Euchemsil 2024

29th EUCHEMS Conference on Molten Salts and Ionic Liquids

22-26th April 2024 Santiago de Compostela, Spain

Book of Abstracts

USC
UNIVERSIDADE
DE SANTIAGO
DE COMPOSTELA

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EUROPEAN SOCIETY OF IONIC MATTER

Welcome Address

On behalf of the local organizing committee, I am delighted to welcome you to this 29th International Conference Euchem on Molten Salts & Ionic Liquids hold in the University of Santiago de Compostela. It is very gratifying to see more than 130 colleagues from Europe and the rest of the world gathered for this very relevant conference on the rapidly evolving fields of densely ionic liquids and molten salts. The meeting evidently will promote discussions and cross-fertilization of people working and researching long distance apart. We all appreciate physical meetings, which cannot be replaced by everyday online connections.

I hope you will find attractive the scientific and social programs, as well as the venue and the city that hosts the meeting for the first time in Spain in the already very long series dating back to 1966 in Norway. I hope you enjoy the visit and these days in Santiago de Compostela, the end of the Camino de Santiago, the unique and ancient medieval route that reunited Europe again after the long centuries following Rome's decadence. Goethe's sentence "Europe was made in the pilgrimage to Santiago de Compostela" brilliantly embodies the deep European tradition of the city and its inseparable University. We are proud of our tradition and of our university, with its secular tradition of excellence and service to Galicia, an autonomous historic nationality of Spain with an ancient and deeply influential culture, and unmatched landscapes.

Luis Miguel Varela

Luis M. Varela
Full professor of Condensed Matter Physics
Chair of 29th Euchemsil Conference on Ionic Liquids and Molten Salts

Foreword

The 29th International Conference Euchem on Molten Salts & Ionic Liquids builds on a highly successful series starting in Norway in 1966. This meeting is promoted by the European Chemical Society and this edition locally co-sponsored by the European Society on Ionic Matter and the University of Santiago de Compostela with a local organizing committee made up with members its Physics Faculty.

The aim of the conference is to cover fundamental aspects, applied research and industrial applications of **ionic liquids and molten salts, promoting cross-fertilization between both research communities**. The conference will host invited presentations by high-impact speakers from the international academic community, oral and poster presentations and will be attended by **more than 130 participants** from all over the world. Moreover, it will include for the first time in the series a **special roundtable on molten salts** and its energy and industrial applications. The contributions to the conference will be published as **special editions of the Journal of Molecular Liquids and Frontiers in Chemistry**.

The Venue

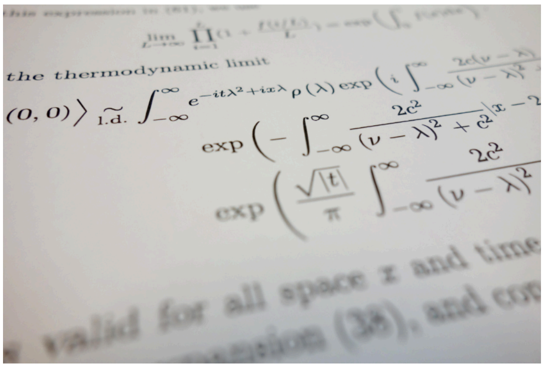
The iconic city of **Santiago de Compostela**, capital of Galicia and see of the Parliament of the region the most ancient university of Galicia and of an Archbishopric, is globally famous for its **iconic cathedral** placed at the end of the Camino de Santiago, destination of the hundreds of thousands of pilgrims from all over the world who make their Camino every year.

The ancient city of Santiago includes an **immense heritage** of churches, monasteries, and palaces, scattered along streets and squares that configure a unique stone monument which has been a **UNESCO World Heritage Site since 1985**, and is world-known as one of the three great pilgrimage centers of Christianity, along with Jerusalem and Rome, hosting the tomb of the apostle Santiago the Greater.

The **University of Santiago de Compostela** is one of the university institutions with a longer and great tradition in Europe offering a significant number of doctoral programs. **More than 260 research teams**, belonging to the different Departments and Research Institutes, has allowed a wide technological cooperation with regional, national, and international institutions, companies, and small and medium-sized enterprises. During the conference, its unique heritage will be toured, including that of the **conference venue, the Chemistry Faculty**, an iconic historic center of the science departments.

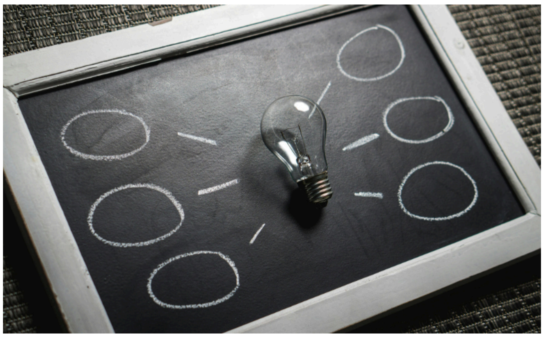
Scientific Committee

- Oscar **Cabeza Gras** (President)
- Christian **Schröder**
- Catherine **Bessada**
- Mathieu **Salanne**
- Andrea **Mele**
- Anna **Martinelli**
- Mireille **Turmine**
- Vasileios **Dracopoulos**
- Luis M. N. B. F. **Santos**
- Bernhard **Roling**
- Vladislav **Ivaništšev**



Organizing Committee

- Luis M. **Varela Cabo** (Chair)
- George **Chen** (Vice Chair)
- Josefa **Salgado Carballo** (Vice Chair)
- Hadrián **Montes Campos** (Secretary)
- María **Villanueva López**
- Elena **López Lago**
- Juan José **Parajó Vieito**
- Trinidad **Méndez Morales**



Conference Schedule

General Schedule

	Monday	Tuesday	Wednesday	Thursday	Friday
8:30		Registration			
8:45					
9:00		Openning	Invited Speaker, Properties: **H. Rodriguez** (USC, Spain) (9:00-9:45)	Invited Speaker, Synthesis, Catalysis and Recovery: **J. Dupont** (UM, Spain and FURG, Brazil) (9:00-9:45)	Invited Speaker, Devices and Applications: **J. Jacquemin** (U. Tours, France) (9:00-9:45)
9:15		Invited Speaker, Theory and Computation: **S. Lam** (UMass Lowell, USA) (9:15-10:00)			
9:30					
9:45			Oral presentations: Properties III **O19-O23** (9:45-11:00)	Oral presentations: Synthesis, Catalysis and Recovery I **O44-O48** (9:45-11:00)	Oral presentations: Devices and Applications II **O61-O65** (9:45-11:00)
10:00		Oral presentations: Theory and Computation I **O01-O04** (10:00-11:00)			
10:15					
10:30					
10:45					
11:00		Coffee Break			
11:15					
11:30		Keynote Speaker, Theory and Computation: **D. Diddens** (HI MS, Germany) (11:30-12:00)	Keynote Speaker, Properties: **M. Bendova** (UCT Prague, Portugal) (11:30-12:00)	Keynote Speaker, Synthesis, Catalysis and Recovery: **TBA** (11:30-12:00)	Keynote Speaker, Devices and Applications: **C. Pozo-Gonzalo** (Deakin University, Australia) (11:30-12:00)
11:45					
12:00		Oral presentations: Theory and Computation II **O05-O09** (12:00-13:30) Oral presentations: Devices and Applications I: **O55-O60** (12:00-13:30)	Oral presentations: Properties IV **O24-O28** (12:00-13:30) Oral presentations: Molten Salts I **O29-O33** (12:00-13:30)	Oral presentations: Synthesis, Catalysis and Recovery II **O49-O54** (12:00-13:30) Oral presentations: Molten Salts III: **O40-O43** (12:00-13:30)	Oral presentations: Devices and Applications III **O66-O71** (12:00-13:30)
12:15					
12:30					
12:45					
13:00					
13:15					
13:30		Lunch Break			**Closure**
13:45					
14:00					
14:15					
14:30		Poster Session (14:30-15:00)			
14:45				**Flash Oral Presentations** (14:45-16:00)	
15:00		Invited Speaker, Properties: **Andreas Taubert** (Universität Potsdam, Germany) 15:00-15:45	Invited Speaker, Molten Salts: **G. M. Haarberg** (NTNU, Norway)		
15:15					
15:30					
15:45		Oral presentations: Properties I **O10-O14** (15:45-17:00)	Special Session Molten Salts. Keynote Speaker: **M. Ether Rojas** (15:45-16:15) and Round-table (16:15-17:30)		
16:00	Registration			Poster Session (16:30-17:00)	
16:15					
16:30				**Social Event**	
16:45					
17:00		Coffee Break			
17:15					
17:30		Keynote Speaker, Properties: **Jose Costa** (UPorto, Portugal) 17:30-18:00	Coffee Break		
17:45					
18:00		Oral presentations: Properties II **O15-O18** (18:00-19:00)	Oral presentations: Molten Salts II **O34-O39** (18:00-19:30)		
18:15					
18:30					
18:45					
19:00	Reception	**Social Event: Camino de Santiago**			
19:15					
19:30					
20:30					
21:00					
21:30				Conference Dinner	

Detailed Program

Day	Hour	Code	Presentation	Author	Title
Tuesday	9:15	I1	Invited Presentation	LAM, Stephen	Artificial Intelligence-Enhanced Understanding and Prediction of Molten Salt Structure and Property
Tuesday	10:00	O01	Oral Presentation	IVANISTSEV, Vladislav	Ionic liquid–electrode interface: partial charge transfer, surface dipole, and quantum capacitance
Tuesday	10:15	O02	Oral Presentation	MACÍAS-SALINAS, Ricardo	Use of a Modified Free-Volume Theory for the Viscosity Modeling of Ionic Fluids
Tuesday	10:30	O03	Oral Presentation	DUCZEK, Carolina	Modelling Mass Transport in NaCl and ZnCl2 Containing Electrolytes
Tuesday	10:45	O04	Oral Presentation	MARTÍNEZ-CRESPO, Pablo	Machine Learning of Interatomic Potentials for Molecular Dynamics
Tuesday	11:30	K1	Oral Presentation	DIDDENS, Diddo	Ion transport mechanism in ionic liquids and related electrolytes: the hydrodynamic picture
Tuesday	12:00	O05	Keynote Presentation	SCHRÖDER, Christian	Decomposition, interpretation and prediction of various ionic liquid solvation parameters: Kamlet-Taft, Catalan and Reichardt's ETN
Tuesday	12:15	O06	Oral Presentation	OTERO-LEMA, Martín	Molecular mechanisms of H2/N2 uptake in bulk and confined ionic liquids
Tuesday	12:30	O07	Oral Presentation	VOROSHYLOVA, Iuliia	Charge Screening at Ionic Liquid-Electrode Interfaces
Tuesday	12:45	O08	Oral Presentation	SCHAMMER, Max	Influence of Solvation on the Structure of the Electrochemical Double Layer: A Continuum Approach for Ionic Liquids
Tuesday	13:00	O09	Oral Presentation	CABEZA, Oscar	New insights on the electrical conductivity of high concentrated electrolytes
Tuesday	12:00	O55	Oral Presentation	PEREIRA, Jorge F. B.	Towards the industrial implementation of cholinium chloride-based aqueous biphasic systems (ABS) – Phase separation hydrodynamics and best biphasic region of operation
Tuesday	12:15	O56	Oral Presentation	BASSON, Jonathan	Ionic liquids and deep eutectic solvents as alternatives to glycerol for plasticization of starch
Tuesday	12:30	O57	Oral Presentation	MEZZETTA, Andrea	Alternative process for the valorisation of microalgal biomass
Tuesday	12:45	O58	Oral Presentation	GUAZZELLI, LORENZO	Natural Deep Eutectic Solvents and bio based-Ionic Liquids for the valorisation of agri-food industry wastes
Tuesday	13:00	O59	Oral Presentation	FARINHA, Artur	Influence of Ionic Liquids on the Growth of Organic Semiconductor Films via Vapor Deposition
Tuesday	13:15	O60	Oral Presentation	MARTÍNEZ-RICO, Óscar	Towards the circular economy in the textile industry: using Deep Eutectic Solvents to decolorize wastewaters and cotton
Tuesday	15:00	I2	Invited Presentation	TAUBERT, Andreas	Having fun with zwitterions: from hydrogels to ionic liquid crystals
Tuesday	15:45	O10	Oral Presentation	RUSSINA, Olga	Solvation of simple and complex carbohydrates in ionic liquids and deep eutectic solvents

Detailed Program

Day	Hour	Code	Presentation	Author	Title
Tuesday	16:00	O11	Oral Presentation	ITOH, Toshiyuki	Origin of Moisture Absorption Capability of Ionic Liquids
Tuesday	16:15	O12	Oral Presentation	ANDRÉ, Julien	The selective leaching of gold by deep eutectic solvents: strengths and limitations
Tuesday	16:30	O13	Oral Presentation	MALHERBE, Cedric	Studying the solvation of the proton in imidazolium ionic liquids using Raman Spectroscopy
Tuesday	16:45	O14	Oral Presentation	KAMIMURA, Akio	A new way to control the solubility of ionic liquids
Tuesday	17:30	K2	Keynote Presentation	COSTA, José	Exploring Morphology, Wettability, and Vacuum Applications of Ionic Liquid Films
Tuesday	18:00	O15	Oral Presentation	MELE, ANDREA	Effect of hydrated ionic liquids and deep eutectic solvents on the thermal transitions of DNA
Tuesday	18:15	O16	Oral Presentation	BUSATO, Matteo	A multidisciplinary approach to unveil the structural arrangement of deep eutectic solvents upon cosolvent addition: from local order to nanoscale organization
Tuesday	18:30	O17	Oral Presentation	SILVA, Rodrigo M. A.	Thermodynamic study of ionic liquids with fluorinated cations
Tuesday	18:45	O18	Oral Presentation	SHAH, Faiz Ullah	Fluorine-Free Electrolytes: Why and How?
Wednesday	9:00	I3	Invited Presentation	RODRÍGUEZ , Héctor	Ionic liquids for a better exploitation of (ligno)celluloses in the biorefinery context
Wednesday	9:45	O19	Oral Presentation	TOWERS TOMPKINS, Frances	Electronic effect of the metal cation on the anion: implications for the reactivity of ionic liquids and concentrated electrolytes
Wednesday	10:00	O20	Oral Presentation	HESSLING, Janis	Influence of internal interfaces on the structure and dynamics of IL-based electrolytes confined in a metal-organic framework
Wednesday	10:15	O21	Oral Presentation	MOTTA, Daniele	A comprehensive study of NaCl-polyol mixtures: affordable and green electrolytes for electrochemical energy storage systems
Wednesday	10:30	O22	Oral Presentation	RODRÍGUEZ FERNÁNDEZ, Carlos Damián	The effect of charge delocalization in the dispersion of the refractive index of ionic liquids
Wednesday	10:45	O23	Oral Presentation	ROCHA DE MORAES, Beatriz	Unveiling the molecular interactions in ether functionalized ionic liquids utilizing DMSO as a molecular probe
Wednesday	11:30	K3	Keynote Presentation	BENDOVÁ, Magdalena	Exploring Morphology, Wettability, and Vacuum Applications of Ionic Liquid Films
Wednesday	12:00	O24	Oral Presentation	GUTIERREZ VEGA, Alberto	Exploiting monoterpenoids in type V deep eutectic solvents: A combined high-pressure experiments and theoretical approach for enhanced carbon dioxide and nitrogen absorption
Wednesday	12:15	O25	Oral Presentation	DI PIETRO, Maria Enrica	A deep dive into structure and dynamics of sustainable hydrophobic eutectics and eutectogels
Wednesday	12:30	O26	Oral Presentation	AROSA, Yago	Investigating the non-linear properties of ionic liquids based on the [NTf2] anion through Z-scan

Detailed Program

Day	Hour	Code	Presentation	Author	Title
Wednesday	12:45	O27	Oral Presentation	D'ANGELO, Paola	Structural Characterization of Lanthanum(III) Solutions in Ethyl Ammonium Nitrate (EAN) Mixtures with Water and Methanol
Wednesday	13:00	O28	Oral Presentation	GLAVATSKIH, Sergei	Self-assembly and lubricity of orthoborate ionic liquids
Wednesday	12:00	O29	Oral Presentation	WEBER, Norbert	Sodium-Zinc molten salt batteries
Wednesday	12:15	O30	Oral Presentation	ATWI, Lamis	Composite solid oxide/molten hydroxide electrolyte for ammonia fuel cell
Wednesday	12:30	O31	Oral Presentation	COSTANTINE, Joelle	Electrochemical behavior of thorium in chloride molten salt
Wednesday	12:45	O32	Oral Presentation	LAIR, Virginie	Molten carbonates towards new CO2 conversion
Wednesday	13:00	O33	Oral Presentation	NOEL, Corentin	The use of molten carbonates for CO2 valorization into calcium oxalate.
Wednesday	15:00	I4	Invited Presentation	HAARBERG, Geir Martin	Electrowinning of Aluminium from Molten Salts Electrolytes
Wednesday	15:45	K4	Keynote Presentation	ROJAS BRAVO, M. Esther	Molten Salts in Thermal Storage Systems
Wednesday	18:00	O34	Oral Presentation	BESSADA, Catherine	From fluorides to chlorides in nuclear energy : detection of anionic complexes by NMR, EXAFS and MD at high temperature.
Wednesday	18:15	O35	Oral Presentation	CARRIÈRE, Charly	New insight of redox potential control by titanium chloride in molten salt: prospects for metals protection?
Wednesday	18:30	O36	Oral Presentation	RAKHMATULLIN, Aydar	Reaction of aluminium metal with NaF-ScF3 melt: Investigation of formation of aluminium-scandium alloy
Wednesday	18:45	O37	Oral Presentation	CARRE, Ludovic	Polymer conversion from pyrochemistry in molten salt for production of hydrogen, carbonates, and energy recovery.
Wednesday	19:00	O38	Oral Presentation	HAMZA, Letissia	Study of the dissolution rate of Mg in NaOH-KOH (51.5-48.5 mol%) eutectic melts at 225°C
Wednesday	19:15	O39	Oral Presentation	CARETERO, Théo	Uranium species stability in molten LiCl-KCl
Thursday	9:00	I5	Invited Presentation	DUPONT, Jairton	Zwitterionic Solutions for Carbon Dioxide Capture and Transformation
Thursday	9:45	O44	Oral Presentation	AHMED, Mukhtiar	Fluorine-Free Ionic Liquids and Electrolytes: From Synthesis to Energy Storage Applications
Thursday	10:00	O45	Oral Presentation	ANTZUTKIN, Oleg N.	Non-Halogenated Functionalised Ionic Liquids
Thursday	10:15	O46	Oral Presentation	CASTIGLIONE, Franca	Eutectogel formulations for cancer therapy: the codelivery of 5-fluorouracil and ibuprofen

