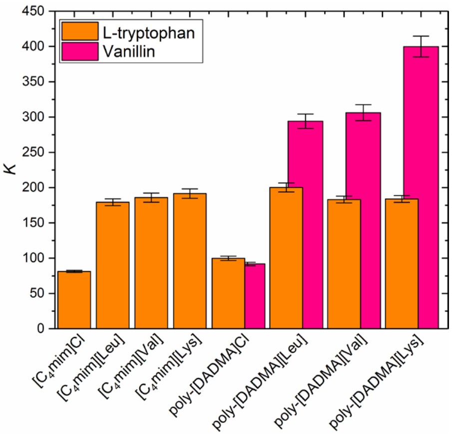

Figure 1. Partition coefficients (*K*) of L-tryptophan and vanillin in ABSs based on PILs at 298.15 K and in the systems based on 1-butyl-3-methylimidazolium ILs [4].

Acknowledgements: We thank RSF (project No. 20-13-00038) for financial support. Experiments were performed at the Research park of St. Petersburg State University (Center for Magnetic Resonance, Center for Chemical Analysis and Materials Research, Center for Thermogravimetric and Calorimetric Research).

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P21

Molecular simulations of salts hydrates

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Classical molecular simulations have become an important tool for studying electrolyte solutions under various thermodynamic conditions. Such simulations are based on microscopic models, force fields, whose use is limited by their ability to reasonably predict solubility of the electrolyte studied and thus avoid spurious precipitation and ion clustering. Previous simulation studies have often focused on the solubility of

anhydrous crystalline salts, but virtually never on crystalline hydrates, except for hydrohalite, $NaCl \cdot 2H_2O$ [1,2], despite there are at least 23 experimentally known different hydrates that can precipitate from alkali-halide solutions.

This work attempts to fill this gap in hydrate simulation studies by systematically investigating the ability of the best force fields selected to qualitatively capture the stability of the individual phases of various alkali-halide hydrates and to quantitatively predict their lattice parameters. First, we show that the nonpolarizable force fields studied often fail to model hydrates containing the Li^+ cations, whereas the polarizable force fields recently refined in our group [3,4] are able to model all the hydrates except for $LiCl \cdot H_2O$. Second, we further refine our FFs for Li^+ to yield stable $LiCl \cdot H_2O$. Third, our simulations clarify the positions of the Li^+ cations in the beta phases of $LiBr \cdot H_2O$ and $LiI \cdot H_2O$, whose distributions were previously described only as stochastic [5,6]. As a byproduct, a simple and reliable simulation methodology suitable also for complex polarizable models and nonorthorhombic crystal lattices is proposed and tested, based on simulations of finite crystals floating in vacuum.

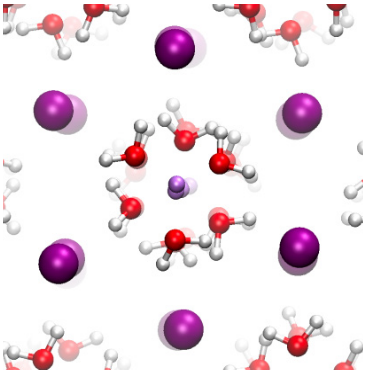

Figure 1. Snapshot from simulation of stable polarizable model of $LiI \cdot 3H_2O$.

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P22

Molecular and process modelling of selected novel solvents for CO_2 capture

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Reducing greenhouse gas emissions is crucial to mitigate the effects of climate change, and CO_2 capture via absorption using aqueous amine solvents remains the most widely used industrial process for this purpose [1]. However, a significant technical barrier is the high energy demand for solvent regeneration such as the benchmark 30 wt.% Monoethanolamine (MEA), increasing the cost of capture, nowadays capped at new US DOE limits of $30 per ton. To overcome this, it is necessary to search for novel amines with desirable thermodynamic properties that can improve the economic design of CO_2 capture plants.However, evaluating the performance of new amines is challenging due to limited experimental data necessary for detailed techno-economic evaluation, and the absence of a practical framework to determine the most suitable solvent.

Given the recent advancement in molecular modeling tools, molecular-based equations of state provide a suitable platform for the design of modelling screening frameworks. The main objective of this work is to develop a robust solvent screening tool using the soft-SAFT molecular-based equation of state (EoS) [2] to obtain relevant thermodynamic properties for assessing novel solvents for CO_2 capture. A collection of 36 alternative novel amines were included in this work, belonging to six families: (1) aminoalcohols, (2) alkylethanolamines, (3) dialkylaminoalcohols, (4) cyclic amines, (5) diamines, and (6) multiamines. This work highlights the predictive power of soft-SAFT EoS in cases where no experimental data was available. The modeling was extended to calculate two key performance indicators, namely, cyclic capacity and regeneration energy, as screening criteria to determinethe most optimal solvent.

In our search for the most efficient replacement amine to the golden standard MEA, both 2-Diethylaminoethanol (DEEA) and Diethylenetriamine (DETA) showed promising potential in terms of a high cyclic capacity (Δα) and low regeneration energy (Q_{regen}), shown from Figure 1.

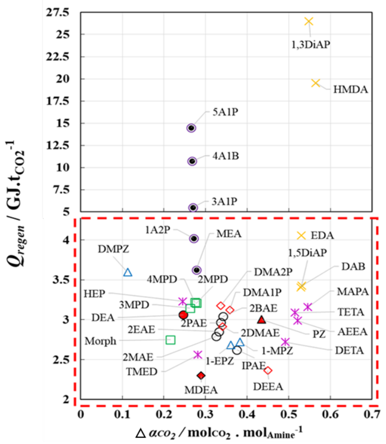

Figure 1. Scatter plot of the Regeneration energy (Q_{regen}) with cyclic capacity (Δα) of 36 novel amines.

Acknowledgments: Financial support for this work was provided by Khalifa University through the RICH Center RC2-2019-007.

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P23

The coupling hydrogen bond shared by water and the energetic explosives

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We show that energetic explosives of the nitrogen-based explosives such as TATB [1], nitromethane [2] and $N_5^-:nH_3O^+$ complex [3] share the coupling hydrogen bond (O:H-O) of water, the anti-hydrogen bond H ↔ H of acid solutions, and the O: ⇔ :O super hydrogen bond of base solutions [4]. The H-O bond of the O:H-O in water and the H-N bond of the O:H-N in TATB show the negative thermal expansivity and compressibility while the H-C bond of O:H-C in the nitromethane undergoes the positive compressibility but negative thermal expansivity (Figure 1.).

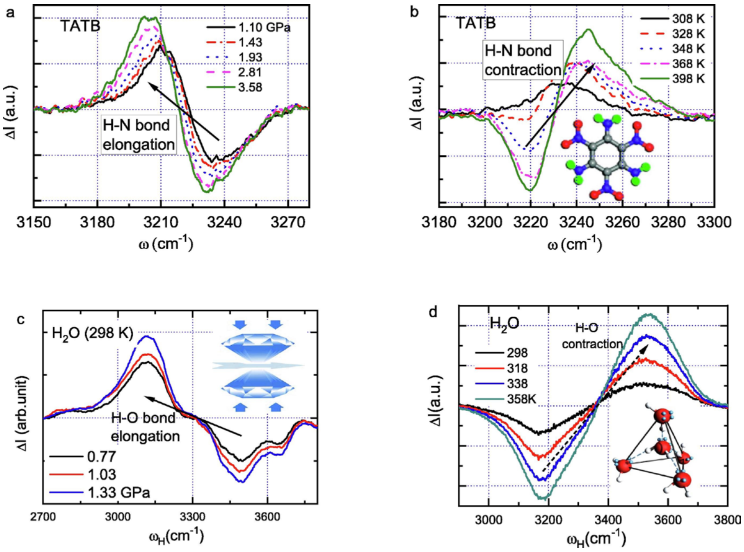

Figure 1. H-N and H-O negative compressibility and negative thermal expansivity in TATB and H_2O.