Detailed Program

Day	Hour	Code	Presentation	Author	Title
Thursday	10:30	O47	Oral Presentation	GARCIA-VERDUGO, Eduardo	Click Chemistry: An Efficient Approach for the Synthesis and application of task-specific ionic liquids.
Thursday	10:45	O48	Oral Presentation	CAETANO, Gabriela	Development of Poly(ionic liquid)s for Removal and Electrochemical Degradation of Azo Dyes
Thursday	11:30	K5	Keynote Presentation	ILIEV, Boyan	Scaling-up Ionic Liquids Production for Industrial Applications
Thursday	12:00	O49	Oral Presentation	SÁNCHEZ, Julián	Efficient Catalytic Hydrogenation of CO2 derived Compounds over Organometallic Supported Ionic Liquid Phases
Thursday	12:15	O50	Oral Presentation	PICCOLI, Vinicius	How do drugs dissolve in deep eutectic solvents?
Thursday	12:30	O51	Oral Presentation	SCHAEFFER, Nicolas	Water-in-salt solution as leaching media for the recovery of platinum group metals from catalytic converters
Thursday	12:45	O52	Oral Presentation	LEGEAI, Sophie	Propeline: a green alternative to Ethaline for electrometallurgy of precious metals
Thursday	13:00	O53	Oral Presentation	GALLEGO, Cristina	Exploring the potential of eutectic solvents for the valorization of fish skin
Thursday	13:15	O54	Oral Presentation	ALVES, Alexandre	Formation and Stabilization of Silver Nanoparticles on Thin Films of Symmetric Imidazolium-Based Ionic Liquids
Thursday	12:00	O40	Oral Presentation	MORSA, Amedeo	Thermodynamics of the Mg2+, Ca2+ // Cl-, SO42- reciprocal system for the identification of potential salt-based high temperature Phase Change Materials
Thursday	12:15	O41	Oral Presentation	NG, Woei Jer	High-Temperature Nuclear Magnetic Resonance Investigation into the Structural Behaviour of Lanthanide Trichlorides in the NaCl-MgCl2 Binary Molten Carrier Salt System
Thursday	12:30	O42	Oral Presentation	FOURES, Thibaut	Influence of oxide concentration on SS316L electrochemical behaviour in molten LiCl-KCl medium
Thursday	12:45	O43	Oral Presentation	KUBIKOVA, Blanka	Solubility investigation of selected RE2O3 in (LiF-NaF)eut vs (LiF-NaF-REF3) molten systems
Thursday	14:45	FP01	Flash Oral Presentation	RIGHETTI, Grazia Isa Carla	SEED4GREEN - A seed for the green transition. Tailoring Deep Eutectic Solvents for 5-Hydroxymethylfurfural (HMF) transformation
Thursday	14:53	FP02	Flash Oral Presentation	BHAKTA, SAYANTIKA	Biomass-Derived Fluorine-Free Ionic Liquid Electrolytes: Synthesis and Energy Storage Application
Thursday	15:01	FP03	Flash Oral Presentation	ALTAVA, Belen	Hydrolysis of polyurethane foam wastes using ionic liquid-superbase catalytic systems
Thursday	15:09	FP04	Flash Oral Presentation	GUTIERREZ VEGA, Alberto	A theoretical study of low concentration per- and polyfluoroalkyl substances (PFAS) remediation from wastewater by novel hydrophobic deep eutectic solvents (HDES) extraction agents
Thursday	15:17	FP05	Flash Oral Presentation	KOEL, Mihkel	Deep Eutectic Solvents and extraction of bioactive compounds
Thursday	15:25	FP06	Flash Oral Presentation	MANNUCCI, Giorgia	Insight into the thermal and structural properties of oxalatoborate-based ionic liquids

Detailed Program

Day	Hour	Code	Presentation	Author	Title
Thursday	15:33	FP07	Flash Oral Presentation	RENSONNET, Aurelie	Probing the acidity level of ionic liquids: implementation of the Hammett acidity functions in Raman spectroscopy
Thursday	15:41	FP08	Flash Oral Presentation	KUNAPULI, Swaroop Venkata Sai	Modeling fragmentation of non-covalent molecular clusters in soft-ionisation mass spectrometry of deep eutectic solvents
Thursday	15:49	FP09	Flash Oral Presentation	KOEL, Mihkel	Supported ionic liquids for efficient thermal energy storage
Thursday	15:57	FP10	Flash Oral Presentation	VERDÍA BARBARÁ, Pedro	Evaluation of cellulosic ionogels for energy storage devices
Thursday	16:05	FP11	Flash Oral Presentation	SOUVENIR ZAFINDRAJAONA, Mahasoa Salina	Green approach for the synthesis of new biosourced ionic liquids and influence of water as a co-solvent on their physicochemical properties for biomass derivatization
Thursday	16:13	FP12	Flash Oral Presentation	BAYAZIT, Sarah	Synthesis and biological evaluation of the new derivatives of kazcaine
Friday	9:00	I6	Invited Presentation	JACQUEMIN, Johan	Current State Applications of Ionic-Based Systems in Industry and in Devices
Friday	9:45	O61	Oral Presentation	COSTA, Renata	Rethinking Circularity of Electrified Interfaces for Sustainable Energy Storage Devices
Friday	10:00	O62	Oral Presentation	ILIEV, Boyan	CO2 Capture and Conversion with Ionic Liquids – Reality or a Dream
Friday	10:15	O63	Oral Presentation	SANTIAGO-ALONSO, Antía	Ionogels: Advanced Battery technology through semisolid electrolytes with enhanced transport and thermal properties
Friday	10:30	O64	Oral Presentation	MANNU, Alberto	Eutectic mixtures from waste cooking oils: application to the recovering of critical elements from spent lithium ion batteries
Friday	10:45	O65	Oral Presentation	JORGE, Alexandre	Design of eco-friendlier cotton dyeing platforms using deep eutectic solvents and natural dyes
Friday	11:30	K6	Keynote Presentation	POZO-GONZALO, Cristina	Sustainability in the supply chain of materials vital in energy storage
Friday	12:00	O66	Oral Presentation	LAHIRI, Abhishek	Understanding the influence of anions on Zn electrochemistry in deep eutectic solvents-water mixtures for Zn-ion capacitors
Friday	12:15	O67	Oral Presentation	ABDOU, Nicole	Structural battery electrolytes: effect of composition on the physico-chemical properties.
Friday	12:30	O68	Oral Presentation	LOIS CUNS, Raúl	Optimizing hybrid water-in-salt electrolytes for energy storage
Friday	12:45	O69	Oral Presentation	ZHAO, Yansong	Application of ionic liquids in iron based battery for large scale wind energy and solar energy storage
Friday	13:00	O70	Oral Presentation	MIRANDA, Carlos	New Small-Volume Coin Cell for the Measurement of Electrical Conductivity of Ionic Fluids
Friday	13:15	O71	Oral Presentation	LORENZ, Samuel	Ionic liquid-Based Electrolytes for next Generation Batteries

Poster Contributions

Code	Author	Title
FP01	RIGHETTI, Grazia Isa Carla	SEED4GREEN - A seed for the green transition. Tailoring Deep Eutectic Solvents for 5-Hydroxymethylfurfural (HMF) transformation
FP02	BHAKTA, SAYANTIKA	Biomass-Derived Fluorine-Free Ionic Liquid Electrolytes: Synthesis and Energy Storage Application
FP03	ALTAVA, Belen	Hydrolysis of polyurethane foam wastes using ionic liquid-superbase catalytic systems
FP04	GUTIERREZ VEGA, Alberto	A theoretical study of low concentration per- and polyfluoroalkyl substances (PFAS) remediation from wastewater by novel hydrophobic deep eutectic solvents (HDES) extraction agents
FP05	KOEL, Mihkel	Deep Eutectic Solvents and extraction of bioactive compounds
FP06	MANNUCCI, Giorgia	Insight into the thermal and structural properties of oxalatoborate-based ionic liquids
FP07	RENSONNET, Aurelie	Probing the acidity level of ionic liquids: implementation of the Hammett acidity functions in Raman spectroscopy
FP08	KUNAPULI, Swaroop Venkata Sai	Modeling fragmentation of non-covalent molecular clusters in soft-ionisation mass spectrometry of deep eutectic solvents
FP09	KOEL, Mihkel	Supported ionic liquids for efficient thermal energy storage
FP10	VERDÍA BARBARÁ, Pedro	Evaluation of cellulosic ionogels for energy storage devices
FP11	SOUVENIR ZAFINDRAJAONA, Mahasoa Salina	Green approach for the synthesis of new biosourced ionic liquids and influence of water as a co-solvent on their physicochemical properties for biomass derivatization
FP12	BAYAZIT, Sarah	Synthesis and biological evaluation of the new derivatives of kazcaine
P13	CHOWDHURY, Hrishikesh	Novel Ionic Liquids: Lubricants for Space and Electrolytes for Supercapacitors
P14	RIZZI, CECILE	Extraction of Ag (I) from acidic media by CYPHOS® IL 104 involving reverse micelle
P15	SILLIKOVA, Veronika	Hydrothermal synthesis of the potassium fluoroscandates
P16	LOZANO, PEDRO	Chemo-enzymatic approaches for carbon dioxide capture and transformation to cyclic carbonate esters for Non-Isocyanate Polyurethane synthesis
P17	ANDREU OLARIA, Jose Juan	From Supramolecular differences to Bioactive properties: Highly modular Ionic Liquids based on Amino Acids
P18	CASU, Paolo	Investigating the Eutectic Mixtures formed by Choline Chloride and Hydroxyphenol Isomers
P19	FILIPPOV, Andrei	Complexation in Ionic Liquid Electrolytes Probed by Multinuclear NMR Diffusometry

Poster Contributions

Code	Author	Title
P20	KLOSINSKA, Agnieszka	Extraction properties of 1-butyl-3-methylimidazolium ionic liquids in the process of butadiene separation from C4 fraction
P21	ARRIBAS, Andrea	Deterpenation of citrus essential oil by extraction with a biocompatible ionic liquid
P22	RABELL MONTIEL, Brenda	Efficient reversible production of hydrogen with CO2 in a catalytic system employing Ru-PNP complexes and ionic liquids.
P23	MÍGUEZ-ROEL, Ángel	Structural and Dynamic Properties in Ionic Liquids Ternary Mixtures with Water as Solvent, a Computational Study
P24	VRANEŠ, Milan	Pharmaceutical Active Ionic Liquid Behavior in Natural Deep Eutectic Solvents: Insights into Solvent Composition Effects
P25	MATSELKO, Oksana	Formation of the ternary fluorides from the molten salts and by means of the mild hydrothermal synthesis
P26	MLYNÁRIKOVÁ, Jarmila	Critical evaluation of volume properties of the zirconium-based fluorides melts MF-K2ZrF6 (M = Li, Na, and K).
P27	EWAZNEZHAD FARD, Darya	Viscosity modelling of pure molten salts and their binary mixtures utilized in heat transfer and storage applications
P28	TRIOLO, Alessandro	Role of hydrogen bonding donor and anion in choline based eutectic media structural organization
P29	CÁCERES, Alexandra	Towards the use of 1-ethyl-3-methylimidazolium propionate in fish waste valorisation: solubilities
P30	DRACOPOULOS, VASSILEIOS	Gas dehumidification using supported nicotine based ionic liquid membranes
P31	GARCÍA GUIMAREY, María Jesús	Tribological Behavior of Hybrid Nanolubricants for Internal Combustion Engines
P32	GAY VILLARET, Narcís	Development of a molten salt electrorefining process suited for the recycling of HALEU fuel production scraps
P33	GINER RAJALA, Óscar	Synergies of a polyoxometalate-ionic liquid hybrid with a phosphonium ionic liquid as transmission fluid additives for electric vehicles
P34	KJAER STEFFENSEN, Astrid	Electroreductive transformations of biomass derived compounds in green solvents
P35	LIÑEIRA DEL RIO, Jose Manuel	Synergistic effects of functionalized WS2 and SiO2 nanoparticles and a phosphonium ionic liquid as hybrid additives of low viscosity lubricants
P36	ZHAO, Yansong	Ionic liquids based breath gas analysis technology for disease screening and diagnosis
P37	BOADO-FERNÁNDEZ, Miguel Ángel	Anomalous transport in Ionic Liquid Mixtures, Theoretical and Computational Modeling
P38	PAPOVIć, Snežana	Enhancing thermal and electrochemical stability of lithium-ion battery electrolytes

Poster Contributions

Code	Author	Title
P39	SOUTO-MONTERO, Paula	Acetate ionic liquids to obtain hydrolyzed collagen from tuna skin
P40	TATRARI, Gaurav	Structurally Flexible Fluorine-Free Ionic Liquid-Based Electrolytes for High-Temperature Supercapacitors
P41	VANOLI, Valeria	Menthol/Thymol DES based eutectogels as drug delivery systems
P42	LAUER BREITENBACH, Gabriela	Thiolactone Chemistry in Action: Creating Task-Specific Hybrid Systems of Functionalized Polymeric Ionic Liquids and Metallic Nanoparticles for Superior Bioactivity
P43	LOBO FERREIRA, Ana I.M.C.	Thermodynamics of alkylsilane-based ILs with different anions
P44	ZHAO, Yansong	Ionic liquid based bio-battery: A self-powered and charged free battery
P45	MARCINIAK, Andrzej	Ionic Liquids in Separation of Sulfur Compounds from LPG
P46	MU, Tiancheng	Deep Eutectic Solvent for recycling of valuable metals from spent lithium-ion battery cathodes
P47	RODRÍGUEZ DELGADO, YLENIA	Integration of experimental techniques and molecular simulations. A multi-scale approach of [EMIM][BF4] + [EMIM][EtSO4] mixture

Invited Presentations

Artificial Intelligence-Enhanced Understanding and Prediction of Molten Salt Structure and Property

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In new molten salt applications such as advanced fission, fusion, or fuel separations, the ability to monitor, test and design materials in high-temperature, corrosive, and even radioactive environments pose significant challenges to design and operation. These challenges are exacerbated by the complex multimodality of salt structures, and its generally unknown impact on thermal properties over large space composition and temperature that is possible. Modern techniques for understanding structure-property relationships such as predictive ab initio simulation or in situ structural spectroscopies are limited by efficiency or information that can retrieved under such challenging conditions. This presentation covers latest advances in applying artificial intelligence to overcome these challenges, particularly in three areas: 1) accelerating predictive simulations using deep learning surrogate models [1][2], 2) learning implicit property relationships that would otherwise be difficult to uncover with human intuition alone [3][4], and 3) enhancing spectroscopic techniques with computer vision-based learning [5]. Examples are given showing how these methods can be applied to dramatically enhance our understanding structure, thermodynamics, and thermophysical properties of molten salts.

Acknowledgements: This work is funded by DOE NE- supported by the US Department of Energy (DOE) NEUP Award DE-NE0009204 and National Science Foundation Award Number 2138456.

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Having fun with zwitterions: from hydrogels to ionic liquid crystals

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Besides many other things, zwitterions can be used to make ionic liquids, ionic liquid crystals, or ionogels. The intriguing aspect of many of these zwitterion-based (soft) material is that already the zwitterions themselves have interesting properties like rather high thermal stabilities. These properties can then further be altered and expended by making ionic liquids from these zwitterions. The group has been researching zwitterion-based materials for roughly a decade [1-5] and the presentation will introduce some of the basic concepts, molecular building blocks, and materials that have been developed. The focus of the presentation will be on a large group of zwitterions, their phase behavior, and their ion transport properties. Moreover, we will show how these zwitterions can be transformed into ionic liquid crystals with a rather high thermal stability, interesting proton transport properties, and again interesting liquid crystallin phases. Some of the zwitterions are also able to enhance the performance of enzymes or are able to stabilize rather reactive media, which would otherwise decompose relatively rapidly. Figure 1 shows the general reaction towards some of our zwitterions, a photograph of zwitterion-based hydrogels, and the texture of a zwitterion-based ionic liquid crystal recently made in the laboratory.

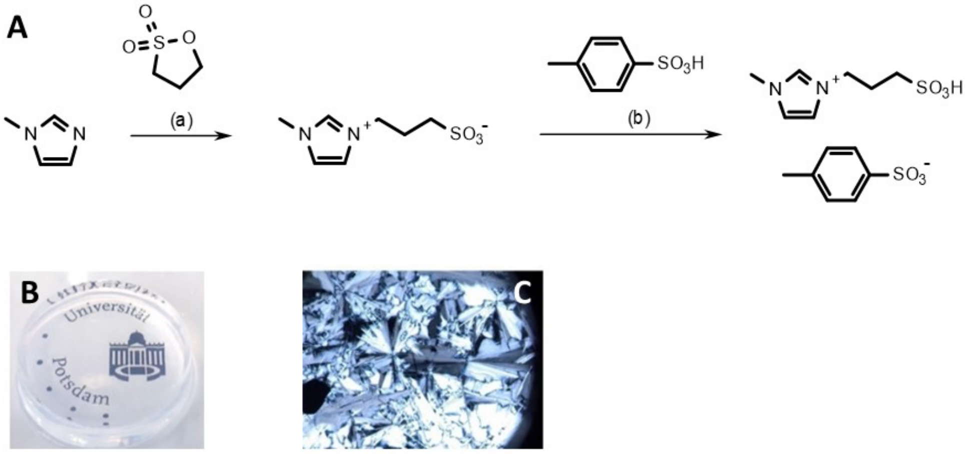

Fig. 1 A) Reaction towards some of our zwitterions and ionic liquids [1], B) photograph of zwitterion-based hydrogels [4,5], C) and the texture of a zwitterion-based ionic liquid crystal.

Acknowledgements: The author thanks A. Lange, S. Shehaj, Dr. T. Mai, Dr. R.B.J. Ihlenburg, Dr. E. Delahaye, Dr. C. Günter, Dr. K. Zehbe, S. Mies, and A. Nitschke for their efforts and hard work in generating all the wonderful data that will be presented at the conference. Funding by the University of Potsdam, the Deutsche Forschungsgemeinschaft DFG, and the Deutsche Akademische Austauschdienst DAAD is gratefully acknowledged.

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Ionic liquids for a better exploitation of (ligno)celluloses in the biorefinery context

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Lignocellulosic biomass is a resource with the potential to constitute the basis of a new technological platform for the biorenewable production of chemicals and materials. It is mainly constituted, in different proportions, by three biopolymers: cellulose, hemicellulose, and lignin; which represent a significant chemical richness already embedded in the natural raw material. In order to get a fractionation of these biopolymers and/or to improve their reactivity in subsequent transformations through biorefinery schemes, (ligno)celluloses are typically subjected to a pretreatment stage for reduction of the recalcitrance of the natural matrix. Conventional pretreatment processes rely on the use of strong acids or bases, or volatile organic solvents, and harsh processing conditions. This hampers the overall sustainability character of the promising lignocellulosic-based platform mentioned above [1].

With their great solvation ability and appealing set of properties, ionic liquids have the potential to contribute to the development of milder and more sustainable processes in the chemical industry. The particular consideration of ionic liquids in biomass pretreatment can be traced back to the discovery, in the early years of the present century, of the capacity of some ionic liquids to dissolve cellulose and lignocellulosic materials in relevant concentrations [2]. Derived from the knowledge generated in this research niche over this period, this presentation will focus on a non-dissolving approach for the pretreatment of (ligno)celluloses with ionic liquids. This approach may help to mitigate important process issues associated with the typical alternatives based on dissolution. Examples of subsequent valorisation of the constituent biopolymers will be also discussed.

Acknowledgements: The author is grateful to MCIN/AEI/10.13039/501100011033 and the European NextGenerationEU/PRTR funds for support through project TED2021-131784B-I00, and also to Xunta de Galicia (project ED431B 2020/21, co-funded by the European Regional Development Fund).

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Electrowinning of Aluminium from Molten Salts Electrolytes

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Metal production is a large and important industry worldwide and many metals and alloys have excellent properties that make them indispensable for a sustainable development of the modern society. Metal production takes place by carbothermal reduction or by using another reducing agent for iron and steel, silicon, manganese, ferro alloys, magnesium and titanium. However, electrolysis offers possibilities to reduce the carbon footprint significantly. Nickel, copper and zinc are produced by electrowinning in aqueous electrolytes. Less noble metals may be produced by molten salt electrolysis. Aluminium is by far the most important metal produced by molten salt electrolysis, around 70 million tons being produced annually [1]. Industrial processes have also been developed for alkali metals and magnesium. Other attractive candidates for future development of molten salt electrowinning are titanium, silicon, and rare earth elements especially within recycling of electronic waste.

Mixtures of salts are excellent molten electrolytes with high electrical conductivity and high thermodynamic stability. Therefore molten salt electrolytes are used for the production of reactive and less noble metals such as sodium, potassium, lithium, magnesium and aluminium.

Primary aluminium is produced by the Hall-Heroult process which is based on electrolysis in molten fluoride electrolyte, Na_3AlF_6-AlF_3, at ~960 °C in which the raw material alumina is dissolved and decomposed into pure aluminium and CO_2 gas due to the use of carbon anodes [2]. Direct CO_2 emissions are due to the anode process including perfluoro carbon (PFC) formation during anode effect. An inert anode to produce oxygen may eliminate direct CO_2 emissions including PFC gases and give possibilities to improve the cell design. CO_2 emissions from generation of electricity are the most important issue globally, especially due to the fact that the largest producer (more than 50 %) China is using coal as the source for electricity. Also the use of pure metals to produce alloys may significantly increase the carbon footprint due to the primary production of alloying elements having a high carbon footprint. A new approach to produce alloys directly during electrolysis is proposed, and results from lab experiments show that this method may give significant reduction of carbon footprint for the production of aluminium alloys. Other sources of CO_2 emissions are production and manufacture of alumina and carbon anodes as well as loss in current efficiency for aluminium. A new process based on aluminium chloride electrolysis and recycling of CO_2 may eliminate CO_2 emissions from the production process. Such an approach is under research and development by the Norwegian company Hydro.

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Zwitterionic Solutions for Carbon Dioxide Capture and Transformation

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Undoubtedly, CO_2 is no longer solely perceived as a contributor to global warming; instead, it is recognized as an abundant and cost-effective raw material. Transforming captured CO_2 into valuable products or fuels not only mitigates emissions to the atmosphere but also emerges as a pivotal solution for realizing a comprehensive carbon cycle [1]. Recent studies highlight the potential of basic phenolic zwitterionic solutions (whether aqueous or alcoholic) to replace industrially utilized aqueous amine solutions as CO_2 sorbents, offering various environmental and economic benefits [2]. In this presentation, we will explore and discuss the catalytic hydrogenation of these captured CO_2 solutions, leading to the production of methanol or formic acid, depending on the catalyst's nature and/or reaction conditions (refer to Figure 1).

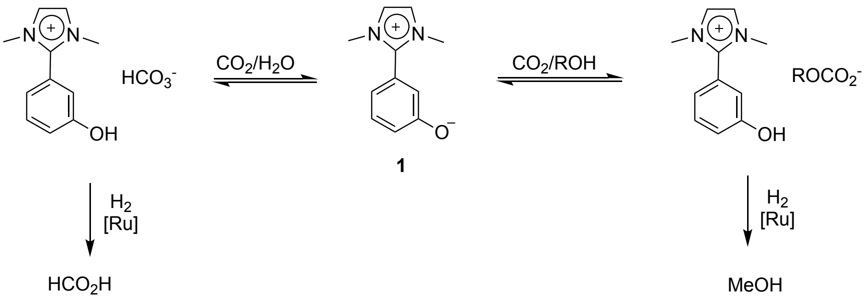

Fig. 1 Scheme showing the tandem CO_2 capture by basic (aqueous or alcoholic) solutions of zwitterion **1** and hydrogenation to methanol of formic acid by Ru-based catalysts precursors.

Acknowledgements: We are grateful to CAPES (001), FAPERGS (22/2551-0000386-9 and 18/2551-0000561-4), CNPq (406260/2018-4, 309111/2021-8), MICINN-FEDER-AEI 10.13039/501100011033 (PID2021- 124695OB-C21 and PDC2022-133313-C21), MICINN – European Union Next Generation EU-PRTR (TED2021- 129626B-C21) and SENECA (20790/PI/18) for financial support. J. D. is fellow of the "Maria Zambrano program" at the University of Murcia (Spain).

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Current State Applications of Ionic-Based Systems in Industry and in Devices

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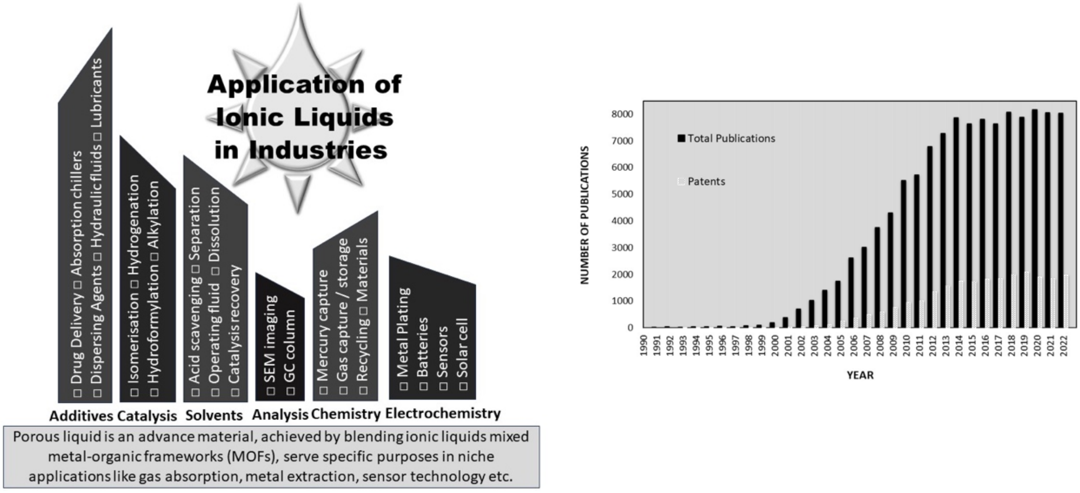
Since several decades, Ionic Liquids (ILs) have garnered substantial attention within the realm of scientific exploration, extending their versatile potential across an expansive spectrum of applications as displayed in Fig. 1. These applications encompass pivotal domains such as solvent chemistry, catalysis, and electrochemistry, where the remarkable feature of ILs, and their use when mixed with other fluids, as tailor-made solutions, both come to the fore. This unique attribute empowers researchers and industrial innovators to finely adjust their physicochemical properties to perfectly align with the requisites of specific applications, thereby heralding a new era of customization and precision in industrial processes. However, it is noteworthy that, despite the conspicuous fervor within the patent literature, the practical realization of IL-based processes into commercially viable ventures remains somewhat constrained, with only a limited cadre of such processes having successfully navigated the arduous path from laboratory innovation to industrial implementation. With this backdrop, this talk seeks to provide an insightful vantage point into the intriguing narrative of the commercialization of IL-based processes, as it stands to date, along with some prospects when formulating solutions containing at least an ionic species (Molten Salt, Deep Eutectic Solvent, IL, etc.). Through a discerning exploration of both the milestones achieved and the challenges encountered along this trajectory, advantages and disadvantages intrinsically associated with the utilization of this unique class of materials in the industrial landscape and devices will be then discussed.



a)

b)

Fig. 1. Applications Showcasing the Versatility of ILs (a), along with the evolution of publications and patents in the SciFinderTM Database (1990-2022) relating to the Concept of 'IL' (b).

Acknowledgements: This work benefited from the support of the Chair “Sustainable Energy” led by Mohammed VI Polytechnic University, sponsored by OCP.

Keynote Presentations

Ion Transport Mechanism in Ionic Liquids and Related Electrolytes: The Hydrodynamic Picture

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We present a hydrodynamic theory describing the pair diffusion in periodic systems, thereby extending earlier work on self-diffusion by other groups [1,2]. The theory describes dynamical ion correlations relevant to compute the Onsager coefficients from Molecular Dynamics (MD) simulations, which we demonstrate for two ionic liquids as well as for other electrolytes relevant for modern energy storages. Overall, we observe good agreement between theory and simulation data, highlighting that hydrodynamic interactions universally dictate ion correlations. However, when summing over all ion pairs in the system to obtain the cross-contributions to the total cationic or anionic conductivity, the hydrodynamic interactions between ions with like and unlike charges largely cancel. Consequently, significant conductivity contributions only arise from deviations from a hydrodynamic flow field of an ideal fluid, which arises due to the local electrolyte structure as well as the relaxation of the latter. For MD simulations of ionic liquids, the momentum-conservation constraint additionally is crucial, which we study by employing different ionic masses in the simulations.

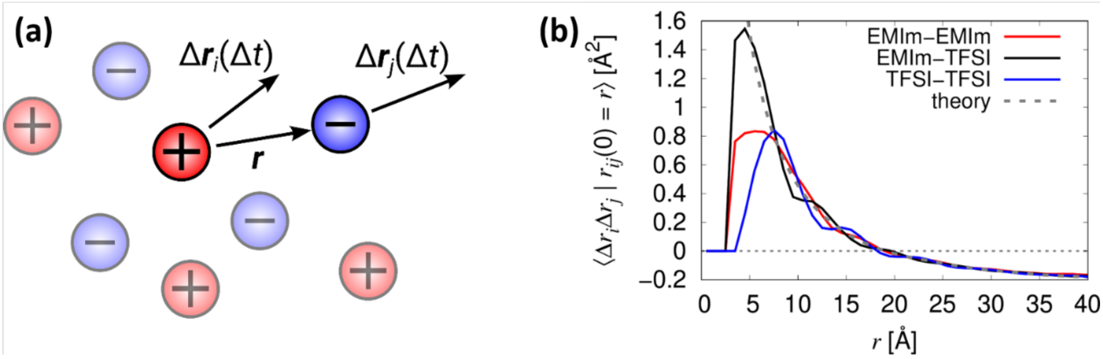

Fig. 1 (a) Schematic illustrating dynamical ion correlations contributing to the Onsager coefficients. During lag time *Δt*, the motion of each ion *i* can be characterized by its displacement vector $\Delta \mathbf{r}_i$. (b) Dependence of the average scalar product between the displacement vectors of ions *i* and *j* as a function of their initial separation *r*. For small *r*, ions of all pair types (EMIm-EMIm, EMIm-TFSI, TFSI-TFSI) move correlated, whereas a global counterflux emerges for large *r* in agreement with the theoretical prediction.

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Exploring Morphology, Wettability, and Vacuum Applications of Ionic Liquid Films

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The wetting behavior of ionic liquid (IL) films holds significant importance across diverse scientific fields and technological applications. Particularly intriguing is the behavior of ILs under vacuum conditions, which has generated significant interest in recent research [1]. Investigations in recent years have especially explored the adsorption, growth, and stability of ultra-thin IL films on metal surfaces [2]. Understanding the surface and interface properties of ILs is crucial for their application in various technologies, including as lubricants, electrolytes in batteries and supercapacitors, solid catalysts with IL layers, and interfacial layer materials fabricated by physical vapor deposition (PVD) methods.

This presentation will highlight recent advancements in the study of IL droplet/film formation through vapor deposition [3-9]. The nucleation and growth of IL films via PVD have been actively explored within our research group, employing a customized thermal evaporation procedure based on Knudsen effusion cells [3-7]. The focus has been on investigating the effects of cations, anions, and alkyl chain length on film wetting and morphology. Additionally, the impact of deposition rate, substrate temperature, and substrate roughness on nucleation, droplet formation, and spreading during film deposition has been examined.

Furthermore, potential applications of ionic liquid films, such as in the formation and stabilization of metal nanoparticles [8], will be highlighted. Emphasis will also be placed on the efficacy of IL-assisted vapor deposition in achieving high-quality and distinctive crystal film growth of organic semiconductor materials [9].

Acknowledgements
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Solution chemistry of menthol-based chiral ionic liquids in aqueous environment

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Aqueous solutions of organic and inorganic compounds, including of ionic liquids, are some of the most studied systems in physical chemistry. In spite of this, there is still a certain lack of understanding of solute-solvent interactions of ionic liquid ions with water molecules. Moreover, investigations of such systems have an increasing practical relevance, as fine tuning the properties of ionic liquids is possible not only by means of their structure modification, but also via their mixing with a suitable molecular solvent, water being a frequent solvent of choice. To fill in some of the blanks, experimental measurements of physicochemical properties and phase behaviour of these systems can be confronted with molecular dynamic simulations [1]. In a general manner, measurements of volumetric, osmometric, thermal and transport properties provide us with a wealth of knowledge on solution chemistry of aqueous solutions of ionic liquids in their own right. MD simulations then constitute a powerful tool to obtain an even deeper insight into the molecular structure of ILs in water. In turn, estimates of bulk volumetric and transport properties by simulations can be validated by the corresponding experiments.

In this contribution, this approach will be illustrated by examples of studies of volumetric, transport and osmometric properties in aqueous solutions of conventional and chiral ionic liquids (e.g. in 1-alkyl-3-[(1R,2S,5R)-(–)-menthoxymethyl]imidazolium chlorides) by means of experiments and MD simulations. In addition to binary aqueous solutions, octanol-water partitioning of the studied ILs will be discussed.

Acknowledgements: Specific university research (A1_FCHI_2022_002), the Czech Science Foundation (grant 20-24155S), MEYS e-INFRA CZ (ID:90140) and National Science Centre, Poland (Grant No. UMO-2020/37/B/NZ9/04201) are greatly acknowledged.

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Molten Salts in Thermal Storage Systems

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In this keynote it will be given an overview of the applications of certain molten salt mixtures, mainly what is known as solar salt, in long term thermal storage systems. Starting from the current commercial configuration of such systems, their goodness and challenges will be highlighted. The development of these systems achieved in concentrating solar thermal power plants has paved the way to extend their used to other applications like industrial processes, both for managing waste heat and for using thermal solar energy as primary energy source, and Carnot Batteries, which allows storing large amounts of the energy provided by electrical renewables –PV and Wind-. Worldwide singular facilities working with molten salts will presented.

Fig. 1 MOSA (Molten Salt loop) at Plataforma Solar of Almería, CIEMAT

Scaling-up Ionic Liquids Production for Industrial Applications

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The diverse areas of applications that have developed with ionic liquids in recent years have led to them no longer being viewed as laboratory curiosities, but as products of industrial interest and utility. However, one of the factors slowing this progress is the assumption that they are both expensive and not available on a large scale. A good example that allows us to refute these rumors is the scaling of ionic liquids for use as antistatic additives for plastics, glues or lubricants.

Scale-up can be achieved either through classic batch synthesis or through the use of flow microreactor technology. The latter has the advantage of a higher surface area to volume ratio, resulting in fewer hotspots, faster reaction kinetics and overall pure product results without the need for lengthy workup.

This technology offers safety benefits such as lower use of VOCs and reduced overall volume in the event of a spill. As with batch reactors, material selection is crucial for the purity of the end material, as even high-quality stainless steel is susceptible to corrosion (Fig. 1).

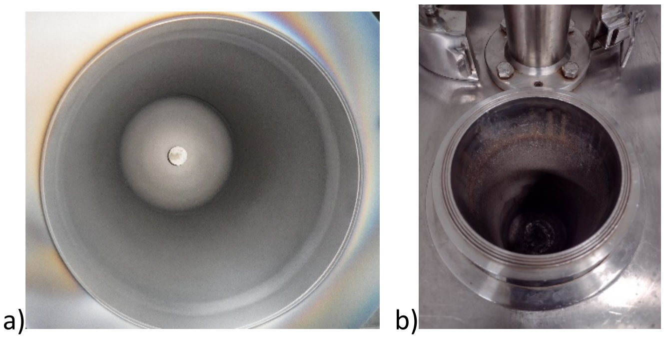

Fig. 1. Effects of corrosion on pressure reactors: a) Hastelloy and b) High grade stainless steel.

Furthermore, scale-up optimization also follows customer requirements and/or market trends. It is rare that a product rises directly from 1 kg to 1 metric ton without the production of intermediate amounts. Manufacturing these allows for smooth and less problematic scaling of the production process.

Finally, we will discuss some aspects of the ongoing discussion about perfluorinated compounds. It is well known that prominent ILs are using perfluorinated anions. Their use offers an interesting combination of properties such as high stability, hydrophobicity and low viscosity. In view of an impending ban on these substances, we are working on the synthesis of new fluorine-free alternatives. In our presentation we will highlight our results and we will demonstrate that it will open new market opportunities.

Sustainability in the supply chain of materials vital in energy storage

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The world is transitioning to reliable and sustainable clean energy technologies at an astounding rate. However, the key metals and resources vital for manufacturing technologies like wind turbines, electric vehicles (EVs), solar cells and batteries are now listed as critical raw materials European Commission,[1] Geoscience Australia[2] and by the US Department of Energy. [3]

It is known that the natural resources for those raw materials are finite, however the expected demand in the next 10-40 years is exponentially increasing, which in turn will generate a significant supply deficit in the next years. Therefore, it is necessary to develop sustainable methods to recover critical metals from metal waste, based on green electrochemical methods, enhanced by knowledge of ion speciation and electrolyte-electrode interactions.

In this work, the potential of deep eutectic solvents (DES) and ionic liquids (IL) as safe solvents on the extraction and recovery of the critical metals using chemical and electrochemical means is evaluated. For instance, we have reported the Nd^{3+} electrodeposition process using an hydrophobic phosphonium IL $[P_{66614}]$[TFSI] (trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide) in the presence of water as an additive, which was necessary to obtain electrodeposits. An in-depth study showed the importance Nd^{3+} solvation shell composition and conformation (e.g cis/trans and mono/bidentate) to give a favorable Nd^{3+} reduction process and better quality deposits.[4] An increased in recovery efficiency (60%) and electrodeposit purity was obtained using non-fluorinated ionic liquids.[5]

On different studies, we have established the importance of adding sulfate anion as an additive to an ethylene glycol- based DES to enhance both electrodeposition recovery efficiency (78 %) as well as purity of the electrodeposit.[6] Those studies will underpin the science to design safe electrolyte mixtures to enhance the chemical and electrochemical recovery of critical metals from secondary sources.

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Oral Contributions

Ionic liquid–electrode interface: partial charge transfer, surface dipole, and quantum capacitance

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This presentation sheds light on the interaction between ionic liquids and electrode surfaces. Such interfaces are essential for many electrochemical devices, from ideally polarisable supercapacitors to non-polarisable catalysts for CO_2 electroreduction. We pay special attention to quantum capacitance and partial charge transfer because their magnitude describes the interfacial electron redistribution.

Using Density Functional Theory (DFT), we compare how quantum capacitance and charge transfer behave at interfaces made of metal (Au) and semi-metal (Bi and C) electrodes with imidazolium (Im^+) tetrafluoroborate (BF_4^-) and iodide (I^-) ionic liquids. Our approach includes different methods for analysing charge (Bader, DDEC, and Voronoi analyses) to quantify the charge transfer, from partial with halide anions to full with redox-active ions, as seen in pseudocapacitors. We also use Molecular Dynamics to show how quantum capacitance contributes to the total capacitance.

The presentation combines our published [1–5] and most recent modelling results to highlight the importance of the surface dipole. This factor originates from electrocatalysis and deserves broader attention as it unites charge transfer, quantum capacitance, and the potential across the interface.

Overall, this research aims to improve our understanding of how ionic liquids and electrodes interact and help design better electrochemical devices for energy storage and conversion.

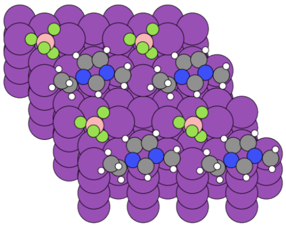

Fig. 1 An example Bi(111)–EMImBF4 interface model for Density Functional Calculations.