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P24

Synthesis and physico-chemical characterization of Co/Al and Cu/Al hydrotalcites

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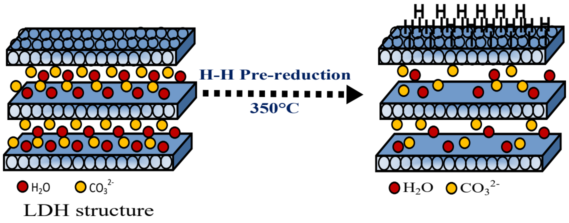
Hydrotalcite-like compounds (HTlcs), representing an important class of layered materials with numerous potential applications as catalysts, catalyst supports, ions exchanger/adsorbents, layered hosts for bio-molecules and precursors for composite materials [1]. The chemical composition can be represented by the general formula: $[M(II)_{1-x}M(III)_x\ (OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} is a bivalent cation, M^{3+} is a trivalent cation, A^{n-} is an anion and x is defined as the $M^{3+}/[M^{2+}+M^{3+}]$ ratio, whose value varies between 0.2 and 0.33.

The structural and textural properties of the LDHs depend on both M^{2+} and M^{3+} nature, interlayer anion and x values (responsible of the charge in the layers), the concentration of the reactants in the synthesis solution and the synthesis procedure (co-precipitation, hydrothermal, microwaves, ultrasound, pH value among others) [2]. These materials can interact with anions by both the interlayer space and external surface.

Co/Al and Cu/Al Hydrotalcites were prepared by co-precipitation method at room temperature with M^{2+}/M^{3+} molar ratio of ~ 2 at pH = 9-10 using carbonates as an interlayer anions. Two aqueous solutions, one containing nitrate salts as such $M^{3+}/[M^{2+}+M^{3+}] = 0.33$, and the other containing a mixture of $NaOH/Na_2CO_3$, were added dropwise. The suspension thus obtained was kept at 60°C for 15 h. The precipitate was filtered and washed with deionised water until pH ~ 7 of the filtrate, dried at 70°C for 24 h and then reduced under hydrogen flow at 350°C.



The chemical composition, structure, morphology and thermal behaviour were investigated using energy-dispersive X-ray (EDX), X-ray diffraction, FTIR spectroscopy, nitrogen adsorption/desorption measurements (BET equation and BJH method), thermogravimetric analysis (TGA/DTG), TEM and SEM techniques. The results confirm that the precipitation process is effective by EDX analysis, and indicate that HTlcs samples with M^{2+}/M^{3+} atomic ratio of 2:1 are successfully prepared by co-precipitation method. The diffractograms obtained by PXRD show that the reflections are typical characteristics of the hydrotalcite and revealed a good dispersion of aluminium in the brucite layers. The textural properties of the LDH reveal that all hydrotalcite-like precursors exhibit low specific surface area (23 - 71 m^2/g), typical values of fresh LDHs and large mean pore diameter of 9-27 nm with total pore volume of 0.04-0.16 cm^3/g. The difference in the specific surface areas can be explained by crystallinity degree different of the LDH phases.

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P25

Structure of a single acetic acid droplet ultrasonically levitated in the air by in situ Raman and X-ray scattering

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Aerosol droplets in the atmosphere are deeply involved in forming clouds and global climate change. It is important to clarify the structure and properties of aerosols at the molecular level. We developed a structural analysis method using in situ Raman scattering and X-ray scattering of a single droplet ultrasonically levitated in the air [1] and reported the structure and properties of inorganic aerosol droplets, such as aqueous magnesium nitrate [1] and magnesium sulfate droplets [2]. In this study, we investigated the structure and properties of acetic acid droplets as a model of organic aerosols generated when plants breathe.

Aqueous solutions of 0.989, 1.98, 2.97, 3.96, 4.99 and 5.89 mol/L acetic acid were prepared. A droplet (size 1~2 mm) was levitated using a syringe in an ultrasonic generation device (Honda Denshi) in a sample chamber. A spectrometer with a CCD detector (Tokyo Instruments) was used for Raman scattering measurements (wavelength: 532 nm). The area ratios of the C=O stretching vibration of 1735 cm^{-1} of acetic acid to the O-H bending vibration of water molecule of 1664 cm^{-1} were plotted as a function of acetic acid concentration. From this calibration curve, the concentration of an acetic acid droplet was estimated. X-ray scattering measurements were performed at SPring-8 BL08W (wavelength: 0.107 Å). The two-dimensional data were converted to one-dimensional data by the Orochi program. The interference function $F(Q)$ was obtained by the KURVLR program. The X-ray scattering data were analysed by EPSR (Empirical Potential Structure Refinement) modeling.

From the Raman spectrum analysis, the droplet concentration was found to be 0.814 mol/L for the 0.989 mol/L bulk sample. Figure 1 shows the structure of acetic acid with atom labels and the interference function $F(Q)$ for the bulk and droplet of acetic acid. EPSR analysis revealed a mean coordination number of the methyl-methyl interactions (C1-C1) increased from 1.9 at 0.9886 mol/L to 6.9 at 5.888 mol/L in bulk solution, but 0.9 for 0.8137 mol/L droplet. The O1-O2 pair correlation function shows a sharp peak at 2.6 Å for the two bulk solutions, but no peaks for the droplet. These findings suggest that the methyl groups are arranged near a droplet surface due to the liquid-air (hydrophobic) interaction.

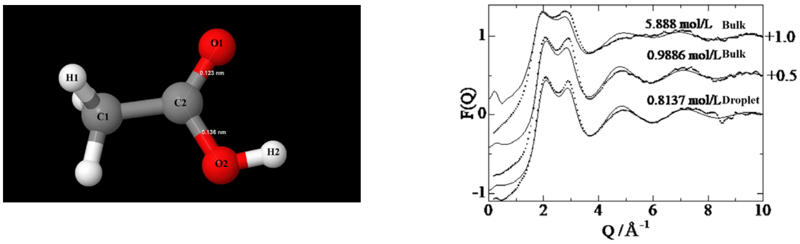

Figure 1. (Left) Acetic acid molecule with labels of atoms. (Right) X-ray interference functions $F(Q)$ of acetic acid with different concentrations in bulk and droplet. Dots: experimental, solid lines: EPSR fits

Acknowledgements: The works were partially supported by KAKENHI (No.19K05551). The X-ray scattering experiments were performed at the BL08W of Spring-8 with the approval of the Japan Synchrotron Radiation Research Institute (No. 2020A0771, 2021A1362).

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P26

Effects of external electric fields on the structure of oligo(ethylene glycol) in explicit solvents by molecular dynamics simulations

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Understanding the structure of polymer solutions under external electric field is very important for applications, such as electrospinning technology [1]. Molecular dynamics simulations were performed under various applied external electric field for oligo(ethylene glycol) of different chain lengths in water or methanol in order to explain the results of our previous study [2]. In a molecular dynamics simulation, we monitor the size of the coil by using the radius of gyration and the end-to-end distance, and we also characterize the anisotropy of the average shape of the coil by quantities derived from the gyration tensor. The distribution of the cosine of the angles of the vector of the monomer unit and the dipole moment vector with respect to the electric field direction is calculated. Finally, the distribution of backbone dihedral angles is calculated, and an attempt to quantify the helicity of the chain is made based on counting monomer units matching predefined helical patterns. Results show that the coil in both solvents becomes an increasingly anisotropic and adopts oblate average shape with stronger fields, but in water this feature seems to be diminished by increasing chain length. In water, the monomer units of the chain orient at angle of about 70° whereas, in methanol, the monomer units orient perpendicular to the electric field. The monomer dipoles of the chain in both solvents point an increasingly in field direction. Regarding the dihedral distribution, electric field promotes gauche population in most cases.

Acknowledgements: This research has been supported by the Jan Evangelista Purkyně University in Ústí nad Labem within the student grant programme (Project No. UJEP-SGS-2022-53-002-3). Computational resources were supplied by the project "e-Infrastruktura CZ" (e-INFRA LM2018140) provided within the program Projects of Large Research, Development and Innovations Infrastructures.

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P27

Local structure and speciation of Li$^+$ and dipole reorientation forsulfolane-based super-concentrated lithium salt solutions

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Lithium-sulfur (Li-S) batteries have a theoretical capacity several times higher than conventional lithium-ion batteries and are expected to become the next generation Li rechargeable ones. However, they are still under studying due to the dissolution of polysulfide, which is considered to be a discharge intermediate, from the positive electrode. Dokko et al. demonstrated good cycle performance of Li-S batteries using a sulfolane (SL: tetrahydrothiophene 1,1-dioxide) based electrolyte. In addition, they found superionic Li$^+$ conduction in highly concentrated lithium salt electrolyte solutions where the Li$^+$ diffuses faster than SL and anions [1]. In this contribution, dipole reorientation dynamics and Li$^+$ speciation in various SL-based Li salt solutions were investigated with dielectric relaxation spectroscopy (DRS) and Raman spectroscopy to discuss this unique superionic Li$^+$ conduction mechanism.

The DRS are recorded as the frequency dependent complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ (ε': permittivity, ε'' dielectric loss), and the dipole response is observed as a relaxation. Figure. 1 shows the dielectric spectra of 0.1–4.3 M $LiBF_4$-SL solutions and 0.4-3.2 M $LiClO_4$-SL solutions. In each case, the relaxation intensity of free SL around 5 GHz decreased with increasing the lithium salt concentration. In addition, with the increase of the lithium salt concentration, a new relaxation appeared at the lower frequencies and the intensity increased. This can be ascribable to the response of solvent ion pairs (SIP) or contact ion pairs (CIP) and aggregates (AGG). On the other hand, the Raman spectra of $LiBF_4$-SL solutions were analysed by the complementary least squares analysis (CLSA) and the formation distribution functions showed that the CIP/AGG formation increases with increasing $LiBF_4$ concentration. Therefore, the relaxation appeared at the lowest frequency side with intensifying should be attributed to the CIP/AGG. Comparing $LiBF_4$-SL and $LiClO_4$-SL solutions, the relaxation intensity of this CIP/AGG was larger in the $LiBF_4$-SL solutions, which indicates that the $LiBF_4$ system is more likely to produce the CIP/AGG than the $LiClO_4$ system. The Li$^+$ local structure was also discussed by means of neutron scattering with $^{6/7}$Li isotope substitution technique.

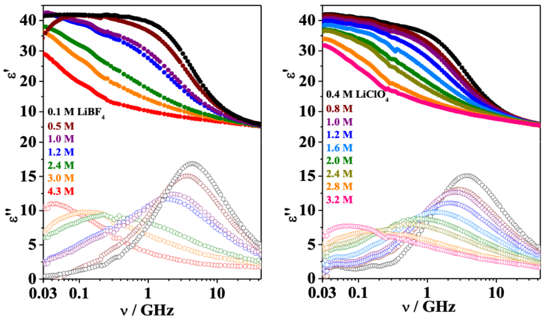

Figure 1. Dielectric spectra of $LiBF_4$-SL (left side) and $LiClO_4$-SL (right side) solutions.

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P28

Alkali metallon recognition by 18-crown-6in aqueous solutions: Evidence from local structure

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Crown ethers can selectively recognize metal ions [1]; however, there is a lack of in-depth understanding of the underlying recognition mechanisms. In the present work, the structure and recognition sequence of alkali metal ions (Li^+, Na^+, K^+, Rb^+ and Cs^+) by 18-crown-6 in aqueous solutions were systematically studied at the atomic level by wide angle X-ray scattering (WAXS)combined with ab initio molecular dynamics (AIMD). The precise positions and orientations of 18-crown-6, cations and water molecules in 18-crown-6/cation complexes and their hydrates were obtained, and the competition and equilibrium between complexation and hydration were expounded. Li^+, Na^+ and K^+ are located in the negative potential cavity of 18-crown-6, with Li^+ and Na^+ deviating from the centroid of 18-crown-6 by 0.95 Å and 0.35 Å, respectively. Rb^+ and Cs^+ lie outside the 18-crown-6 ring, and deviate from the centroid of 18-crown-6 by 0.05 Å and 1.35 Å, respectively. The formation of the 18-crown-6/alkali metal ion complexes is dominated by electrostatic attraction between the cations and the oxygen atoms (Oc) of 18-crown-6. Li^+, Na^+, K^+ and Rb^+ form the $H_2O\cdots$18-crown-6/cation$\cdots H_2O$ “sandwich” hydrates, while water molecules only hydrate with Cs^+ of the 18-crown-6/Cs^+ complex on the same side of Cs^+. Based on the local structure, the recognition sequence of 18-crown-6 for alkali metal ions in the aqueous solution follows $K^+ > Rb^+ > Na^+ > Li^+$, which is completely different from that in the gas phase [2], confirming that the solvation medium seriously affects the cation recognition of crown ethers. This work provides detailed local structure information of crown ether/alkali metal ion complexes and their hydrates, and visualizes the relative positions and interactions between molecules and ions.

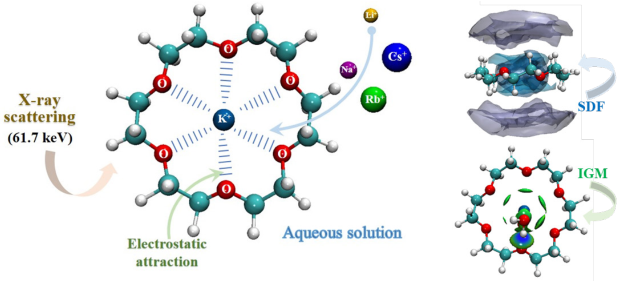

Figure 1. Recognition of 18-crown-6 to alkali metal ions in aqueous solution.

Acknowledgements: The National Natural Science Foundation of China (No.201973106),the Innovation Platform Construction Project of Qinghai Province (2019-ZJ-T03), the CAS Project for Young Scientists in Basic Research (No. YSBR-039) and the SPring-8 team.

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P29

Excited state proton transfer processes in bulk and confined deep eutectic solvents

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Excited state proton transfer (ESPT) reactions play an important role in many natural processes and have applications in photo stabilizers, humidity sensors, photochromic switching, white light generation, photochromic switching, and many more [1]. These reactionsare highly dependent on their surroundingsand have been studied in many media [2-4]. In deep eutectic solvents (DESs), it's still unexplored.

ESPT reaction of 8-hydroxy-1,3,6-pyrenetrisulfonate (HPTS)photoacid has been performed in tetraethylammonium bromide (TEAB) based deep eutectic solvents (DESs) confined in polyether sulfone membranes with a pore size of ~ 350 nm and in bulk media. For this purpose, we have used three DESs constituted of TEAB with various hydrogen bond donors (HBD), ethylene glycol, glycerol, and 1,3-propanediol. The photoprotolytic process has been studied using steady-state and time-resolved fluorescence spectroscopy. We found that both protonated and deprotonated forms of the photoacid exhibit fluorescence in the confined environment of DESs, however, only the protonated form shows fluorescence in bulk media. Moreover, the fluorescence intensity decay of the photoacid fits with a bi-exponential function of time (~ 1.5 and 4 ns) in the confined DESs. In contrast, it fits with a single-exponential function of time (~ 3 ns) in bulk liquids. Therefore, both steady-state and time-resolved fluorescence studies confirm that ESPT is a favorable process in the confined DESs although the pores of the confinement are large but it is an unfavorable process in the bulk environments. We have also carried out an excitation wavelength-dependent fluorescence study of a solute, coumarin 153, in the confined as well as in bulk DESs and observed a significant red-edge excitation shift (~600 cm^{-1}) in the confined environments, while a negligible shift (< 100 cm^{-1}) has been seen in bulk media. This indicates that the DESs confined in the polyether sulfone membranes are more heterogeneous than in the bulk environments and suggests that the extent of microheterogeneity plays an important role in controlling the rate of ESPT in confined DESs. We have also found that the rate of proton transfer is modulated when the hydrogen bond donor of DES was changed from ethylene glycol to glycerol, and then to 1,3-propanediol.