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Use of a Modified Free-Volume Theory for the Viscosity Modeling of Ionic Fluids

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The present work introduces a modification of the free-volume theory (FVT) in order to obtain improved representations of the dynamic viscosity of various representative modern ionic fluids: pure ionic liquids (ILs) and deep eutectic solvents (DESs). The thermodynamic potentials (residual internal energy and liquid densities) present in the resulting modified FVT model were estimated from two simple cubic equations of state of the van der Waals type: Soave or Peng-Robinson. The modifications introduced to the FVT approach were successfully verified during the correlation and prediction of experimental dynamic viscosities of 3 families of imidazolium-based ILs ([$C_X$mim][BF_4], [$C_X$mim][PF_6] and [$C_X$mim][Tf_2N]), one pyridinium-based IL ([b3mpy][BF_4]), one pyrrolidinium-based IL ([P14][Tf_2N]) and one ammonium-based IL ([N1114][Tf_2N]) over a temperature range varying from 273.15 to 353.15 K and at pressures from 1 to 3,000 bar. We also considered three archetypal choline chloride-based DESs for model validation: Reline, Ethaline and Glyceline within a temperature range varying from 293.15 to 373.15 K and at pressures from 1 to 1,000 bar.

Modelling Mass Transport in NaCl and $ZnCl_2$ Containing Electrolytes

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Due to the ongoing energy transition from fossil fuels to renewable energies, the topic of energy storage is more present than ever. Here, liquid metal batteries (LMBs) are one promising option for low-cost stationary storage of electrical energy. The working principle in general is quite simple – the system of liquid metal anode, molten salt electrolyte and liquid metal cathode self-assembles due to density differences and during operation electroactive species migrate from electrode to electrode through the electrolyte.

The battery in the present study uses sodium as anode and zinc as cathode material as well as a two layered molten salt mixture being separated by a diaphragm. Figure 1 shows this setup. Flow phenomena due to the liquid nature of the battery will arise during operation [1]. Most interestingly and very likely to occur in the electrolyte are thermal and solutal convection, which are consequences of unstable density distribution due to species transport and temperature differences. So far, those have mostly been investigated in the cathode of traditional LMBs only [2, 3]. Recently, mass transport in the electrolyte of a LiBi LMB was numerically investigated [4].

For NaZn cells, the electrolyte where two active species – Na^+ and Zn^{2+} – are transported primarily is the most important region to consider. The consequences of the mentioned convection phenomena are improved mixing of the electrolyte and reduced concentration overpotentials, but also self-discharge is promoted by mass transfer. Thus, knowing and understanding the species transport in the electrolyte is a major step in improving cell performance. Also, a charge-discharge asymmetry for solutal convection will be present during operation. Hence, solutal convection might evolve in the upper part of the electrolyte during charge and at discharge in the lower one. Additionally, the diaphragm influences the species transport and the evolving flow.

When operated above a critical current density, solutal convection can be observed in form of plumes evolving and sinking down/rising up, as it is exemplary shown in Fig. 1.

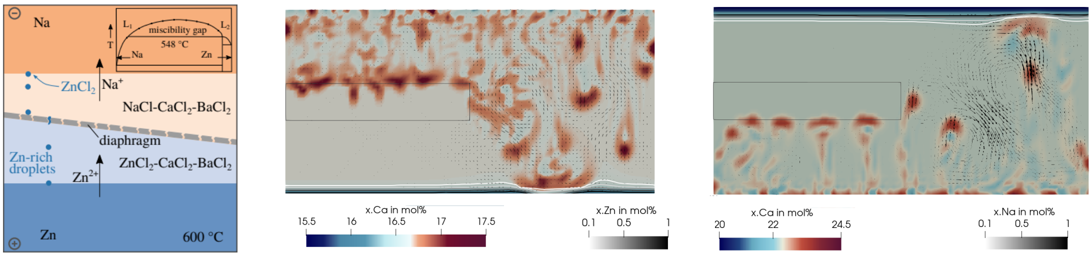

Fig. 1: Working principle for the NaZn LMB at charge (left) and solutal convection in the electrolyte during charge (middle) and discharge (right).

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Machine Learning of Interatomic Potentials for Molecular Dynamics

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Molecular Dynamics simulations that rely on classical force fields have been among the main tools for modeling atomic systems at nanoscopic length- and time- scales. Alas, they lack the accuracy of *ab initio* methods. In these, the ground state electronic density determines the Potential Energy Surface (PES) that dictates the movement of the atoms in the Born-Oppenheimer approximation. Nevertheless, the explicit treatment of electrons comes at a great computational cost and poor scaling.

On the way towards overcoming the computational cost of *ab initio* Molecular Dynamics without compromising their accuracy, Interatomic Potentials fitted from Density Functional Theory calculations via Machine Learning have emerged as a promising option. These potentials interpolate the Born-Oppenheimer PES from only the atomic positions, skipping the explicit treatment of electronic degrees of freedom. In this contribution, the mathematical foundations and the capabilities of this type of approach will be summarized. Results obtained with the NeuralIL[1,2] Neural Network Force Field for Ionic Liquids will be presented as a specific case.

Acknowledgements: The financial support of the Spanish Ministry of Science and Innovation (PID2021-126148NAI00 funded by MCIN/AEI/10.13039/501100011033/FEDER, UE) is gratefully acknowledged. Moreover, this work was funded by the Xunta de Galicia (GRC ED431C 2020/10). P. M. C. wishes to thank the Xunta de Galicia for his “Axudas de apoio á etapa predoutoral” grant (ED481A 2022/45). H. M. C. thanks the USC for his “Convocatoria de Recualificación do Sistema Universitario Español-Margarita Salas” postdoctoral grant under the “Plan de Recuperación Transformación” program funded by the Spanish Ministry of Universities with European Union's NextGenerationEU funds.

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Decomposition, interpretation and prediction of various ionic liquid solvation parameters: Kamlet-Taft, Catalan and Reichardt’s ETN

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In the realm of solvent characterization, a multitude of multiscale methodologies are employed, each offering detailed insights into specific solvent properties. For instance, the polarity of a solvent can be compared to others using the prominent Reichardt’s ETN values. Concurrently, hydrogen bond donor and acceptor capabilities are discernible by applying Catalan and Kamlet-Taft parameters. Such detailed characterization facilitates the accurate prediction of various chemical phenomena, including reactant solubility, compound stability, and the identification of transition states. The relevance of these solvation parameters extends to selecting optimal solvents for processes such as solvation, extraction, and catalysis. They are also vital for understanding solute interactions, acquiring specific spectroscopic data, and ascertaining the position of chemical equilibria.

In this study, we report a successful application of designed regression analysis to decompose the Kamlet-Taft, Catalan, and Reichardt’s parameters of ionic liquids into their constituent ionic components. Our method provides a systematic pathway to accurately predict the solvation parameters of yet-unexplored combinations of cations and anions. Moreover, this decomposition into singular ionic constituents has been coupled with quantum-mechanical calculations of the ionization potential, the electron and proton affinity, permitting a direct correlation between the solvation parameter and the physico-chemical as well as quantum-mechanical properties at the molecular level. This integrated approach provides a sophisticated interpretation of the values associated with ionic liquids, thereby advancing our comprehension of their intricate nature.

Molecular mechanisms of H_2/N_2 uptake in bulk and confined ionic liquids

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In recent years the advance of climate change has exacerbated the need for an energy transition towards a greener economy, in order to both meet the increasing needs of our societies and reduce our carbon footprint. One key agent that has risen in popularity as a clean alternative to fossil fuels is hydrogen. However, one major problem arises when dealing with this gas, and it is the matter of its safe and efficient storage. To tackle this matter, porous liquids such as ionic liquids (ILs) have been proposed as potential candidates for hydrogen storage. However, a fundamental understanding of the process of hydrogen solvation within ILs is still lacking. In this contribution we present a computational study of hydrogen sorption in a wide variety of bulk ionic liquids. Solvation properties were studied both by means of classical molecular dynamics (MD) and density functional theory, and it was found that the principal mechanism behind hydrogen uptake is the presence of structural voids within the liquid[1]. Moreover, it was determined that the key factor was not only the amount of free space, but rather the presence of cavities that allow for the accommodation of gas molecules.

Additionally, for two of the ionic liquids, the solvation properties of both hydrogen and nitrogen were studied when the ILs are subject to confinement within carbon nanotubes (CNTs), by means of both MD and hybrid Monte Carlo/MD simulations. A large increase in gas uptake was found, specially for certain CNT sizes, which displayed a gas uptake maximum. These maxima were found to be correlated with structural rearrangements of the ILs within the nanotubes.

Acknowledgements: The financial support of the Spanish Ministry of Science and Innovation (PID2021-126148NA-I00 funded by MCIN/AEI/10.13039/501100011033/FEDER, UE) is gratefully acknowledged. Moreover, this work was funded by the Xunta de Galicia (GRC ED431C 2020/10). A. R. P. thanks the Spanish Ministry of Education for his FPU18/01597 grant. M. O. L. and P. M. C. wish to thank the Xunta de Galicia for their ``Axudas de apoio á etapa predoutoral" grants (ED481A 2022/236 and ED481A 2022/45). T. M. M. acknowledges her contract funded by the pilot program of the USC for the recruitment of distinguished research personnel—call 2021 under the agreement between the USC and the Santander Bank for 2021–2024. H. M. C. thanks the USC for his "Convocatoria de Recualificación do Sistema Universitario Español-Margarita Salas" postdoctoral grant under the "Plan de Recuperación Transformación" program funded by the Spanish Ministry of Universities with European Union's NextGenerationEU funds. R. L. C. acknowledges his Predoctoral Contract under the framework of the project PID2021-126148NA-I00 funded by MCIN/AEI/10.13039/501100011033/FEDER, UE. Facilities provided by the Galician Supercomputing Centre (CESGA) are also acknowledged.

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Charge Screening at Ionic Liquid-Electrode Interfaces

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Ionic liquids (ILs), known for their high electrochemical stability and negligible vapour pressure, are under investigation for applications in fuel cells, solar panels, supercapacitors, and actuators. [1] As electrolytes consisting solely of ions, ILs display a distinctive layering structure at IL-electrode interfaces, [2] giving rise to characteristic potential-capacitance curves of bell or camel shapes. [3]

In this communication we move a step forward and present results of a systematic molecular dynamics (MD) simulation study to elucidate the behaviour of pure IL 1-butyl-3-methylimidazolium hexafluorophosphate, $BmimPF_6$, and its mixtures with 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, BmimFAP, confined between gold electrodes with various crystallographies (Au(111), Au(110), Au(100)) (refer to Fig. 1 for an example of cation orientations in the $BmimPF_6|Au(hkl)$ systems). Our MD results reveal that the initial application of an electric potential induces a separation in the ionic layers of the ionic liquid, with counter-ions being attracted to the electrodes and co-ions expelled from the first adsorption layer. At this potential, the capacitance reaches its maximum. Subsequent increases in potential lead to capacitance decay, accompanied by subtle reorientations and an increase in ion density at the interfacial layers. [4] We posit that this behaviour represents a universal phenomenon in IL electrolytes confined between electrodes. These findings hold both fundamental and practical significance for applications in electrochemical devices.

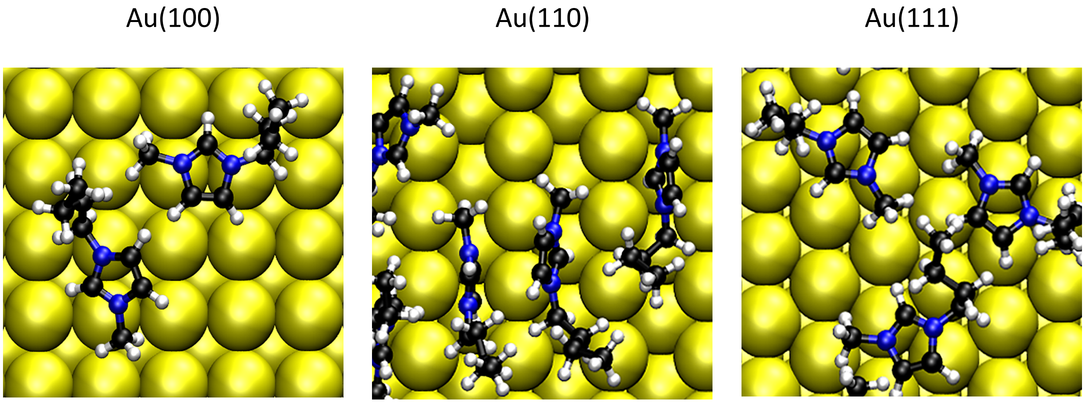

Fig. 1 Schematic representation of $BMIm^+$ cations configurations on cathodes at −16 μC cm^{-2} for each studied gold surface.

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O08
Oral Presentation

Influence of Solvation on the Structure of the Electrochemical Double Layer: a Continuum Approach for Ionic Liquids

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Here, we present a holistic framework for the description of IL based electrolytes, which couples nonequilibrium thermodynamics with mechanics and electromagnetic theory. Our continuum approach applies both to the bulk phase and to charged regions near electrified interfaces, thus spanning a wide range of length-scales from cell-level (micrometers) to microscopic interactions (nanometers).

For bulk electrolytes, e.g. in battery applications, our description comprises all transport mechanisms (diffusion, migration, convection), and predicts the evolution of the electrolyte species. In a series of publications, we validated this theory with experimental results [1,2].

To describe the electrochemical double layer (EDL), we supplemented our bulk description by non-local ion interactions. For pure ILs, our theory predicts that the structure of the EDL is governed by three energies scales related to short-ranged ion-correlations, thermal energy, and electrostatic energy of Coulombic interactions [3] (in particular, dominant correlations lead to nanostructuring). We validated this approach with AFM experiments [4].

Recently, we extended our EDL model to also account for solvation effects. Analysing the differential capacitance, our approach reproduces known effects, as the shift from "camel"-shape to "bell"-shape for larger salt concentrations. As novel features, it describes the effect of ion asymmetry on the capacitance minimum, and predicts the emergence of additional peaks in the differential capacitance resulting from stripping of the solvation shell in the EDL.

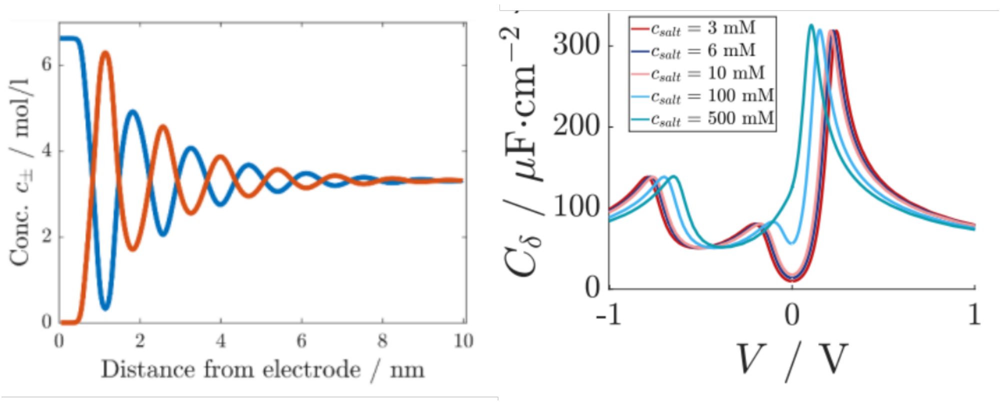

Fig. 1 Left: Charge oscillations in the EDL for a pure ILs. Right: Differential capacitance curve.

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New insights on the electrical conductivity of high concentrated electrolytes

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Electrical (or ionic) conductivity is one of the main properties of electrolytes, which determines their applicability for different purposes. For low concentrated electrolytes, both aqueous or non-aqueous, the Nerst-Einstein theory works fine, relating conductivity with diffusion constant of the different ionic species present. As well, Walden plot, based on the Stokes-Einstein relationship, works well to relate molar conductivity and fluidity [1].

The problem complicates to understand electrical conductivity for high concentrated electrolytes, and more with the discovery of ionic liquids and of deep eutectic solvents, both pure as mixed with different solvents. In these systems the ionic interaction between ions cannot be ignored, and classical theories do not work appropriately. Based in previous works, some of us developed an ideal pseudolattice model of charge transport in high concentrated ionic solutions, obtaining the corresponding states law for the electric conductivity [2]. The equations derived from this model apply from volumetric to transport properties with fine fitting between the measured data in electrolyte mixtures and the predicted behaviour of the different magnitudes with the composition. For electrical conductivity in ionic liquid mixtures, the model works very well for mixtures with low salt concentration, but no so fine for high concentrated mixtures, where the model fails for salt volume fractions higher than 0.5. The ideal pseudolattice model was refined to correct those discrepancies. The resulting model, called “random”, presents a high capability of prediction for majority of electrolytes at all range of concentrations studied up to the date of publication [3]. Unexpectedly, last experimetnal results measured in our own laboratory seems to contradict the theoretical model developed, and those discrepancies comes from three very different systems. First, ionic liquid based hydrogels do not change their electrical conductivity when they transit from a liquid state to a quasi-solid gel one, while their fluidity becomes null in gel state (i.e., they present an infinite viscosity, but a quite good conductivity) [4]. Second, some deep eutectic solvents mixed with methanol present a giant peak, much higher than that predicted by the mentioned random model [5]. Third, when mixing some protic ionic liquids with some non-aqueous solvents, the mixture decreases its electrical conductivity respecting its value when pure for all solvent concentrations, which does not fit with the predicted behaviour from our random model. A new version of that model, trying to generalize it to fit also these new system, is in progress and results will be published soon.

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Solvation of simple and complex carbohydrates in ionic liquids and deep eutectic solvents

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Carbohydrates (CH) are the most abundant organic compound available to humanity. They are characterized by the presence of several hydroxyl groups and, depending on their chemical nature, they can show an amphiphilic nature. Simple CHs such as glucose and sucrose show high solubility in water; while more complex CHs, such as cyclodextrins (CD) or cellulose show small to poor solubility. On the other hand, it is desirable to individuate alternative, bio-sustainable media that can nicely perform in solubilizing small, as well as complex CHs for further handling and transformation.

Ionic Liquids (ILs) and Deep Eutectic Solvents (DES) can help in this respect. For decades it has been known that chloride and acetate based ILs can efficiently dissolve cellulose[1] and recently DES have been proposed for similar tasks.

Here we show our recent results on the determination of thermodynamic (solubility) and structural properties of mixtures of simple CHs (e.g. glucose, fructose) and different CDs in ILs[2] and DES[3], highlighting general features of the solvation mechanism.

By the integration of experimental (solubility, viscosity, scattering experiments) and computational (Molecular Dynamics) tools, we access a detailed picture of the solvation mechanism in terms of atomistic properties, highlighting the role of hydrogen bonding interactions as well as of dispersive ones.