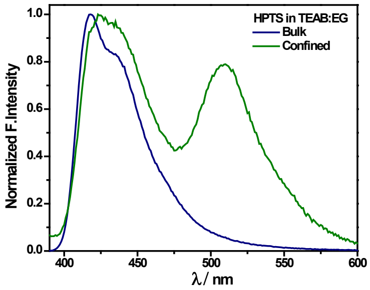

Figure 1. Steady-state emission spectra in HPTS in Bulk and confined TEAB:EG DES.

Acknowledgments: Dr. Biswajit Guchhait (Supervisor), Shiv Nadar Institution of Eminence

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P30

Determination of anomalous regions and phase transitions in continuous shouldered well model

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Molecular dynamics and Monte Carlo simulations in the canonical and isothermal-isobaric ensembles were used to determine anomalous regions in a two-dimensional system of particles interacting through continuous shoulder well (CSW) potential. The potential is isotropic and consists of three parts: a steep repulsive wall, a soft repulsive shoulder, and an attractive Gaussian well. The model is therefore characterized by two characteristic distances. Regions of density, diffusion, and structural anomalies were determined and by determining their hierarchy, the possibility that the model fluid reproduces anomalous behavior of liquid water was checked.

P31

Molecular dynamics study of thermodynamical and structural properties of naphthalene and its derivatives

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Molecular dynamics simulations of naphthalene, 1-methylnaphthalene and 2-methylnaphthalene were carried out in order to investigate their structural and thermodynamic properties. OPLS force field was used in all-atom molecular dynamics simulation of naphthalene and its derivatives. The goal of the study was to investigate possible differences in thermodynamic and dynamic properties of naphthalene and its derivatives and connect these differences to the structure and structural properties of each derivative.

The systems were simulated at various temperatures, from temperatures where compounds are in the solid state to temperatures where the gas phase appears. Furthermore, different thermodynamic properties, such as density, enthalpy, heat capacity, thermal expansion coefficient, and isothermal compressibility, as functions of temperature were calculated for all derivatives. Dynamic properties such as diffusion coefficient and viscosity were also calculated. Results from naphthalene and derivatives were compared to each other.

The differences in thermodynamics usually originate from differences in structure, therefore, we also explored the structure of naphthalene and derivatives in the liquid and solid states. Radial distribution functions for each derivative were calculated and compared. We obtained different amorphic and crystal structures which were characterised. The position or lack of methyl in (methyl) naphthalene has a significant effect on the structure both in the liquid and solid state, and consequently also on thermodynamic and dynamic properties.

P32

Automated quantum chemical microsolvation in arbitrary solvents

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Molecules in solution, typically denoted as solutes, are surrounded by solvent molecules with which they interact. These interactions have a direct influence on the properties and reactivity of the solute at hand. To obtain a more accurate chemical model, as well as improve the description of the system behaviour, it is vital that solvent effects are taken into account.

In quantum chemical descriptions, those solvent effects are either treated implicitly, accounting for bulk properties only – in its simplest way by an electrical permittivity – or explicitly, by defining an arbitrary number of solvent molecules around the solute. This approach poses two questions:

- Where and how should those solvents be placed?
- How many are needed to capture most of the relevant interactions while minimizing the computational workload?

In a previous work [1] we succeeded in devising a protocol for systems solvated in water, that extracts energetic and entropic information from MD simulation derived data. This protocol makes use of the Grid Imhomogenous Solvation Theory (GIST) [2,3] to determine solute-solvent interaction on a grid. The centerpiece of this approach, however, is the in house developed program “Free Energy Based Identification of Solvation Sites” (FEBISS). This uses the GIST generated thermodynamic data to find the most favorable water interaction sites around the solute and places the solvent molecules automatically, based on the free energy. Using the interaction strength, the user has a quantitative measure to decide how many water molecules to include in their quantum chemical microsolvation model.

Here we present the revised and extended protocol, which is now fit to evaluate favorable solvation sites for arbitrary solvents, such as dichloromethane or methanol. We highlight the applicability of this methodology at the example of a solvatochromic system.

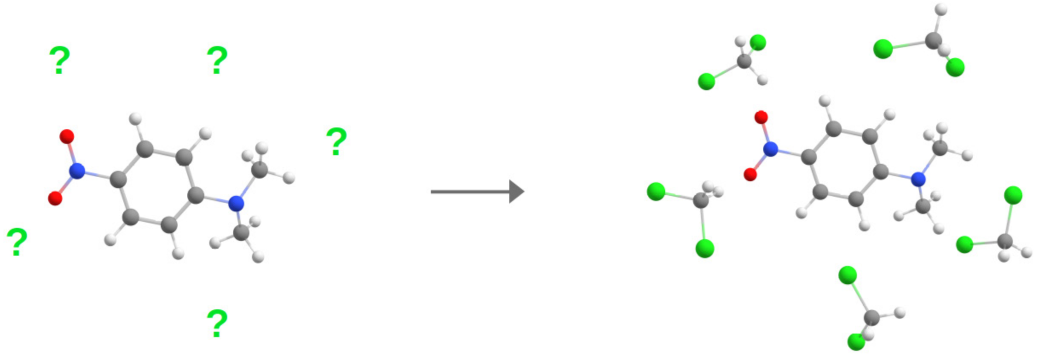

Figure 1. Automated placement of arbitrary solvents

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P33

Electronic fluctuation in dilute aqueous osmolyte solutions: An effective fragment potential – molecular dynamics study

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Small organic molecules in cells have been considered important to control the functions of proteins [1], however, their electronic fluctuation and the intermolecular interaction under physiological conditions has never been clarified due to the lack of observation methods with both accuracy and efficiency. Herein, the time evolutions of the interactions, which is physicochemical origin of the molecular functions, in dilute aqueous trimethylamine *N*-oxide (TMAO) and tert-butyl alcohol (TBA) solutions were analysed via *ab initio* molecular dynamics simulations accelerated with the fragment molecular theory (effective fragment potential: EFP [2]). It has been known that TMAO and TBA have similar structures, but opposite physiological functions to stabilize and destabilize proteins. It was clarified that TMAO induced stable polarization and charge-transfer interactions with water molecules near the hydrophilic group, and water molecules were caught even near the CH_3– group [3]. Understanding the solution dynamics will contribute to artificial chaperone design in next generation medicine.

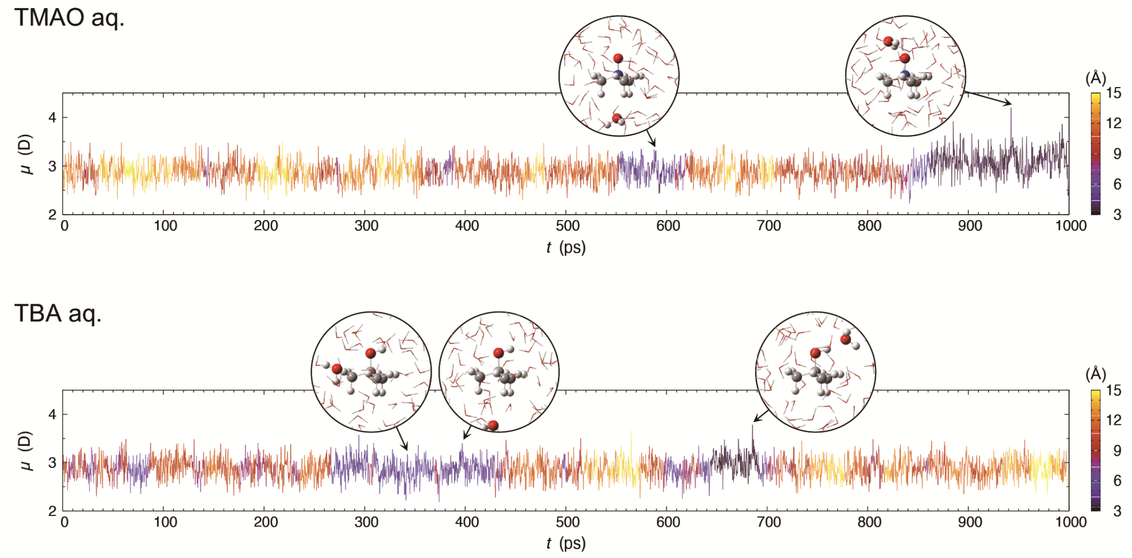

Figure 1. Temporal evolution examples of water dipole moments along 1 ns EFP-MD. The plot color represents the distances (N_{TMAO}–O_{water}/C_{TBA}–O_{water}) as indicated by the key on the right.

Acknowledgements: NK acknowledges support from the JST ACT-X project of the Japan Science and Technology Agency (grant no. JPMJAX20A9). HM acknowledges support from the JSPS KAKENHI (grant no. 21H01894). The calculations were performed using supercomputer resources provided by the Research Center for Computational Science (RCCS) at the Okazaki Research Facilities of the National Institutes of Natural Sciences (NINS), Japan(project no. 22-IMS-C015).

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P34

The behaviour of two-dimensional rose water model in a static electric field: Molecular dynamics simulations

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We studied how a homogenous static electric field affects different properties of water. To model water, we used the rose water model [1], which is a simple two-dimensional model in which molecules are modelled as two-dimensional Lennard-Jones disks with added hydrogen-bonding potential. For hydrogen-bonding potential 3-petal rose functions are used, two different parametrisations of the model were used. The rose water model has already been shown to exhibit many water-like anomalous properties. We made some adjustments to the original model, in order to be able to interact with the external electric field the model has two partial charges added. Using molecular dynamics simulations at constant pressure we studied how a static electric field influences the properties of the rose water model.

The static electric field affects both the structural and thermodynamic properties of water. When an external electric field is present in the system the tendency of molecules is to align their electric dipoles along the direction of the static electric field, however, water molecules also have the tendency to form hydrogen bonds. Therefore, the competition between the influence of hydrogen bonds and the electric field appears, as both want different ordering of water molecules. At first, when the strength of the electric field is low the effect of the field on properties is minimal. Then as the strength of the electric field increases the influence of the field on the water becomes noticeable. With the increasing strength of the electric field position of the extrema of various thermodynamic functions as functions of temperature shift, moreover, the anomalous properties become more distinct. On the other hand, when the strength of the electric field is increased beyond a certain limit the ordering of the system changes and the water model loses its water-like anomalous properties.

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P35

Novel approaches for viscosity prediction: predictive models and machine learning

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Thermophysical properties play a vital role in optimizing the process of mass and energy exchange and are helpful in understanding the nature and strength of molecular interactions between constituent components. Ultrasonic velocity and Viscosity measurements of pure, binary and higher order liquid mixtures have been a primary factor leading to designing and optimizing various chemical processes. In the past few years, prediction of these properties has gained significance due to the global lockdown arising out of COVID-19 pandemic.

There is a critical need for developing predictive models with a high degree of consistency and predictive efficacy, especially for viscosity as it is very challenging to predict its behavior under conditions of varying temperature. The challenges are amplified for systems with Ionic Liquids due to their high viscosity and non-ideal behavior in a mixture. The recently developed Dey-Biswas model, which has been successfully tested on more than 500 binary and a large number of higher order liquid mixtures has been put to test with several well-stablished and some newly developed approaches [1-3].

In the present investigation, viscosity predictions have been carried out on 70 binary mixtures with widely varying physical and chemical characteristics like size, shape, polarity, orientation etc. by using various predictive approaches. The Dey-Biswas model is observed to outperform all the other predictive models. Furthermore, Random Forest [4], which is a machine learning algorithm used for combining the output of multiple decision trees to single result, has been applied on 42 randomly selected systems. A comparative study has been drawn between Dey-Biswas model and Random Forest regression technique.

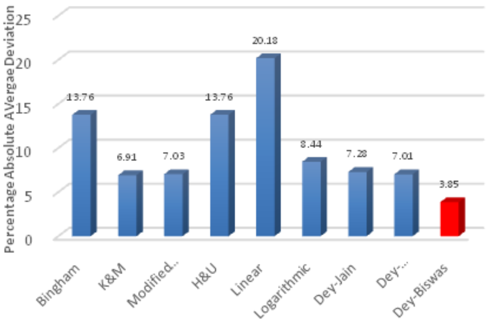

Figure 1. Grand % AAD of 42 Binary liquid mixtures

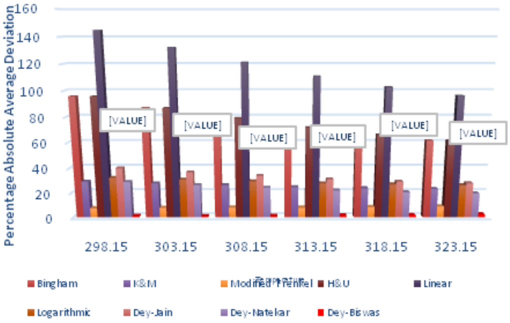

Figure 2. % AAD of various approaches for Trifluoro-propyl trimethoxy silane + n-octanol at various temperatures.

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P36

How does the presence of taurine affect caffeine hydration and self-aggregation?

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Caffeine and taurine are two commonly found compounds in energy drinks. Caffeine is a central nervous system stimulant that can improve alertness, reduce fatigue, and enhance cognitive performance. It works by blocking the adenosine receptors in the brain, which are responsible for promoting sleep and relaxation.

Caffeine can be found in many sources, like coffee and tea. In energy drinks, caffeine is often used to promote wakefulness and energy. On the other hand, taurine is an amino acid naturally produced by the body. It has been associated with several health benefits, including improved athletic performance, reduced muscle damage, and improved insulin sensitivity. In energy drinks, taurine is often added for its supposed ability to enhance physical performance and mental alertness.

Our earlier research showed that the presence of biologically active molecules, such as ATP [1] and salicylate [2], leads to the self-aggregation of caffeine in water. The binding of caffeine molecules into self-aggregates significantly affects its solubility and bioavailability.

Since water molecules surround caffeine and taurine molecules in the human body and energy drinks, it is important to examine how taurine affects caffeine's structural organisation in water.

Based on the results of measuring the density, speed of sound and viscosity of caffeine in a 0.1 molar water solution of taurine in the temperature range $T = 293.15 - 313.15$ K and computational simulations, we can conclude that the presence of taurine leads to the self-aggregation of caffeine (Figure 1).

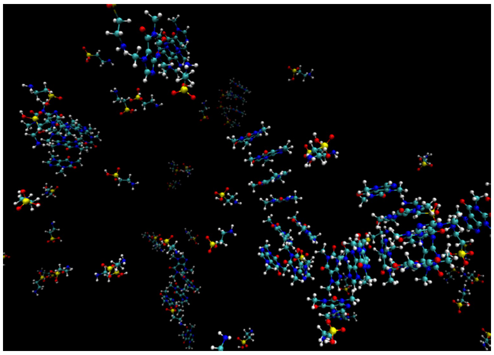

Figure 1. Visual representation of caffeine self-aggregation in the presence of taurine in water.

Acknowledgements: The acknowledgement for the support of the Cost Action CA18202 " NECTAR - the Network for Equilibria and Chemical Thermodynamics Advanced Research", and the Secretariat for Higher Education and Scientific Research of the Autonomous Province of Vojvodina, Serbia (Grant No. 142-451-2545/2021-01/2).

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P37

Investigation of ionic condensation and solvation of SDS and TTAB micelles in aqueous dilute solutions from semi-analytical calculations of radial distribution functions

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It is well known that the determination of the different radial distribution functions (RDF) $g_{ij}(r_{ij})$ in a mixture allows usto describe the structure of the solution and to calculate all the thermodynamic quantities. That can be done by molecular dynamics simulation. However, MD simulation of micellar solutions concerns for practical reasons, rather concentrated solutions with macroions of rather limited sizes.