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Origin of Moisture Absorption Capability of Ionic Liquids

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Relationship between the structure of Ionic Liquids (ILs) and their physical properties has received a great deal of scientific attention.[1] Among other physical properties of ILs, we have been deeply interested in their moisture absorption capability because this makes ILs possible candidates for desiccants for the liquid desiccant-type air conditioners (LDAC).[2] We discovered that tributyl(methyl)phosphonium dimethylphosphate ([P4441][DMPO4])[3a], cholin dimethylphosphate ([Ch][DMPO4])[3b], and dicationic quaternary ammonium bis(dimethyl or diethylphosphates) [3c] exhibit extremely high dehumidification capability (DC). To gain insights into the origin of ILs' DC, we systematically synthesized 26 different types of ILs by combining dimethylphosphonium anions with various types of alkyl group-substituted cyclic cations, including imidazolium, pyrazolium, 1,2,3-triazolium, and 1,2,4-triazolium cations. The DC was found to vary with the alkyl substituent of the cations. Among these 26 ILs, 1-(cyclohexylmethyl)-4-methyl-1,2,4-triazolium dimethylphosphate shows the best DC; its DC (mol) value is 14-times higher than that of the popular solid desiccants $CaCl_2$. For additional insights, we conducted small- and wide-angle X-ray scattering (SWAXS) analysis of 8 types of 1,2,4-triazolium dimethylphosphate; we found that three types of nanostructures exist in these ILs aqueous solutions and these forms depend on the alkyl substituents of cationic part of ILs and water contents. Water from air is absorbed mainly into polar regions of nanostructured ILs, defined primarily by phosphonium anions (in the space between the phosphonium anions in the nanostructure of aggregation form of the IL) and the resulting water-rich domains function as the so-called "water pockets" [4] as illustrated in Figure 1. Since the stability of the aggregated forms of the ILs, we studied depend on the cations; the results suggest that the introduction of an appropriate alkyl side chain in the cationic moiety can be the key to the design of efficient desiccant ILs for LDAC.[5]

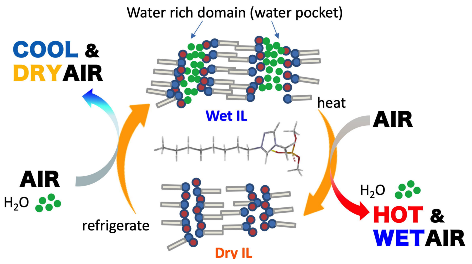

Figure 1. Plausible mechanism of moisture absorption by the 1,2,4-triazolium dimethylphosphate IL

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O12

Oral Presentation

The selective leaching of gold by deep eutectic solvents: strengths and limitations

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Deep eutectic solvents (DES) are an emerging solvents' family under intense scrutiny for a large scope of industrial applications including natural products extraction, metal ore leaching and electrodeposition [1]. For gold hydrometallurgy [2], DES offer notable technical advantages when compared to aqueous-based processes, involving a larger electrochemical window which allow stronger oxidants to be used [3] and a promising metals extraction efficiency [4]. Here, eutectic systems (ES) containing a quaternary ammonium salt based on an ionic organic compound such as choline chloride (ChCl) and a non-ionic organic compound such as urea (U) and ethylene glycol (EG) have been employed between 20 and 50 °C. However, the leaching of gold necessitates the addition of an oxidizing agent, as well as a complexing agent. The most effective agent for this purpose is iodine, which plays the role of both an oxidizing agent and a complexing agent [5]. The above-mentioned iodine enriched ES have proven their ability to leach gold but the selectivity is low as others metals are also attacked. Furthermore, gold etch rate is limited at 50 °C. These limitations have been addressed by carrying out investigations to gain a deeper understanding of these systems, with a specific focus on enhancing Cu/Ni selectivity towards gold. Corrosion inhibitors, such as benzotriazole (BTA) for Cu and carvacrol (CRV) for Ni, were explored as potential additives or ES components to mitigate co-leaching issues.

Two new ES based on ChCl and either BTA or CRV have been prepared. One of the advantages of ChCl:CRV ES is to possess very high species concentrations, which will facilitate the iodine solubilization, while the same species might have a limited solubility in conventional solvents, such as water. These ES showed greater Cu/Ni leaching inhibition capacities when the same inhibitors were used as simple additives in ChCl:EG or ChCl:U. Despite this improvement, the gold leaching efficiency was still lower than in aqueous-based processes. This limitation might be explained by different factors, including the availability of Cl^- which can be evaluated through Walden ionicity (Figure 1), the stability of I_2 with ES compound, or the high viscosity that affects the mass transport through the mechanically assisted convection.

This presentation will encompass a comprehensive dataset including ionic conductivity, density, viscosity and voltammetry analyses to explore the strengths and limitations of the ES.

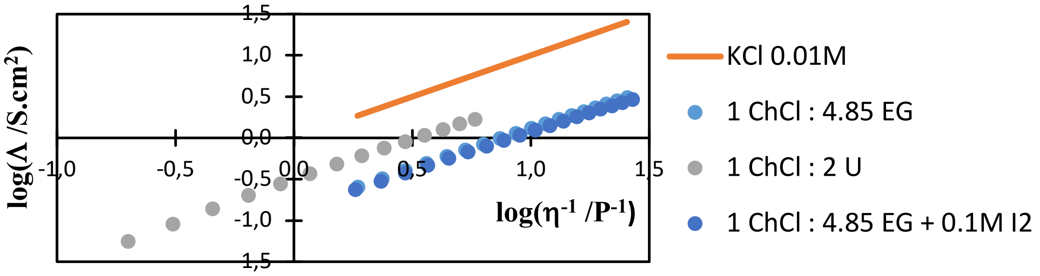

Figure 1: Ionicity (< 100%) of eutectic mixtures compare to ionicity (100%) of KCl in water

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Studying the solvation of the proton in imidazolium ionic liquids using Raman Spectroscopy

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Understanding fundamental levels of acidity accessible in non-aqueous solvents is critical for developing new chemical syntheses and applications in non-aqueous media[1]. Often the level of accessible acidity is expressed as the proton transfer activity coefficient, which is related to the free energy of transfer when the proton is transferred from one solvent to another, experiencing difference in solvation[2]. For the proton, values for the transfer activity coefficient can only be experimentally estimated from extra-thermodynamic models applied to electrode potentials, solubility or spectroscopic measurements[3,4]. Experimental values for the transfer activity coefficient of proton are essential to confront the computed values, as determining free energies of proton solvation, either experimentally or theoretically, in non-aqueous solvents is one of the most discussed questions in physical chemistry[5]. Proton solvation are particularly interesting to study in stable room temperature ionic liquids (RTILs), which emerged as alternative to volatile organic solvents for inorganic and organic syntheses, catalysis, electrolytes and microextraction[6–10]. The presence of small fractions of molecular impurities in RTILs has major impacts on their physico-chemical properties, especially the acidity levels accessible in these solvents, which need to be addressed to develop more robust applications. Here we report on the estimation of the free energy of solvation for proton in stable N,N′-substituted imidazolium ionic liquids using far-field classical Raman spectroscopy and the acidity function proposed by Hammett[11] in different RTILs, built from four different cations (C_2, C_4, C_6 and C_8 N-alkyl, N′-methyl imidazolium) and 4 different anions (OTf^-, NTf_2^-, BF_4^- and PF_6^-).

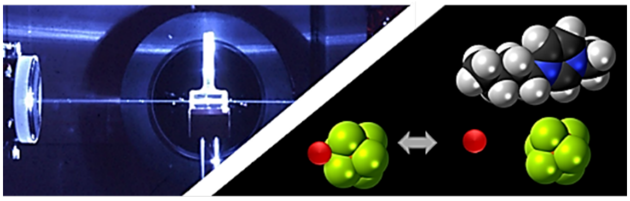

Fig. 1 Raman spectroscopy to evaluate the solvation energy of proton in RTILs.

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A new way to control the solubility of ionic liquids

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Ionic liquids are recognized as a unique solvent that shows different physical properties from any other solvents. So far the chemistry of ionic liquids has enjoyed its own progress derived from these unique properties. On the other hand, ionic liquids suffer severe drawbacks due to such physical properties. One example is the problem of separation. Due to non-volatility of ionic liquids, liquid-liquid extraction is the only method for the conventional removal. However, this method works only if ionic liquid is hydrophilic and desired solute is lipophilic, or vice versa. If both of the ionic liquids and the desire compounds are lipophilic, they will come to the same organic phase. As a result, there seems almost no chance to achieve efficient separation. To solve the serious problem, we proposed a new type of ionic liquids, solubility-switchable ionic liquids (SSILs), which may change solubility and partition properties by simple and mild chemical transformation between acetal and diol [1]. In this presentation, we will discuss chemical and physical properties of this new type of ionic liquids and show how SSILs solve the problem of the separation.

The preparation of SSILs started from the common intermediate **1**. Ammonium-, phosphonium-, and imidazolium-type cations were synthesized via reductive amination of substitution reaction. Following anion exchange completed the preparation of SSILs. The acetal group in all of the SSILs was quantitatively removed by acidic hydrolysis catalyzed by the presence of Nafion resin, and acetalization of the diol-type SSILs was effectively achieved by treatment with 2,2-dimethoxypropane under acidic conditions. Partition experiments of all of SSILs were examined. Most of the acetal-type SSILs were distributed to organic phase and insoluble in water. On the other hand, the diol-type ionic liquids generally preferred to be partitioned to aqueous phase as long as the carbon number of the cationic part of SSILs was relatively small. Such diol-type SSILs showed good solubility in water. We will discuss on the change of solubility and partition properties of SSILs in detail.

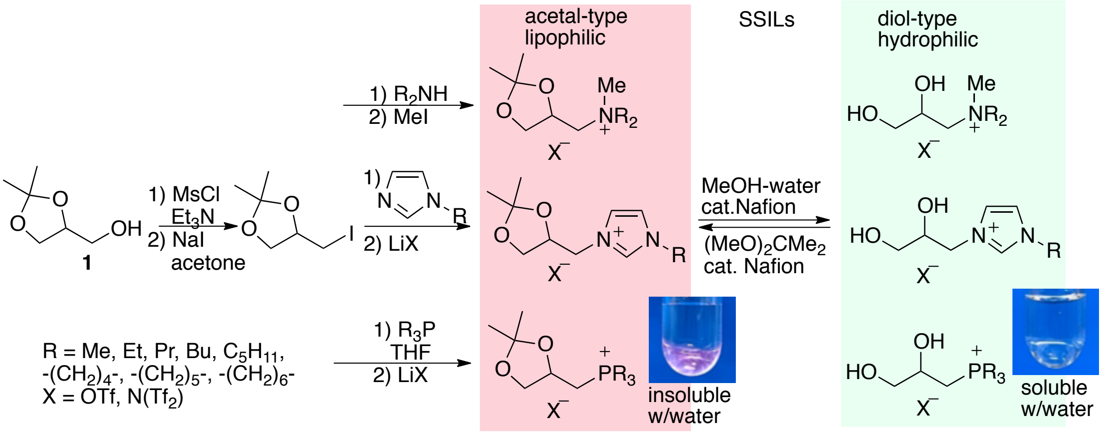

Fig. 1 Preparation and physical properties of SSILs.

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Effect of hydrated ionic liquids and deep eutectic solvents on the thermal transitions of DNA

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The potential use of ionic liquids (ILs) and deep eutectic solvents (DES) as alternative solvents to maintain the original structure of DNA for extended periods holds promise for biotechnological and biomedical applications in the near future.

The influence of cations, anions and molecular components in imidazolium-based ILs and choline-based DES on the thermal structural stability of model nucleic acids is here presented and discussed. Multi-wavelength UV resonance Raman spectroscopy provides selective observation of heat-induced structural transitions in DNA at specific base sequences.

Paradigmatic case studies indicate the formation of preferential interactions between imidazolium cations and guanine bases in the DNA groove, promoting more effective stacking between guanine bases even at elevated temperatures. In the case of DES, the hydration shell of adenine-thymine pairs is strongly perturbed in the presence of DESs. The preferential interaction between H-bond sites of guanine residues and DES is the source of the stabilization of dsDNA.

The outcomes of this investigation contribute to a more comprehensive understanding of the interactions of IL and DES in with A–T and G–C base pairs during thermal unfolding. [1-4]

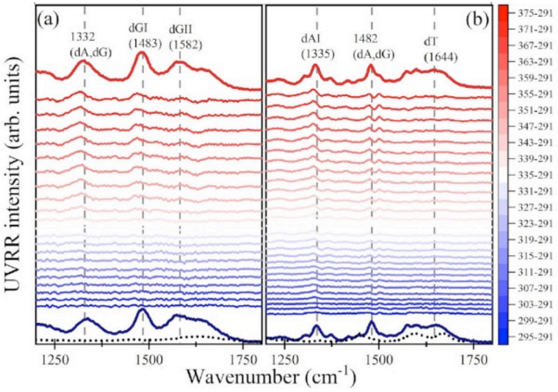

Fig. 1 UVRR spectra collected at the excitation λ = 250 nm (a) and 266 nm (b) of 10 μM dsDNA solution in Tris buffer / ChCl-U DES.

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

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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. Besides the study of “pure" DESs, interest has recently been devoted to DES mixtures formed upon cosolvent addition. Indeed, the addition of molecular solvents like water, alcohols, or alkanes, has been shown to dramatically affect several DESs physical-chemical properties, eventually providing eutectics with enhanced performances and lower costs.

Here we present a study about the structural characterization of a DES formed by choline chloride (ChCl) and sesamol in 1:3 molar ratio through a multidisciplinary approach combining small- and wide-angle X-ray scattering (SWAXS), ATR-FTIR spectroscopy, and molecular dynamics (MD) simulations. This eutectic has shown a peculiar behavior upon the addition of cosolvents like water and methanol (MeOH). For high water content, segregation between sesamol- and water-rich regions occurs, up to the formation of water pores able to confine most of the ChCl and disrupt the DES internal structure, while not provoking macroscopic phase-separation [1]. Differently, segregation was not displayed by MeOH mixtures due to the different interplay between the DES components and the co-solvent [2]. The inspection of such pseudo-phase aggregations has important implications in light of the applicative conditions of these DESs in liquid-liquid microextractions [3]. The obtained fundamental insights provided knowledge about the link between the structural arrangement of these systems and their macroscopic physical-chemical properties, being a step forward in the development of DESs as advanced processing media for more sustainable applications.

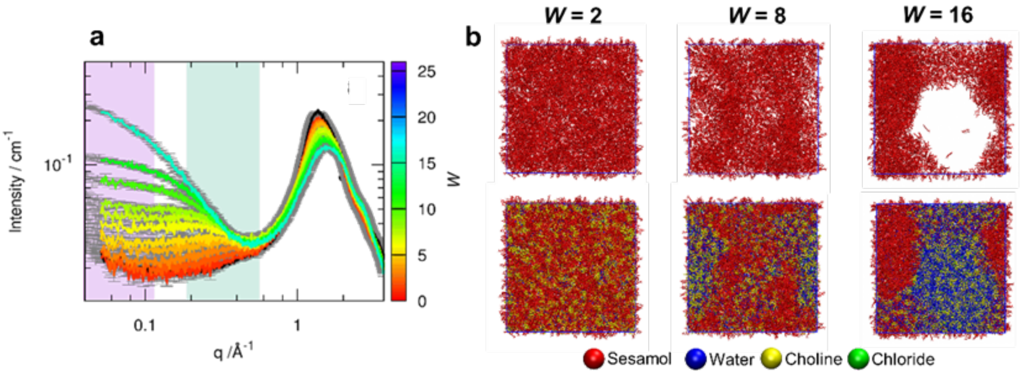

Fig. 1 a) SWAXS and b) MD characterization of ChCl:sesamol:water mixtures at different 1:3:*W* molar ratios.

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Thermodynamic study of ionic liquids with fluorinated cations

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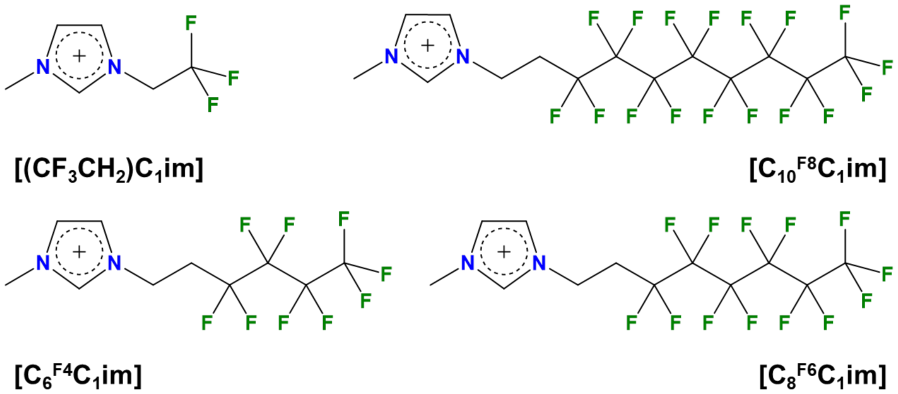
Fluorinated ionic liquids (FILs) have attracted great interest from the scientific community, especially due to their promising properties for application in gas capture and separation [1]. In this study we have investigated the phase behavior, thermal stability, heat capacity and volatility of several FILs in which the cation bears perfluorinated *n*-alkyl chains, paired with the bis(trifluoromethylsulfonyl)imide ($[NTf_2]$) anion.

The phase behavior of these FILs was studied by differential scanning calorimetry (DSC), and their thermal stability was evaluated using thermogravimetric analysis (TGA). The heat capacity measurements were performed, from T = 283 K up to T = 333 K, using a customized differential scanning microcalorimeter. Furthermore, the heat capacity was also determined at T = 298.15 K, by high-precision drop calorimetry [2]. The volatility of these compounds was investigated through Knudsen effusion coupled with quartz crystal microbalance (KEQCM) [3]. Melting properties were only successfully determined for the longest member of the series. However, it was not possible to obtain its glass transition temperature, given that it readily crystallized on cooling. For all the other FILs, only glass transition was detected. The study of the heat capacity allowed us to obtain an estimation for the contribution of each fluorinated methylene group, −CF2−, to the heat capacity of the liquid phase, at T = 298.15 K. The KEQCM studies revealed that the FILs are more volatile than their hydrogenated analogs.



$[(CF_3CH_2)C_1im]$

$[C_{10}{}^{F8}C_1im]$

$[C_6{}^{F4}C_1im]$

$[C_8{}^{F6}C_1im]$

Fig. 1 Structures and nomenclature of the studied fluorinated cations.

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Fluorine-Free Electrolytes: Why and How?

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The electrolytes of our modern energy storage devices contain flammable organic solvents and fluorinated lithium/sodium salts that are intrinsically unsafe when exposed to heat and fire – this can be very problematic in confined spaces. The decomposition of these fluorinated salts produces hydrofluoric acid (HF), among other toxic gases. Another challenge is the recycling and handling of spent energy storage devices with high fluorine content – posing a chemical hazard and a serious threat to occupational safety, human health and environment. To develop next-generation energy storage devices, the development of new fluorine-free and non-flammable electrolytes is indispensable; these electrolytes should conduct ions efficiently and also directly influence the safety, service life and overall performance of the energy storage devices.

Ionic liquids (ILs) with desired properties can potentially replace the conventional electrolytes. We develop novel fluorine-free IL-based electrolytes that can be used as electrolytes with unique properties; they are non-flammable, liquid at low temperature, thermally and electrochemically stable. The synthesis and characterization including multinuclear (^{7}Li, ^{23}Na, ^{31}P, ^{13}C, ^{11}B, etc.) solution-state NMR, solid-sate MAS-NMR, MS, FTIR and Raman techniques, thermal properties (TGA and DSC), ionic conductivity and NMR diffusivity are performed. A range of new classes of IL-based electrolytes have been recently synthesized that can potentially be used as electrolytes in various energy storage devices [1-4].

Acknowledgements: The financial support from the Swedish Energy Agency, Swedish Research Council, Kempe Foundation and European Union is gratefully acknowledged.

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Electronic effect of the metal cation on the anion: implications for the reactivity of ionic liquids and concentrated electrolytes

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Concentrated electrolytes, electrolytes where the concentration of the salt is far greater than the standard battery concentration of ~1 M, have been found to give far wider electrochemical potential windows, which is of great importance for battery development.[1,2] From DFT-based molecular dynamics (DFT-MD) calculations, it has been suggested that the observed wider windows arise from changes in the anion solvation environment and consequent differences in the liquid phase electronic structure.[1-3] However, there are no experimental measurements of the liquid phase electronic structure for concentrated electrolytes, meaning that these very tricky calculations have not been validated against experimental data.