Therefore, the main objective of this work is to present a new semi-analytical molecular and statistical approach by resolving the BBGKY hierarchy integral equation [1,2], in order to compute micelle-solvent and micelle-counterions RDFs in SDS ant TTAB dilute solutions. All the RDFsaround a central micelle “1”can be written as:

$$g_{1j}(r) = \mathrm{g^{HS}}_{1j}(r)\exp\left(-\frac{W'_{1j}(r)+W^{P}_{1}(r)}{kT}\right) \text{ , and } g_{1w}(r) = \mathrm{g^{HS}}_{1w}(r)\exp\left(-\frac{W'_{1w}(r)}{kT}\right)$$

j≡Na^+ or Br^- and w ≡ water molecule.
$W'_{1j}(r)$ is the charge-chargecontributionto the total potential of mean force (PMF). $W^{P}_{1j}(r)$ is the polarization contribution.$W'_{1w}(r)$ is the charge-water dipole PMF.
$g^{HS}_{1j}(r)$: is the hard sphere (HS) contribution.

Integration of the BBGKY equation for $W'_{1j}(r)$ can be simplified to obtain a generalization of the Debye-MSA theory. We obtain:

$$W'_{1j}(r) = \lambda_2 z_j e\,\Psi_1(r) + (1-\lambda_2)\frac{z_1 z_k}{\varepsilon(r)\mathrm{r}}\mathrm{e}^2 \text{ ; With: } \Psi1(r) = \lambda_1\frac{(Z_1\,e)}{\varepsilon(r)\mathrm{r}}\exp(-2\Gamma\mathrm{r})$$

ε(r)is the local permittivity around “1” given by the Booth-Grahame equation [3]:

$$\varepsilon(r) = n^2 + \frac{(\varepsilon_0-n^2)}{1+\sqrt{\mathrm{b}}E_1(r)}Arctg[\sqrt{\mathrm{b}}\,E_1(r)] \text{ ; With: } E_1(r) = -\nabla\Psi_1(r)$$

n is the refractive index, ε_0 is the bulk dielectric constant, and $b = 1.08\ 10^{-8}$ for water at 25°C.

$$W^{P}_{1j}(r) = \frac{3\varepsilon(r)\alpha_j[E_1(r)]^2}{8\pi[2\varepsilon(r)+n^2]} ; W'_{1w}(r) = (\lambda_w/4\pi)\,[\,\varepsilon(r)-1\,](E_1(r))^2\,C^{\circ}{}_{w}\,g_{1w}(r)$$

α_j is the polarizability of “j” ; C°w is the water concentration of the bulk solution.

$$\mathrm{g^{HS}}_{1k}(r) = 1 + \{\mathrm{g^{HS}}_{1k}(\sigma)-1\}e^{-\gamma k(r-\sigma)}cos\left(\frac{2\pi r}{\lambda}\right);\ \mathrm{g^{HS}}_{1k}(\sigma) = \left[\frac{1+a_1(b_0C)+a_2(b_0C)^2}{1+a'_1(b_0C)+a'_2(b_0C)^2}\right] \equiv \mathrm{PA}$$

σ, b_0 are respectively the mean diameter and the mean covolume of the particles “k ≡ j, w”. C is the total bulk concentration. PA is the Ree-Hoover Padé Approximant [2]. λ is the mean wavelength.

Note that λ_1, λ_2, λ_w, γ_k, and λ are adjustable parameters determined from the two Stillinger-Lovett conditions and the normalization of the $g_{1j}(r)$ and $g_{1w}(r)$ RDFs.

The integration of this system of equations allows obtaining the parameters of micellization (degree of ionic condensation, apparent charge, hydration number, activity...). As a test, we compare our calculations to experimental conductimetric results analyzed according to the Onsager–Kim–MSA-Zwanzig conductivity theory of mixed electrolytes [4,5], taking into account the dielectric friction effect on micelles.

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P38

Interactions of selected psychoactive substances and their synthetic precursors in aqueous solutions

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Experimental measurements of density and viscosity for aqueous MDMA-HCl (ecstasy), metampfetamine-HCl, *N*-ethylpentylone (so-called B,k-ethyl K), ephedrine-HCl, MDMA-HCl + 0,1 $\text{mol} \cdot \text{kg}^{-1}$ D-lactose and ephedrine-HCl + 0,1 $\text{mol} \cdot \text{kg}^{-1}$ D-lactose have been investigated in different temperature and molality ranges: from (293.15 to 313.15) K and from (0.05 to 0.5) $\text{mol} \cdot \text{kg}^{-1}$, respectively. In order to study interactions between solute and solvent, besides obtained experimental results for density and viscosity computational calculations were conducted. From calculated apparent molar volumes, apparent molar volume at infinite dilution, *Hepler*'s coefficient and viscosity *B*-coefficients for investigated systems, their structure *making/breaking* properties were discussed. The tastes of investigated systems were evaluated through calculated values of apparent specific molar volumes at infinite dilution. All studied systems of selected psychoactive substances and their precursors were found to have *structure making* properties (the systems with lactose have atypical *structure making* properties), which indicates a reduction in the mobility of water molecules and the appearance of a bitter taste. By adding lactose to these systems, the bitter taste becomes more pronounced compared to these systems in water.

Spectrofluorometric measurements in combination with computational simulations and molecular docking were carried out for the aqueous systems containing *N*-ethylpentylone, MDMA-HCl and MDMA-HCl + 0.1 $\text{mol} \cdot \text{kg}^{-1}$ D-lactose. Also, an intermolecular deactivation of ethidium bromide (EB) complex with DNA was investigated in the presence of *N*-ethylpentylone. Obtained results indicated good affinity and efficiency of *N*-ethylpentylone to substitute EB from the EB-DNA complex via intercalation mode. Using molecular docking, it was found that the binding energy obtained for *N*-ethylpentylone indicates its higher affinity to interact with DNA, comparing to methamphetamine and amphetamine, but lower compared to ecstasy.

The tests carried out in this work will significantly contribute to the improvement of the understanding of the therapeutic and toxicological potential of the studied psychoactive substances and their precursors, and at the same time additionally indicate certain forensic specificities of them.

Acknowledgements: The acknowledgement for the support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200125)

P39

Application of thin-layer chromatography in the assessment of *N*,*N* - disubstituted chloroacetamides' bioactivity properties

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The first steps in drug development process include complex screenings from usually a large number of compounds, identification of those with an increased probability to be active, their iterative structural modification and modeling of their pharmacokinetics, toxicity and safety. The quantification of the effect of structural changes on the relevant physico-chemical property and bioactivity of the examined newly synthesized or still unsynthesized compounds is possible by application of structure-activity relationships methods. Among numerous molecular descriptors used for established these relationships, lipophilicity is the most frequently used because it is closely related to the bioavailability of the substance and has a crucial role in defining its pharmacokinetic and pharmacodynamic profile.

Lipophilicity of novel derivatives of *N*,*N*-disubstituted chloroacetamides was determined computationally as well as experimentally by using reversed-phase thin-layer chromatography (RPTLC18F254s) in the presence of the selected protic and aprotic organic modifier. The chromatographic behavior of the studied chloroacetamides is influenced to a greater extent by the nature of the present substituent in the molecule and less by the nature of the used organic modifier. Chromatographic parameters of chloroacetamides, R_M^0 and m, as alternative measures of their lipophilicity were correlated with the software obtained values of the standard measure of lipophilicity, logarithm of partition coefficient, log$P$, and selected pharmacokinetic parameters, whereby valid mathematical models were obtained.

Acknowledgements: The authors gratefully acknowledge the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-47/2023-01/200125).

P40

The interactions of biologically activevanillin derivatives with biomolecules

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Due to increased antibiotic resistance, in recent years there has been a growing interest in the discovery of new antimicrobial agents from different sources. Bacteria that are resistant to most antibiotics are a global public health concern [1-2]. With the aim of finding a new antimicrobial drug, we tested two vanillin derivative compounds on some Gram-positive(Staphylococcus aureus and Bacillus subtilis) and Gram-negative bacteria strains (*Klebsiella oxytoca, Proteus mirabilis and Escherichia coli*), and fungi (*Trichophyton mentagrophytes, Mucor mucedo, Penicillium italicum, Aspergillus flavus and Aspergillus niger*). Both compounds showed very good antibacterial activity against *Staphylococcus aureus* and *Bacillus subtilis*, respectively. *Trichophyton mentagrophytes* proved to be the most sensitive of the tested species regarding antifungal activity.