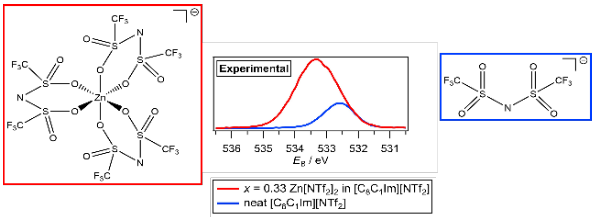

Figure 1. XPS of $[Zn(NTf_2)_3]^-$ versus free $[NTf_2]^-$

The liquid phase electronic structure of ionic liquids (ILs) with large metal cation concentrations were characterised using a combination of X-ray photoelectron spectroscopy (XPS), synchrotron resonant XPS, X-ray absorption spectroscopy (XAS) and DFT calculations, along with the characterisation of the free anions in ILs with no metal cations present. ILs were used rather than concentrated electrolytes with neutral solvent molecules present, as ILs are non-volatile at room temperature, allowing the use of standard ultrahigh vacuum XPS apparatus to study them. Our measurements were performed on a combination of laboratory-based and synchrotron-based XPS apparatus, including beamline B07-B at Diamond Light Source. These large metal cation concentrations gave ILs where the amount of free anions and anions bound to a metal cation were similar. This approach allowed us to characterise the electronic effect of metal cation binding to anions. The metal cations studied include Li^+, Zn^{2+} and Sn^{2+}, which facilitated the probing of the importance of the metal cation formal oxidation state on the anion electronic structure. Our experimental results match very well to our calculations, validating the calculations and allowing further insight into the anion electronic structure. The anions studied include $[NTf_2]^-$, $[TfO]^-$, Br^- and Cl^-; $[NTf_2]^-$ is especially crucial for concentrated electrolytes. Our results are the first step towards experimentally characterising the full influence of salt concentration on electrolyte electronic structure and therefore electrolyte reactivity; we will discuss the implications of our results towards both concentrated electrolytes and ionic liquids.

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Influence of internal interfaces on the structure and dynamics of IL-based electrolytes confined in a metal-organic framework

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Ionic Liquids (ILs) are promising electrolyte components for electrochemical energy storage devices due to their high electrochemical stability and low volatility and flammability. Especially in Li-ion batteries, these favourable properties represent an advantage over commonly used organic electrolytes. However, the poor Li-conductivity, high viscosity and unfavorable Lithium-anion clusters are major drawbacks of ILs as battery electrolytes.[1] Recent results strongly suggest that confinement of an IL-based electrolyte in the metal-organic framework (MOF) ZIF-8 can break Li-anion clusters and thus enhance local Li^+ dynamics.[2]

In our present work we systematically investigate the influence of internal interfaces on the structure and dynamics of confined IL-based electrolytes. To this end, 5 different bis(trifluormethyl-sulfonyl)imide(TFSA)-based ILs are mixed with LiTFSA and confined in the MOF ZIF-8. Resulting samples are investigated by NMR methods, mainly temperature-dependent ^7Li spin-lattice relaxation rates (R_1), which are analyzed using the Bloembergen, Purcell, and Pound (BPP) model. Impedance spectroscopy is used to get information about the ion transport and Raman spectra elucidate the Li-anion coordination and interactions with the ZIF-8 framework. MD simulations are used to support and interpret the results.

The BPP-model provides a very good fit of measured ^7Li spin-lattice relaxation rates, enabling statements on the local environment, the local dynamics and its activation. A correlation between the interaction strength of the IL cation with the ZIF-8 framework and the activation of the local Li^+ dynamics can be observed. Additionally, for the samples with lower activation energies of local Li^+ dynamics, higher conductivities are measured. These results are supported by Raman spectroscopy showing a strong influence of the IL cation on the Li-TFSA coordination in confinement, which is confirmed by MD simulations. These results demonstrate a strong influence of internal interfaces on IL structure and dynamics and might bear potential for tailoring ion dynamics.

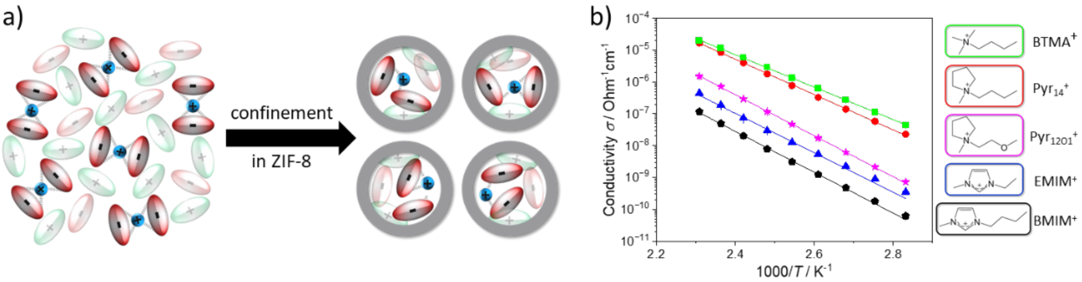

Fig. 1 a) Sketches of Li-TFSA clusters in the bulk and ZIF-8. b) Impedance data of the IL-based electrolytes confined in ZIF-8.

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A comprehensive study of NaCl-polyol mixtures: affordable and green electrolytes for electrochemical energy storage systems

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Efforts to decrease reliance on fossil fuels have led to significant improvements in photovoltaic and wind energy systems. However, the intermittent nature of these renewable sources requires the integration of efficient electrochemical energy storage systems (EESS), such as batteries and supercapacitors, to guarantee a continuous and reliable energy supply [1]. The search for alternative electrolytes to the traditional unstable ones has led to the proposal of Liquid Ionics (ILs), which instead are expensive and generally corrosive to current collectors [2,3]. Consequently, Deep Eutectic Solvents (DESs) have emerged in recent years as a solution to these issues since they are more affordable, non-corrosive and possess favorable properties such as high thermal stability, low vapor pressure, biodegradability and inertness to air and humidity [4].

Our contribution in this field is dedicated to the investigation of sodium-based Deep Eutectic Solvents (DESs): in particular, the study has been devoted to NaCl-Glycerol and NaCl-Ethylene glycol mixtures. To deeply comprehend our mixtures, and to provide all the information necessary for the development in this area, a multilateral analysis has been conducted following the basic roadmap shown in Figure 1. Through thermal analysis (DSC) and vibrational spectroscopic techniques (Raman and FIR), we have managed to classify our mixtures as DES or "salt-in-solvent" and to find a correlation with both the structural features of the molecular components and the occurring intermolecular interactions (hydrogen bond) [5]. These latter play a pivotal role in establishing the ionicity of each system, as well as the electrochemical behavior in fully assembled devices (supercapacitor and sodium-ion battery).

Fig. 1 Essential measurements to have a thorough overview of DESs.

Acknowledgements: this project has received support from Project CH4.0 under the MUR program "Dipartimento di Eccellenza 2023–2027" (CUP D13C22003520001). This study was carried out within the GENESIS project funded by the Ministero dell'Università e della Ricerca within the PRIN 2022 program.

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The effect of charge delocalization in the dispersion of the refractive index of ionic liquids

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The refractive index, n(λ), and refractive index dispersion, δn(λ)/δλ, are relevant magnitudes to describe the optical response of any material, being fundamental parameters for a large set of photonic applications. However, in the field of ionic liquids (ILs) the experimental measurements of wavelength-dependent refractive indices are scarce and the knowledge about how chemical structure affects their dispersion is limited [1]. In order to shed some light on this issue, in this contribution we explore the influence of the chemical structure of cations in the refractive index dispersion of ILs.

We have measured the refractive index curves of several ILs in the spectral range from 320 nm to 1700 nm using white-light refractometry [2]. The ILs studied were combinations of the bis(trifluoromethylsulfonyl)imide anion, $[NTf2]^-$, with different heterocyclic cations bearing alkyl chains of variable length. Since the dispersive behavior of refractive index has its microscopic origins on the dispersion of the molecular electronic polarizability, α(λ), we employed the Lorentz-Lorenz equation to calculate the electronic polarizability of the ILs:

$$\alpha_{IL} = \sum_i \alpha_i \tag{1}$$

Afterwards, using the well-known additivity of electronic polarizability [3] , we identified and analyzed the α_i contributions to the overall electronic polarizability of i different parts composing the IL. We observed that the presence of charge delocalization in the cations increases the dispersion, producing an important rising of the value of the refractive index as wavelength decreases. On the other hand, the contribution of alkyl chains to dispersion is much more limited, without any important influence of the cation they are attached to.

In conclusion, the additivity of electronic polarizability on ILs can be exploited to understand the dependence of refractive index as a function of the chemical structure of the liquid of interest. According to our results, charge delocalization plays a major role in the behavior of the refractive index dispersion by making it stronger. Hence, the careful designing of regions with and without charge delocalization in ions is expected to be a powerful mechanism to develop task-specific ILs with tailored refractive index dispersion for optical applications.

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Unveiling the molecular interactions in ether functionalized ionic liquids utilizing DMSO as a molecular probe

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The intricate balance of interactions that determines the physicochemical properties of ionic liquids (ILs) with ether-functionalized cations, particularly those including highly coordinating anions like acetate, remains unclear. In the present study, the influence of ether linkages on the interactions between the ions and on the physicochemical properties of two acetate-based ILs —1-butyl-3-methylimidazolium ($[C_4C_1Im][OAc]$) and 1-(2-methoxyethyl)-3-methylimidazolium ($[(C_1OC_2)C_1Im][OAc]$) — was assessed through a combination of Raman spectroscopy and thermodynamic measurements using DMSO as a molecular probe. When mixed with ILs, changes in the DMSO structure, evident in the Raman spectra, are suitable to investigate cation-anion interactions.

Mixtures of DMSO with both ILs have negative excess molar volumes for all compositions (x_{IL}= 1.0, 0.75, 0.50, 0.25 and 0.0) and temperature ranges (293 to 353 K) showing that the liquids contract upon mixing. The lowest measured values were −0.55 cm^3/mol (at 353 K and x_{IL}=0.33) and −1.05 cm^3/mol (at 353 K and x_{IL}=0.37) for $[C_4C_1Im][OAc]$ and $[(C_1OC_2)C_1Im][OAc]$, respectively. As expected, the viscosity of the mixtures decreases with increasing mole fraction of DMSO. The deviations from the linear average of the viscosities of the pure components show negative and positive deviations for $[C_4C_1Im][OAc]$ and $[(C_1OC_2)C_1Im][OAc]$, respectively. The positive deviation is attributed to hydrogen bonding between DMSO and the cation. Raman spectra of the mixtures at different compositions highlight that, for $[(C_1OC_2)C_1Im][OAc]$, DMSO preferentially forms clusters that solvate the individual ions. Alternatively, when mixed with $[C_4C_1Im][OAc]$, DMSO is solvated by the IL with no evidence of clusters being formed, in line with previous literature results [1]. The fragile cation-anion interaction in the ether-functionalized IL stems from the folding effect of the side-chain, which creates an intramolecular hydrogen bond between the ether group and the imidazolium ring (Figure 1). This weakens the cation-anion interaction, thereby facilitating the disruption of hydrogen bonds in $[(C_1OC_2)C_1Im][OAc]$.

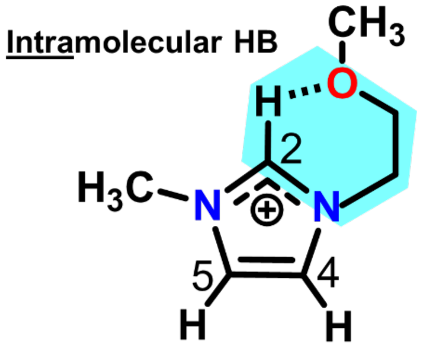

Figure 1. Coiling and intramolecular hydrogen bonding in ether-functionalized cations in acetate-based ILs.

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O24
Oral Presentation

Exploiting monoterpenoids in type V deep eutectic solvents: A combined high-pressure experiments and theoretical approach for enhanced carbon dioxide and nitrogen absorption

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This comprehensive study investigates the development, characterization, and application of natural hydrophobic deep eutectic solvents (HDES) in high-pressure gas capture, focusing specifically on carbon dioxide (CO_2) and nitrogen (N_2). Two binary HDES systems were formulated, using Linoleic acid (LnA) as a hydrogen bond donor (HBD) and carvone (CAR) and cineole (CIN) as hydrogen bond acceptors (HBA). The HDES materials were thoroughly characterized, examining properties such as density, viscosity, conductivity, acidity, surface tension, and hydrophobicity across varying temperature ranges using state-of-the-art equipment. High-pressure gas solubility experiments were conducted to assess CO_2 and N_2 sorption capacities, demonstrating promising results. Simultaneously, an integrated computational approach was applied: COSMO-RS was used to predict solid-liquid equilibria (SLE) and the eutectic point of the natural HDES, while Density Functional Theory (DFT) calculations aided in optimizing molecular geometries and understanding the dispersion interactions. Furthermore, molecular dynamics (MD) simulations were employed to evaluate solubility of CO_2 and N_2 in the natural HDES and their interaction energies. The results from this dual experimental and computational approach show the potential of these HDES systems in high-pressure gas capture. This study represents a significant addition to the knowledge of deep eutectic solvents, their synthesis, characterization, predictive modeling, and practical applications.

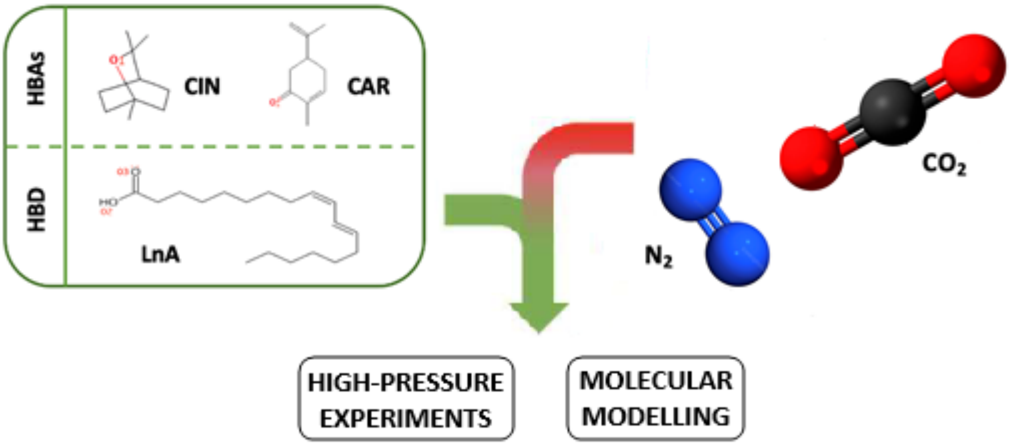

Fig. 1. Compounds used in this work for enhanced carbon dioxide and nitrogen absorption using a dual experimental and computational approach.

Acknowledgements: This work was funded by Ministerio de Ciencia, Innovación y Universidades-Agencia Estatal de Investigación (Spain, project PID2022-142405OB-I00), WORLD project (European Union's Horizon 2020 research and innovation programme under Marie Sklodowska Curie grant agreement n° 873005), European Union NextGenerationEU/PRTR funds and Western Michigan University Faculty Research and Creative Activities Award (FRACAA-23-0039670). We also acknowledge SCAYLE (Supercomputación Castilla y León, Spain) for providing supercomputing facilities.

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O25
Oral Presentation

A deep dive into structure and dynamics of sustainable hydrophobic eutectics and eutectogels

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Hydrophobic non-ionic eutectic solvents (HES) are recently standing out from the crowd of (deep) eutectic solvents, (D)ES [1], thanks to their low viscosities, chloride-free nature and water-immiscibility. To expand the combinatorial playground of HES, their immobilization in a solid-like scaffold to prepare hydrophobic non-ionic eutectogels (HEG) is a unique option [2]. If considerable progress has been achieved in the understanding of intermolecular interactions and mobility within traditional hydrophilic (D)ES, very little is known for HES, and even less for HEG.

Here we illustrate how a multifaceted investigation of HES at the molecular level is key to understanding the complex interplay between H-bond, electronic and steric factors in driving the formation of HES and ruling their peculiar properties [3].

We also show that stable and homogeneous gels are swiftly obtained in non-ionic HES, using the low molecular weight gelator dibenzylidene-D-sorbitol (DBS) at a very low loading, with a simple one-pot preparation process ranked as "excellent" in the EcoScale metrics [4]. A multidisciplinary approach sheds light into structure and dynamics of both liquid and semi-solid samples, proving that the liquid-like nature of the hydrophobic mixture is retained upon gelation. Noteworthy, we observe an unexpected increase of the translational motion of the HES components under confinement compared to pure HES, and a non-linear trend of thermal, rheological and diffusive properties of the HEG as a function of DBS content.

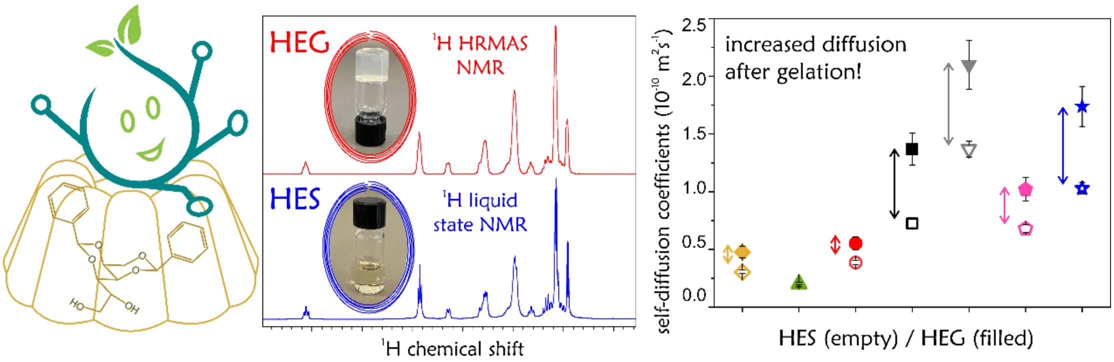

Fig. 1 Sketch of a DBS-based eutectogel (left). Liquid-state and High-Resolution Magic Angle Spinning (HRMAS) ^{1}H spectra of a representative HES and HEG (middle). Averaged self-diffusion coefficients measured for a set of HES and HEG (right).

Acknowledgements: A portion of this study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 – D.D. 1551.11-10-2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

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O26

Oral Presentation

Investigating the non-linear properties of ionic liquids based on the [NTf$_2$] anion through Z-scan

<u>Yago Arosa</u>[1,*], Alejandro Doval[1], Tigran Mansuryan[2], Carlos Damián Rodríguez-Fernández[3], Alessandro Tonello[2], Vincent Couderc[2], Elena López-Lago[1] and Raúl de la Fuente[1]

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In this work we report the variation of the non-linear refractive index (n_2) as a function of the repetition rate of the laser for several ionic liquids based on the [NTf$_2$] anion. We have measured the non-linear refractive index by means of Z-scan using a femtosecond laser at 1030 nm, varying the repetition frequency between 1 kHz and 300 kHz. The results show a smooth progression between negative and positive values of n_2 [1,2] for several cations with different aromaticity, undercovering interesting trends, Fig. 1. The tunability of this magnitude in liquids can be of great interest in frequency conversion processes or ultrafast optics, where the sign change in the non-linear refractive index can impact pulse compression and shaping [3].

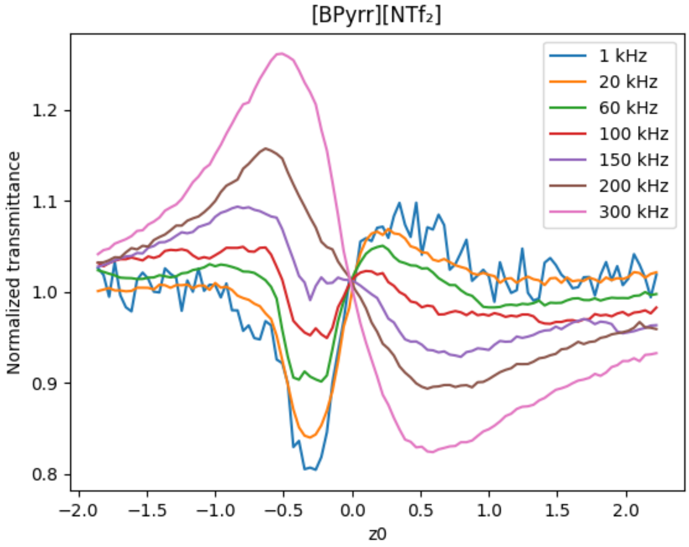

Fig. 1 Z-scan curves of [BPyrr][NTf$_2$] for a given peak power of 10 GW as function of the repetition rate.

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Structural Characterization of Lanthanum(III) Solutions in Ethyl Ammonium Nitrate (EAN) Mixtures with Water and Methanol

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Ionic liquids (ILs) have attracted much attention as a more sustainable alternative to traditional organic solvents owing to their negligible vapor pressure, non-flammability, thermal stability, and low toxicity. Due to these reasons, this class of solvents has been proposed for a variety of applications among which, several are those involving the solvation of metal ions and/or their complexes in ILs. In particular, lanthanide(III) ions (Ln^{3+}) are attracting ever-growing attention due to their employement in a wide horizon of fields, ranging from medical diagnostic to organic synthesis, making their solvation chemistry a topic of great interest [2]. In this framework, the achievement of a clear picture about a metal ion coordination in solution is an essential starting point to understand and improve the applications. In this work, we present the recent developments of a study about the coordination of the La^{3+} ion in the ethylammonium nitrate (EAN) IL and its mixtures with water and methanol (MeOH). Water can be present in ILs also at relatively high concentrations, both due to the hygroscopic nature of these solvents and to the operative conditions of the applications, like liquid-liquid extractions of lanthanoid ions from aqueous solutions. On the other hand, MeOH is the organic solvent that most shares its properties with water, due to the hydroxyl group that allows it to form an intricate H-bonds network, but the presence of the methyl group also allows one to get insights into the interaction of the studied system with an organic compound. In the present work, X-ray absorption spectroscopy (XAS) and molecular dynamics (MD) simulations have been employed in conjunction to shed light into the coordination of the La^{3+} ion in EAN aqueous and MeOH mixtures with different EAN mole fractions (χ_{EAN}). MD simulations showed that the dominant La^{3+} species in EAN/water mixtures is a 10-fold complex showing a remarkable flexibility to adapt for changes coming from the different water content. The amount of nitrate anions in the La^{3+} coordination sphere is found to change gradually with the χ_{EAN} value, differently to what was previously observed for Ln^{3+} ions aqueous mixtures with other ILs, where either water or the IL anion were found to coordinate the metal for wide composition ranges. The MD structural results are confirmed by XAS data collected on 0.1 M solutions of La(NO3)3 on EAN/water mixtures [1]. A similar picture is obtained for La^{3+} solutions in EAN/MeOH mixtures, where both nitrate anions and MeOH molecules are present in the metal ion first solvation sphere across the explored compositional range.

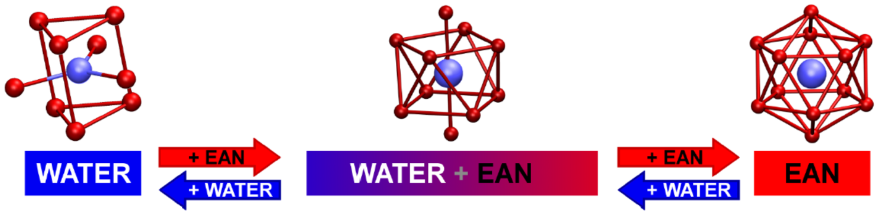

Fig. 1 Pictorial representation of the coordination shown by the La^{3+} ion in aqueous solution, EAN/water mixtures, and pure EAN solution, respectively

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Self-assembly and lubricity of orthoborate ionic liquids.

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Ionic liquids provide a set of properties unavailable with conventional molecular lubricants. They also allow additional functionality by enhancing lubricant electric conductivity [1] and enabling in-situ lubrication control [2-4]. The lubrication mechanisms of ILs are complex. The situation becomes even more challenging when ILs are added to oils [5] or greases [6,7]. Tribofilms formed by ILs can be sacrificial, non-sacrificial or hybrid. The films may also be influenced by the self-assembly properties of ILs in the bulk [8].

Here we compare lubricity of imidazolium and phosphonium bis(oxalato)borate ionic liquids (ILs) in a reciprocating sliding contact at different temperatures. Both the influence of the alkyl chain length and the cation architecture on friction, wear and lubricant breakdown are investigated [9-11]. Imidazolium ILs showed lower friction than phosphonium ILs though only phosphonium-based ILs reduced wear. A longer alkyl chain reduced friction only in the case of the imidazolium-based ILs. Analysis of the wear scars was consistent with chemical breakdown solely of the anion. Chemical changes in the ILs after the tribotests were more pronounced for imidazolium-based ILs, and comparison of breakdown and tribofilm formation implicated catalysis by the imidazolium center, which, in turn, had a strong dependence on the surface self-assembly.

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Sodium-Zinc molten salt batteries

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Within the Horizon 2020 project SOLSTICE [1], sodium-zinc molten salt batteries are being developed. The first cell concept employs solid zinc powder embedded in molten salt electrolyte, together with a solid ceramic electrolyte – operating at 300°C, similarly to the commercially available ZEBRA batteries [2]. Secondly, a high-temperature cell operating at 600°C with fully liquid electrodes and electrolyte is being investigated [3].
The talk will give an overview of the current state of research on high-temperature Na-Zn batteries, including electrochemistry, molten salt chemistry, salt corrosion, cost aspects, cell design and risk assessment.

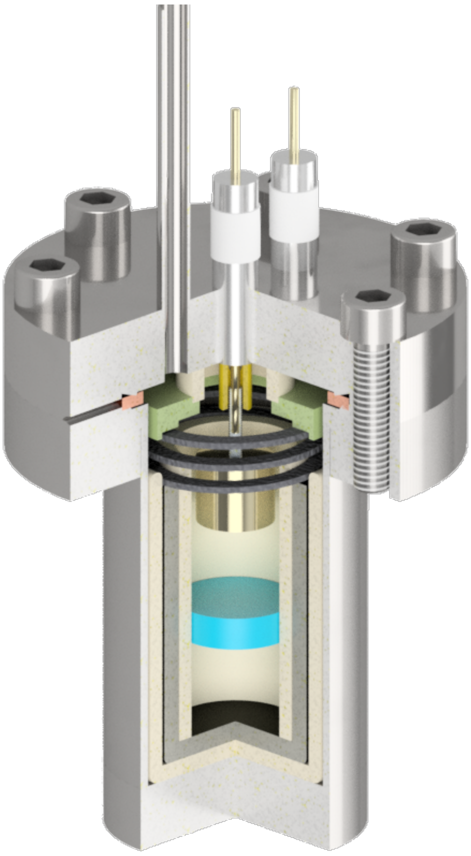

Fig. 1 Cell design of a Na-Zn cell operating at 600°C.

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Composite solid oxide/molten hydroxide electrolyte for ammonia fuel cell

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The current energy context calls for the development of new technologies for the production of electrical energy. Fuel cells can meet this demand and the main fuel considered today is Hydrogen (H_2). However, it is still difficult to store and transport it from the production site to the consumption site. Other vectors need to be deployed, including ammonia (NH_3).

Two common technologies for ammonia-fed fuel cells have been explored in previous research: alkaline fuel cells (AFC) and solid oxide fuel cells (SOFC). Ammonia AFCs operate at low temperatures (50-400°C) using a hydroxide salt-type electrolyte and have achieved a power density of 450 $mW.cm^{-2}$ at 100°C [1]. On the other hand, Ammonia SOFCs operate at high temperatures around 700°C and have recorded a power density of 1190 $mW.cm^{-2}$ at 650°C [2]. Although high-temperature fuel cells demonstrate impressive performance, the extreme operating conditions can lead to material aging and degradation. To strike a balance between performance and material degradation, an intermediate-temperature operation (450-600°C) is desirable. This can be achieved through a NH_3 hybrid cell, which combines the advantages of both AFC and SOFC. While the principle of hybrid cells is relatively new for ammonia fuel cells, it has already been investigated in the literature for hydrogen fuel cells utilizing composite materials of oxide/carbonates [3]. Hydrogen hybrid fuel cells (HFC) have demonstrated power densities exceeding 1000 $mW.cm^{-2}$ from 450°C [4].

This work aims to investigate a new hybrid electrolyte of oxide-alkaline hydroxide salt in view of using ammonia directly in fuel cells. The project focused on the hybrid system composed of Samarium-doped ceria (SDC) with different types of molten salts. The first part of the research was devoted to the synthesis and characterization of the electrolytic phase. A 0.02 S/cm conductivity was achieved with SDC-NaOH; 70-30 wt% under single atmosphere at 400 °C. In the next step, the focus will be on assessing the stability of the various electrolyte and electrode materials in an ammonia-rich atmosphere. At the same time, electrochemical tests will be carried out in gaseous NH_3 using the most promising materials. Based on the results obtained, a complete high-temperature cell will be built and tested. There are, of course, a number of challenges ahead, notably the selection of new materials and their long-term stability.

Acknowledgements:
The authors would like to thank PSL (doctoral school ED621).

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Electrochemical behavior of thorium in chloride molten salt

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Molten salt nuclear reactors are one of the six selected concepts for fourth-generation nuclear reactors [1]. The first molten salt reactor concept developed by Oak Ridge National Laboratory, USA, was designed to operate a fuel salt based on fluorides. These concepts relied on a thermal spectrum conferred by the moderating nature of the fluorides. These neutronic and chemical environments are compatible with a Th/U nuclear cycle but not with a U/Pu nuclear cycle, the latter being the French historical cycle. Chloride salts are more suitable to operate a reactor with the U/Pu cycle or for an actinide burner concept [2],[3]. The base salt chosen is NaCl, to which $MgCl_2$ or $ThCl_4$ is added to reduce the melting temperature to 460 and 330°C respectively. Therefore, it is interesting to study NaCl-$ThCl_4$-$PuCl_3$ salt since it has the lowest melting temperature [4].

There are currently uncertainties regarding the different degrees of stable oxidation of thorium in molten chloride salts. Indeed, the existence of stable $ThCl_2$ has sometimes been identified [5]. The construction of thermodynamic diagrams (based on Pourbaix methodology) using HSC.Chemistry database [6] giving the stability domain of elements as a function of potential and oxo-acidity (oxo-acidity is defined in molten salts by Na_2O activity) shows that a $ThCl_2$ stability domain would reduce the molten salt's electroactivity domain and intrinsically controls the corrosion of structural materials. Thorium was studied in a chloride medium by oxidizing metallic Th powder. Two oxidizing agents were tested: $MgCl_2$ and $ZnCl_2$.

Based on thermodynamic calculation and voltammetric investigations, the potential of the redox system $MgCl_2$/Mg is higher than $ThCl_2$/Th and lower than $ThCl_4$/Th couple, and therefore $MgCl_2$ can only oxidize Th to oxidation state (II) **(Fig. 1).**

Electrochemical measurements show that $MgCl_2$ could not oxidize the metallic Th powder. On the contrary, electrochemical measurements show the oxidation of Th metallic powder after the addition of $ZnCl_2$. In consequence, the experimental results then proved that Th(IV) is the only stable soluble oxidation state in the chloride salt.

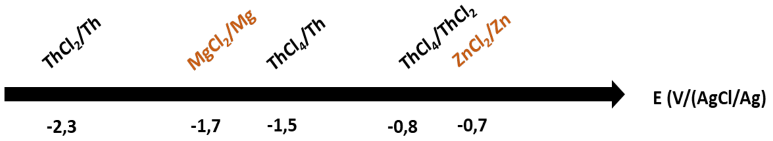

Fig. 1: Potential stability scale calculated based on thermodynamic and electrochemical data.

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Molten carbonates towards new CO_2 conversion

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Today, there is no doubt that the reduction of anthropogenic CO_2 emissions is unavoidable. Among the various technologies for reducing CO_2 emissions, the capture, storage and conversion of CO_2 are being studied. In particular, it is possible to “reuse” CO_2 by converting it into a useful and valuable carbon compound. Electroreduction of CO_2 is an attractive option, particularly in molten carbonate-based environments where its solubility is high. What's more, since commercial fuel cell systems are now mature, this technology would appear to be an ideal solution.

The aim of this paper is to give an overview of the electroreduction of CO_2 into molten alkali carbonates. First, the solubility of CO_2 in various systems will be presented, as a function of temperature as it is a significant parameter for the development of carbon capture and electrolysis systems such as molten carbonate cell (Molten Carbonate Fuel Cell, MCFC and Molten Carbonate Electrolysis Cell, MCEC). Then, from thermodynamics data and electrochemical characterizations, different mechanisms of CO_2 reduction will be discussed. Finally, new opening possibilities will be addressed, thanks to electrolysis cell development and performances.

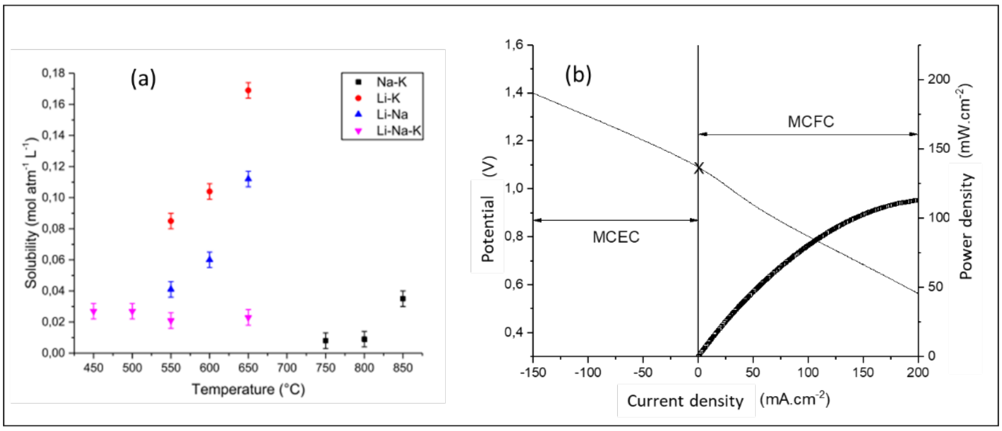

Fig. 1 (a) solubility of CO_2 in various molten carbonates, as a function of temperature. (b) Polarization and current density curves obtained in Li-K molten cell at 650°C. [1, 2, 3]

Work was supported by the French programs PLANEX ANR-11-EQPX-0–01 and ANR MCEC 17-CE05–0025–01. PhD grant supported by the French MESRI (Ministère de l'enseignement supérieur, de la recherche et de l'innovation, France) as well as PSL (Paris Sciences et Lettres University)

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The use of molten carbonates for CO_2 valorization into calcium oxalate.

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CO_2 emissions keep rising and the effects of global warming are more and more significant, despite decisions taken during Paris agreement in 2015 at the COP 21. The 3rd part of the IPCC report : Mitigation of Climate Change emphasizes on the need of solutions to capture, store and valorize CO_2. A solution would be to valorize CO_2 into a solid phase such as calcium oxalate CaC_2O_4, which could be reused in some industries. Previous results paved the way for the formation of intermediates - such as oxalate ion $C_2O_4^{2-}$ - during the electroreduction of CO_2 [1].

This work deals with CO_2 reduction mechanisms into molten carbonates[2]. In this kind of medium, the solubility of CO_2 depends on the composition of the mixture and the operating temperature and can be 100 times higher than in water at room temperature[3].

The goal of this project is to highlight the formation of calcium oxalate by CO_2 electroreduction in alkali molten carbonates.

First, TGA/DSC analyses have shown that the ternary $(LiNaK)_2CO_3$ eutectic was the only alkali carbonate eutectic available for the formation of calcium oxalate, its melting point (397°C) being lower than CaC_2O_4 thermal degradation temperature (480°C).

Then, to quantitatively generate calcium oxalate, its solubility in the ternary eutectic has been determined through electrochemical techniques. The solubility of lithium, sodium and potassium oxalates have also been measured to identify the least soluble oxalate and ascertain the electrochemical conditions necessary for the electrodeposition of calcium oxalate.

Finally, electrochemical analyses, (e.g. cyclic voltammetry and square wave voltammetry) have evidenced a multi-step reduction process. Notably, the initial step involves a one-electron process, aligning with the formation of oxalate intermediates.

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From fluorides to chlorides in nuclear energy : detection of anionic complexes by NMR, EXAFS and MD at high temperature.

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Because of severe experimental hindrances, the knowledge on molten halogen salts chemistry has long remained limited to few experimental approaches. Molten fluorides and chlorides mixtures can be strongly organized at unusually long distances due to the predominance of coulombic interactions and thus described by the formation of an intermediate range ordering [1]. The description of free anionic species content evolution is also of primary importance for a better understanding of their properties. NMR and EXAFS spectroscopy are one of the techniques able to provide such information. Nevertheless, these molten salts cumulate high temperatures (from 500 K to 1800 K), corrosive properties towards most of the materials and sensitivity to moisture and oxygen making these experiments a real challenge [2]. Thanks to specific design of the sample container and of the heating system it is now possible to obtain NMR and EXAFS spectra in the melt and to follow the evolution of the local structure with temperature and composition up to 1500°C.

The local structure of molten AX-MX$_4$ systems (A=Li+, Na+, K+; X=F, Cl, M= Ln^{3+}, Th^{4+}, U^{4+}) can be described as composed of free fluoride or chloride with anionic species $[MX_7]^{3-}$, $[MX_8]^{4-}$ and $[MX_9]^{5-}$ whose distribution varies with the amount of MX$_4$ (X= F, Cl and M= Ln^{3+}, Th^{4+}, U^{4+}) [3].

We are now able to calculate directly the signals obtained, thanks to the coupling between molecular dynamic calculations and theoretical approach of signals by DFT calculations. This new step towards a better description of the speciation in such molten salts will provide a new capability to determine the physical and chemical properties of molten salts used in nuclear energy.

Keywords

Molten salts, chlorides, fluorides, NMR, EXAFS, speciation

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New insight of redox potential control by titanium chloride in molten salt: prospects for metals protection?

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Molten salt (MS) systems have many attractive features including nuclear MS reactors, thermal energy storage, solar power plants… Due to a low melting point, a high thermal stability and the low cost of molten chloride salts (MCS), the possibility to develop MS reactors and especially Generation IV nuclear reactors has been studying since decades. However, such an aggressive medium could be responsible for material degradation caused by corrosion. One of the best challenges regarding safety and sustainability is the compatibility between high temperature MCS and materials. Because no passivation layer is sufficiently protective to limit the corrosion in MCS, the best way could be the salt redox potential control [1-2].