Also, research was conducted on biomolecule bovine serum albumin. Examining these interactions, we concluded that both compounds have the appropriate affinity for binding to bovine serum albumin, which is of vital importance. To determine the binding position of our compounds to BSA (site I and/or II), competition experiments were performed with site markers such as eosin (site I) and ibuprofen (site II) [3].

Further, to investigate potential antitumor activity, the interactions with DNA have been conducted. Examining the interactions between our compounds and DNA using fluorescence, we concluded that our compounds interact with the DNA molecule through intercalation, which was additionaly confirmed by viscosity measurements. In addition, a molecular docking study was performed to investigate the binding mode of the tested vanillin derivatives to DNA and bovine serum albumin. In conclusion, all the results indicate a great potential for the future application of these compounds in clinical practice in the future [3].

Acknowledgements: This work was supported by the Serbian Ministry of Education, Science and Technological Development (Agreement No. 451-03-47/2023-01/ 200122).
This contribution is based upon work from COST Action CA18202, NECTAR – Network for Equilibria and Chemical Thermodynamics Advanced Research, supported by COST (European Cooperation in Science and Technology).

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P41

Physicochemical properties of metformin hydrochloride aqueous solutions

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Metformin is a biguanide used mainly for the treatment of non-insulin-dependent diabetes mellitus. While the antidiabetic effect of metformin, usually in the form of metformin hydrochloride (Figure 1), is well documented, its taste is rather bitter, leading to problems in patient compliance with this drug [1]. In combination with a suitable anion which would replace the chloride anion, its taste and even its pharmacological properties could be improved. Combining metformin cations with a pharmacologically active anion makes it possible to obtain new salts or ionic liquids with double or even synergistic action as drugs [2].

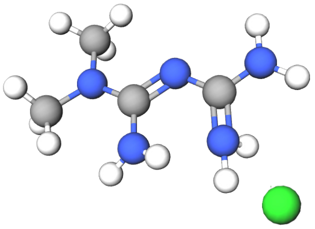

Figure 1. 3D model of metformin HCl

To better understand the behavior of metformin hydrochloride in the presence of some pharmaceutically important anions, the density, sound velocity, and viscosity of metformin hydrochloride water solutions and solutions in 0.1 molar solutions of acesulfame potassium, sodium saccharin, glutamine, and sodium salicylate in the temperature range from 278.15 K to 318.15 K were measured in a concentration range of 0.02 to 0.1 $mol \cdot kg^{-1}$. From the experimental data (Figure 2), the value of the Masson slope (Sv) was determined and found to be negative, suggesting relatively weak interactions between metforminium and hydrochloride ions. The viscosity coefficient B of the Jones-Dole equation was found to be positive and decreases with temperature, indicating that this substance acts as a structure maker in water. The values of the apparent molar volume (V_ϕ), the apparent molar volume at infinite dilution (V_ϕ^0), the Hepler coefficient, the apparent molar limiting expansion (E_ϕ^0), the hydration number, and the thermodynamic parameters of viscous flow was estimated and will be further discussed in terms of solute-solute and solute-solvent interactions.

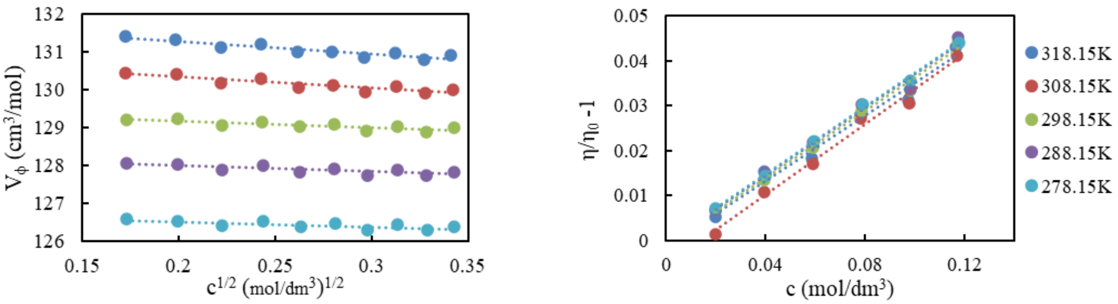

Figure 2. The dependency of a) apparent molar volume, V_ϕ on the square root of concentration and b) the reduced viscosity, η/η_0 -1, on concentration of metformin in a water solution within a temperature range from 278.15K to 318.15 K

Acknowledgements: A.V. is grateful to the Erasmus mobility program for enabling him to perform the necessary measurements at the University of Ljubljana.

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P42

Formation and evolution of an oxide film on titanium alloys of the first circuit of a nuclear reactor with a water coolant

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In the nuclear power industry, titanium alloys are widely used as construction materials for heat exchange equipment at stationery and transport nuclear power plants (NPPs). High mechanical strength and radiation resistance as well as a low cross-section of neutron activation reactions of titanium allow us to count on the further use of these materials in the design of nuclear power plants - in particular, as materials for the shells of fuel elements and reactor housings. In the primary circuit, a solid protective oxide layer on the surface of construction materials is formed consisting of titanium dioxide on top of which discrete crystallites composed of complex oxides of titanium and other metals forming during the corrosion process present. The study of their formation is a fundamental basis necessary to solve actual problems of corrosion prevention, ensuring stable heat exchange, and decontamination of surfaces.

In this communication, we are going to present the results of model autoclave experiments simulating the conditions of the light-water nuclear reactor first circuit. Surface studies were carried out using SEM and EDX methods, and the compositions of solutions were determined using ESI-MS and ICP-AES. Experiments have shown that the fast growth of oxide film takes place only during the first week of the experiment. The resulting oxide film consists of a mixture of oxides, dense (100-200 nm) and loose (600-1000 nm) layers stand out in it. Study of solutions have shown that Ti dissolves first, followed by polymerization of hydroxo forms in solution, their precipitation and dehydration leading to the formation of oxide compounds, and then solid-phase transformation of oxide forms occurs.

Acknowledgements: This study was supported by Russian Science Foundation (grant 22-29-00604). Authors acknowledge Saint-Petersburg University Research Park (Centre for X-Ray Diffraction Studies and Chemical Analysis and Materials Research Centre) for their assistance in experimental work.

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Theoretical investigation of melt-vacuum and melt-scCO$_2$ interfaces using molecular dynamics: the case of curcumin

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Supercritical solvents, such as supercritical water or supercritical CO$_2$ (scCO$_2$), offer many advantages over their traditional, often organic, counterparts. In particular, they are often more environmentally friendly, safer (often non-flammable, non-explosive), cheaper and easy to separate from the solute if needed. Moreover, supercritical fluids have wide ranges of viscosities, densities and diffusivities that can be "tuned" by varying the thermodynamic conditions (temperature, pressure).

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 (scCO$_2$ 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-scCO$_2$ 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, scCO$_2$ 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 scCO$_2$) 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.

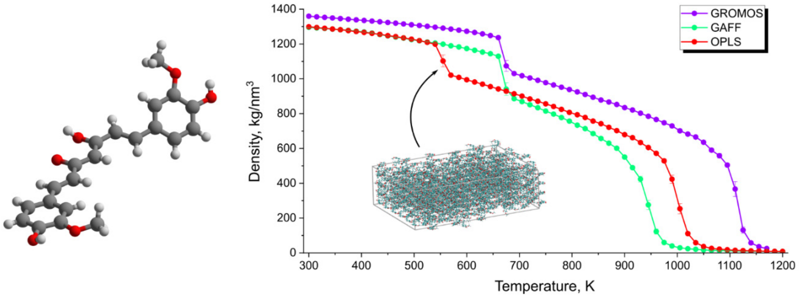

Figure 1. Curcumin (left) and the dependence of the density of curcumin on temperature (right).

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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[2] H. Hatcher, R. Planalp and J. Cho, Cell. Mol. Life Sci., 2008, 65, 1631.

P44

Poly(diallyldimethylammonium) chloride in water and in a salt solution: Chain conformation and ion mobility from molecular dynamics

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Poly(diallyldimethylammonium) chloride (PDADMAC) is an important water-soluble cationic polyelectrolyte used as a coagulant/flocculant in water treatment and as a surface modifier in different industrial and biomedical applications. In the present work, full-atomic molecular dynamics modeling of PDADMAC in water and in an aqueous solution of NaCl has been performed using OPLS-AA force field and SPC/E model for water. Structural characteristics (chain conformations, distribution of ions around the chain), ion diffusion coefficients and electrophoretic mobility are estimated from the simulations and compared with available experimental data and with simulations by other authors who used more approximate models.

The preferred polycation conformation looks like a sequence of stretched fragments separated by kinks (Figure 1). Adding the salt to the aqueous solution makes the chain only slightly more compact, despite significant counterion condensation.

The combined impact of the polyion concentration and the periodicity of MD environment (finite box size) on the calculated transport characteristics is appreciable but not substantial.

The diffusive behavior of polycations for different chain lengths (from 20 to 400 monomers) is examined, as well as ionic migration under electric field, with the competition between the external field and ionic interactions affecting the transport characteristics.

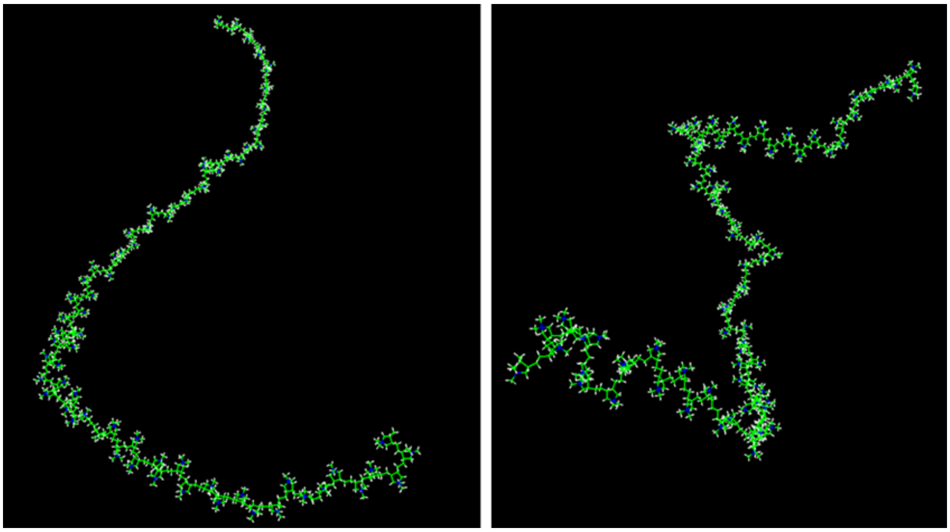

Figure 1. Typical conformations of a poly(diallyldimethylammonium) cation chain (the polymerization degree is 80) in water (left) and in 0.504*m* aqueous solution of NaCl (right).

Acknowledgements: We thank Russian Science Foundation (project 20-13-00038) for financial support. The calculations were partly performed at the Research Park of St. Petersburg State University using the Computer Center facilities.

P45

Nonaqueous analogues of aqueous two-phase systems based on formamide

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In recent years, in the field of extraction techniques and phase equilibria, aqueous two-phase systems have attracted a lot of attention. There appears a miscibility gap in the liquid phase in these systems which is formed by two incompatible compounds mixed with water. In our work we were looking for an analogues system, where the water would be replaced by an organic and strongly polar solvent. Such research has almost never been undertaken before [1-2].

It was proved that such a phenomenon is equally common in nonaqueous mixtures. Our latest work provided information on the formation of a miscibility gap in more than 300 systems (of more than 2500 checked), by addition of salt or carbohydrated to a mixture composed of two fully miscible organic solvents [3]. Among them, phase separation was most often observed when formamide was the substitute of water. Having this in mind, I investigated the liquid-liquid equilibria in several formamide systems, namely: formamide + {acetonitrile + D-fructose}, or {pentan-1-ol + NaBr}, or {pentan-1-ol + $NaNO_3$}, or {butan-1-ol + $NaNO_3$}, or {butan-1-ol + D-sorbitol}. Additionally, the water + acetonitrile + D-fructose was measured for comparison. The temperatures at which liquid biphasic mixtures becomes homogenous was detected for known overall composition. This way the points located on the binodal $T(x_1,x_2)$ surface was detected. Exemplary diagram is depicted on fig. 1.

For the collected data the correlations were made using typical empirical equations, with parameters expressed by the appropriate temperature function. For most applications, the following equation turned out to be sufficient: $x_1 = a(T) + b(T)\ln x_2 + c(T)x_2$. The temperature dependence was assumed to be linear with respect to temperature or its reciprocal.

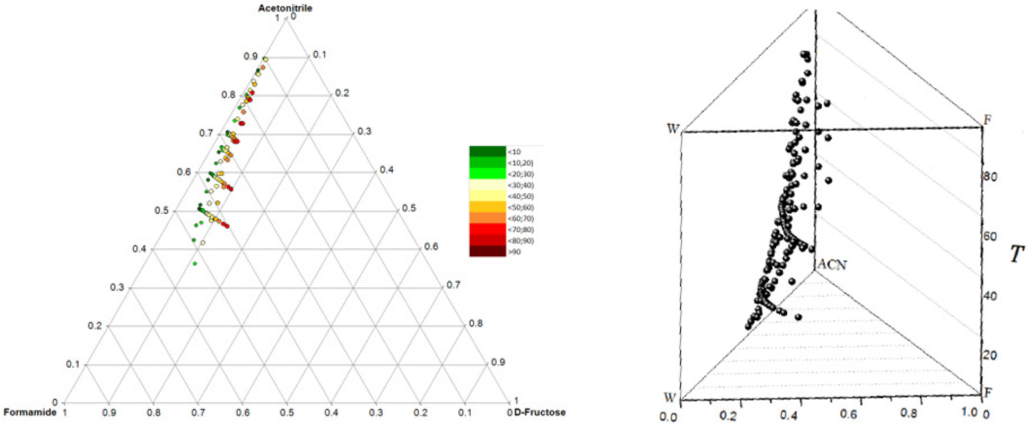

Figure 1. Liquid-liquid equilibria in formamide + acetonitrile + D-fructose (left) and in water + acetonitrile + D-fructose (right) systems (concentration in mole fractions). On the left, the points were projected onto the Gibbs triangle.

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[2] J. Liu, J. Zhao and Z. Chen, *Acta Phys. - Chim. Sin*. 1982, **22**, 845-850.
[3] P. Sikorski, W. Tomaszewski, K. Kosiek and T. Hofman, *Fluid Phase Equilib*. 2023, **570,** 113790.

P46

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. While 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, 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.

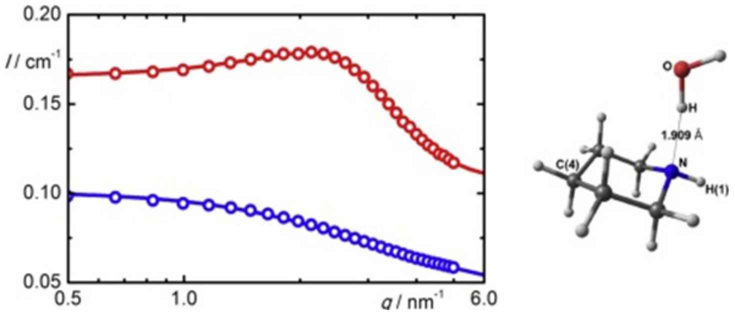

Figure 1. Small angle neutron scattering of piperidine clusters in water and ab initio structure of piperidine-water complex in vacuum.

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