The aim of the presented research was the development of a fast and reliable method to significantly lower the salt redox potential and to fix it over time. For this purpose, the titanium chloride $TiCl_2$ was chosen as the amphoteric species capable of imposing a lower potential of the molten salt. This couple was synthetized from Ti^0, inserted into the molten salt. For a fast oxidation of Ti^0 into Ti^{II}, $ZnCl_2$ was previously added to perform the following redox reaction thermodynamically favorable: $Ti+ZnCl_2=TiCl_2+Zn$ (ΔG = - 87 kJ)
In presence of $TiCl_2$, the molten salt redox potential is decreased from -0.35 V to -1.0 V vs Ag/AgCl (Figure 1a). $ZnCl_2$ was chosen as it prevents oxidation of $TiCl_3$ in $TiCl_{4\,(g)}$ (ΔG = 172 kJ). Indeed, boiling point of $TiCl_4$ is lower than the temperature of the MCS. It is then not stable in the salt.
In presence of $TiCl_2$, the redox potential of the MCS is significantly lowered, around - 1 V/(Ag/AgCl) and stable over one month (Figure 1b). In these conditions, the redox potential of many metals and alloys are in the immunity domain, suggesting an effective means against corrosion.

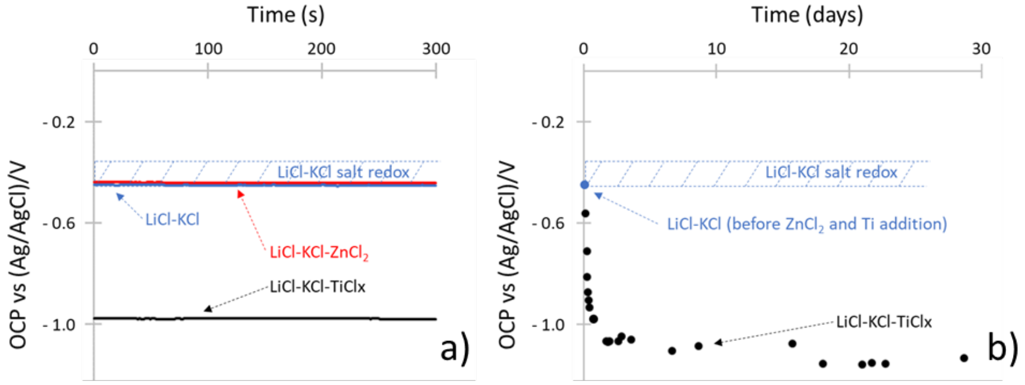

Figure 1: OCP recorded on W working electrode at 450°C in LiCl-KCl before and after $ZnCl_2$ then Ti addition (a) and evolution of the LiCl-KCl-TiClx MCS redox over one month.

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Reaction of aluminium metal with NaF-ScF_3 melt: Investigation of formation of aluminium-scandium alloy

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It is well established fact that tiny infusion of a rare earth metal scandium to aluminum alloys radically improve the tensile strength and desirable physical properties of the alloy product. Scandium influences the alloy structure, promotes formation of a subgrain structure and prevents the recrystallization.

In this study, the mechanism of metal aluminum dissolution in NaF−ScF_3 eutectic melts and the chemical interaction between the constituents of this mixture have been thoroughly studied by a combination of differential thermal analysis (DTA), high temperature and solid-state nuclear magnetic resonance (NMR), and X-ray diffraction (XRD) coupled with the molecular dynamic simulations. The formation of an insoluble Al_3Sc alloy in molten $(NaF-ScF_3)_{eut}$ system was proven and the chemical mechanism of this aluminothermic Al_3Sc alloy production was elucidated. The molecular dynamics calculations of the bath allow us to construct the structural model and to predict viscosity, density and electrical conductivity of the reagent melt to help to optimize the conditions of the alloy synthesis. [1,2]

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Polymer conversion from pyrochemistry in molten salt for production of hydrogen, carbonates, and energy recovery.

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Global plastics production exceeds 390 Mt per year, making it the 3rd most produced material in the world, after cement and steel. However, the amount of plastic collected and recycled is still too low, with almost 2/3 going to landfill and only 32% of plastics are recycled in EU. They are treated in three main ways: mechanically, chemically and, to a lesser extent, biologically. Performance plastics such as polyamides, polyacrylics and fluorinated polymers contain additives that make them even more difficult to recycle [1]. These engineering plastics can be found in a wide range of applications, particularly in Waste Electrical and Electronic Equipment (WEEE). In France, collection rates for WEEE vary from 44 to 70% depending on the type of waste (household or professional), and almost ¾ of it is recycled. However, while metals are recovered and recycled, plastics are not, or are rarely recovered [2].

In this project we are studying the pyrochemical conversion of plastics in molten hydroxide salts to produce hydrogen [3], carbonates, and energy recovery, according to the following hypothesis :

$$\boldsymbol{C_xH_yO_z} + 2x\,\boldsymbol{MOH} + (x-z)H_2O \rightarrow x\,\boldsymbol{M_2CO_3} + \left(2x + \left(\frac{y}{2}\right) - z\right)\boldsymbol{H_2}$$

Moreover, it seems that some molten salts can trap CO_2 as well as toxic compounds such as halides which are present in many WEEE (brominated epoxy resins), batteries (PVDF) or solar panel (PVF).

To achieve this goal, model molecules as well as polymers will be studied to properly identify the products and optimize the conditions as well as the reactor. Several parameters were studied, such as temperature, reaction time, salt/polymer ratio, etc. The gaseous reaction products were characterised by gas chromatography and quantified by water displacement. The solid phase obtained after cooling the liquid bath is studied by IR and NMR. So far, preliminary results have enabled hydrogen production to be validated and approximately quantified. Carbonates have also been observed under certain conditions.

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Study of the dissolution rate of Mg in NaOH-KOH (51.5-48.5 mol%) eutectic melts at 225°C

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Nuclear waste stored in silos 115 and 130 at La Hague (Orano) is mainly made up of structural waste from the reprocessing of fuel from first-generation reactors, the natural uranium graphite gas reactors. These silos contain mostly graphite, magnesium, and uranium metal and are of various sizes, from bulk waste at the top of the silos to the finest particles expected at the bottom. Graphite powder is relatively easy to manage, while magnesium and uranium powders are highly reactive with the portal solution in cementitious matrices, releasing hydrogen gas and oxidation products, which can lead to the cracking of the cementitious matrix and loss of integrity over time. Thus, due to their high specific surface area, bottom reactive waste cannot be treated using current conditioning techniques. The proposed way to manage the powdery nuclear wastes is to dissolve them in a molten hydroxide salt NaOH-KOH (51.5-48.5 mol%) at 225°C containing water and then confine the inert oxidized metal into a conditioning matrix. Thermodynamically, Mg dissolution can occur through water and Na^+ oxidation, generating respectively hydrogen gas in the salt medium or Na, a pyrophoric compound.

Experimental electrochemical studies have shown that the dissolution reaction is controlled by the water diffusion in the molten salt and that Na is not formed by the dissolution of Mg. Moreover, it was observed that the Mg (II)/Mg redox potential is higher than the Na^+/Na potential, regardless of the molten salt's water percentage. Magnesium metal is, therefore, oxidized by water to produce hydrogen gas, as shown by the following reaction:

$$Mg+H_2O=MgO+H_{2(g)}$$

To study the impact of the water content and the specific surface of the magnesium on the kinetic of Mg dissolution, a gas phase micro-chromatograph (µGC) was coupled to the reactor outlet to monitor the hydrogen released. The variations in the quantities of hydrogen produced as a function of time are illustrated in the form of cumulative curves. The slope at the origin of these curves is used to determine the dissolution rates. These slopes vary linearly with the water content at low water contents, which means that the water diffusion controls the corrosion of the magnesium.

The influence of Mg granulometry on dissolution kinetics was also studied. The same experimental protocol was used for different Mg particle sizes and a water content of 0.257 mmol/cm^3, and the amount of H_2 produced was monitored by gas chromatography. The results show that the dissolution kinetics increase linearly with the specific surface area, confirming that the higher the specific surface area, the greater the reactivity of the particles.

Uranium species stability in molten LiCl-KCl

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Uranium is an element mainly used as a fuel in nuclear energy production. One of the key elements of the fuel cycle is its reprocessing. Electrolysis in molten salts is a pyrochemical processes that can be used in order to recover fissile and fertile materials. This recovery process is initiated with an anodic dissolution of metallic spent nuclear fuel in molten halides such as LiCl-KCl. Then uranium, plutonium and minor actinides are recovered by electrolysis using solid cathode and liquid cadmium electrode. A good understanding of actinides behavior in the media is mandatory for a proper process operation. Thus, studies were made over the past decades in order to gather data towards uranium species behavior in molten chlorides [1][2][3].

The goal of this work was to obtain data on the U(IV)/U(III)/U systems equilibrium in LiCl-KCl. Hence, the U(III) and U stability was studied. Cyclic voltammetry (fig.1) and chronopotentiometry were performed in order to characterize the evolution of bath chemistry over time. It was found that neither U(III) nor U is stable in LiCl-KCl. A reaction mechanism for the involved reactions was proposed.

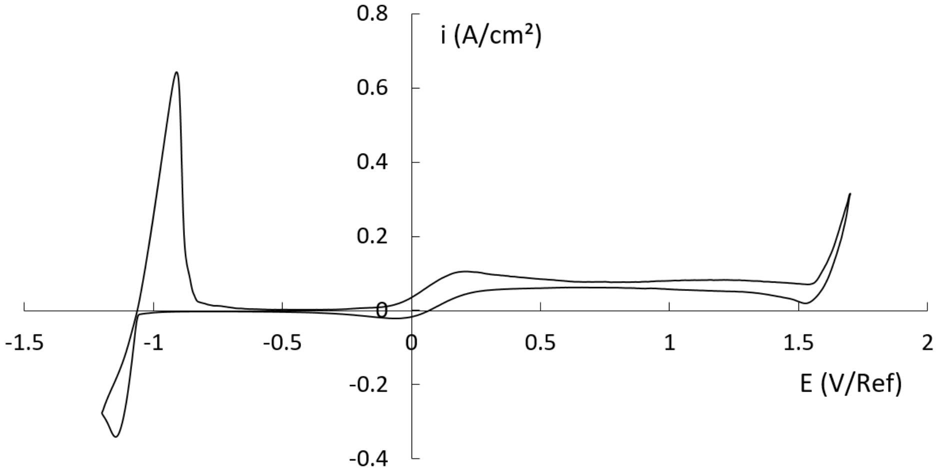

Fig.1 Cyclic voltammogram on a tungsten electrode in LiCl-KCl-UCl_3 at 450 °C, counter electrode: tungsten, reference electrode: LiCl-KCl-AgCl (1 wt%)/Ag, [UCl_3]: 0.144 mol/kg, scan rate: 0.1 V/s

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Thermodynamics of the Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} reciprocal system for the identification of potential salt-based high temperature Phase Change Materials

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The thermodynamic properties of the Mg^{2+}, Ca^{2+}// Cl^-, SO_4^{2-} reciprocal system, as part of the six-component systems Mg^{2+}, Ca^{2+}, Na^+// Cl^-, SO_4^{2-} and Mg^{2+}, Ca^{2+}, K^+// Cl^-, SO_4^{2-}, play a crucial role for the identification of phase change materials (PCMs), within the framework of our current project "PCM-Screening-2". Salt systems can be used as PCMs for charging and discharging latent heat at constant temperature during melting and solidification in latent heat thermal energy storage (LHTES) technologies [1, 2]. Therefore, the thermodynamic properties of pure compounds, binary, ternary and reciprocal systems need to be considered in order to select the suitable system for such applications. Several eutectic mixtures identified in the respective phase diagrams are investigated in order to verify whether they meet the requirements for applications as potential PCMs [3]. The systems (I-VIII) shown in Fig.1 are studied using various methods: differential thermal analysis coupled with thermogravimetry (DTA/TG), differential scanning calorimetry (DSC) and high temperature X-ray diffractometry (HTXRD). In order to pursue our goal, decomposition of sulphates [4], vaporization of chlorides and possible reaction with crucible materials need to be taken into consideration. The experimental results are integrated in a CALPHAD-based database for prediction of thermodynamic properties of the multicomponent salt system.

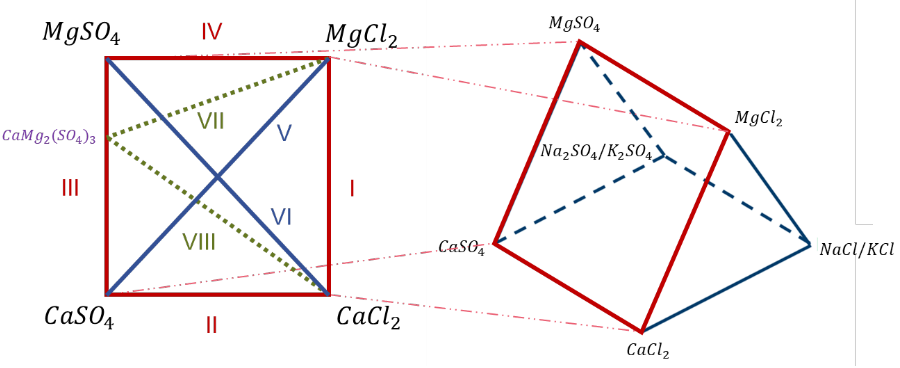

Fig. 1 Graphical representation of the complex six-component systems under analysis: Mg^{2+}, Ca^{2+}, Na^+// Cl^-, SO_4^{2-} and Mg^{2+}, Ca^{2+}, K^+// Cl^-, SO_4^{2-}.

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High-Temperature Nuclear Magnetic Resonance Investigation into the Structural Behaviour of Lanthanide Trichlorides in the NaCl-MgCl$_2$ Binary Molten Carrier Salt System

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Molten chloride fast reactors (MCFRs) are rapidly gaining momentum as promising Generation IV nuclear reactors, mainly due to their reactor design that promotes inherent safety and their ability to reduce the nuclear waste inventory [1]. While many variations to the MCFR fuel compositions have been proposed, the NaCl–MgCl$_2$ binary stands out as a propitious carrier salt system for the fissile/fertile actinide trichlorides due to its ability to sufficiently lower the fuel melting temperature, thus ensuring the integrity of reactor structural materials over its operational lifetime [2]. In this study, High-Temperature NMR studies have been performed on the NaCl–MgCl$_2$–CeCl$_3$ and NaCl–MgCl$_2$–LaCl$_3$ molten systems using CO$_2$-laser heating developed in Orléans, France to probe the structural behaviour of actinide trichlorides in MCFR fuels. Measurements of the ^{25}Mg, ^{35}Cl and ^{139}La chemical shift as a function of fuel composition provide insight into the coordination and complexation behaviour of lanthanide species in molten chloride salts. Furthermore, by coupling NMR measurements with Molecular Dynamics simulations, the fraction of the different complex species ($LaCl_6^{3-}$, $LaCl_7^{4-}$, $LaCl_8^{5-}$, $LaCl_9^{6-}$….) present can be quantitatively deduced [3]. This integrated approach provides a more precise assessment of the thermophysical and transport properties of MCFR fuels, crucial for optimizing heat transfer efficiency and the economic viability of molten salt reactors.

Acknowledgment: This work was carried out as part of the ISAC project funded by the France 2030 government program.

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O42

Oral Presentation

Influence of oxide concentration on SS316L electrochemical behaviour in molten LiCl-KCl medium

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Molten salts reactors have the potential to reduce the amount of spent nuclear fuel produced during electricity production [1]. One of the key issues is the corrosion resistance of the materials involved in this kind of reactors [2].

The main goal of this work is to study the behaviour of pure metals and alloys in a molten chloride media, with a high degree of control over the experimental conditions (atmosphere, temperature, oxide ions concentration). The first step was the characterization and the treatment of LiCl-KCl eutectic (59.2/40.8 mol%) at 550°C. Calibration methods, via square wave voltammetry, were used to monitor in situ oxide ions concentration and electrolyses were also performed to purify the solvent. The behaviour of pure metals such as nickel, chromium, iron, molybdenum and tungsten, was studied by electrochemical techniques and long duration immersions followed by SEM observations coupled with element analysis. The influence of oxide ions was also evaluated on each metal. This methodology was then transposed to the behaviour of 316L stainless steel (SS316L).

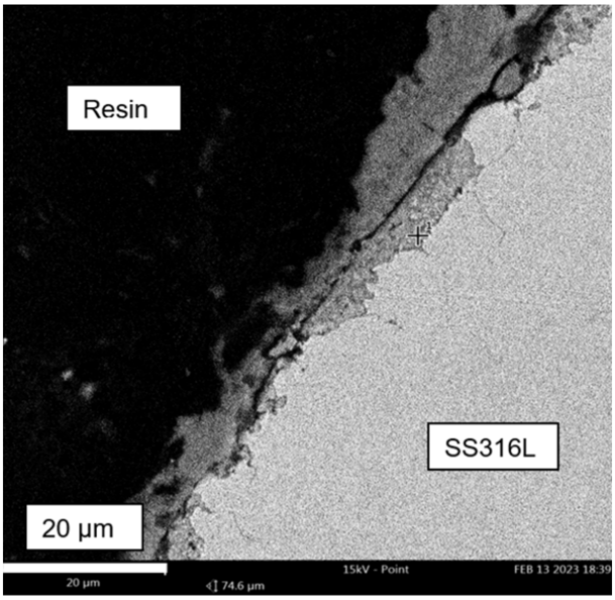

Fig. 1 Micrography of a 316L stainless steel electrode immersed in LiCl-KCl at 550°C; oxide concentration = 0,150 mol/kg

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Solubility investigation of selected RE_2O_3 in $(LiF\text{-}NaF)_{eut}$ vs $(LiF\text{-}NaF\text{-}REF_3)$ molten systems

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Rare earth (RE) elements play important role in the material chemistry and this fact causes a constant increasing demand of these metals. European Union (EU) suffers from the lack of raw materials in general, RE elements including. These elements belong to the group of critical raw materials defined by the EU with very low recycling level [1]. The recycling seems to be the efficient way how to reduce the dependence on imports of raw materials, reduce the volume of waste and how to increase the sustainable development.

Molten salt electrolysis is an industrial method for the extraction of RE elements from corresponding mixtures, including oxides. It is known that the solubility of rare earth oxides (REO) is not high but the presence of RE fluorides increase the solubility.

Our recent work was focused on solubility study of selected RE_2O_3 in the molten mixture of $LiF\text{-}NaF\text{-}REF_3$. The composition of $LiF\text{-}NaF\text{-}REF_3$ was constant with the lowest temperature of primary crystallization obtained in previous studies. To see the positive effect of REF_3 presence on solubility of RE_2O_3, the experiments on solubility of REO were performed also in the LiF-NaF eutectic mixture. The solubility investigation was measured by thermal analysis of molten mixtures and XRD analysis of the solidified samples. Solubility limit was finally determined based on the presence of RE_2O_3 patterns in the XRD records of solidified mixtures.

Acknowledgements: This work was supported by the Slovak Research and Development Agency under the contract No. APVV-19-0270 and by Slovak grant agency: VEGA 2/0083/24.

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Fluorine-Free Ionic Liquids and Electrolytes: From Synthesis to Energy Storage Applications

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Since their introduction by Sony in 1990, lithium-ion batteries (LIBs) have acquired a sizable market share. They have the best energy densities, a high open circuit voltage, a low selfdischarge rate, no memory effect, and a slow loss of charge when not in use. These properties make them the most popular rechargeable batteries for portable gadgets, electric vehicles and aerospace applications. They do, however, pose major safety issues since the conventional electrolytes are made of fluorinated salts dissolved in volatile organic solvents, the former being meta-stable at ambient temperature and the latter being flammable with a high vapour pressure. Thus, there is an urge to develop thermally and electrochemically stable nonfluorinated electrolytes to improve the safety and performance of batteries. Electrolytes based on ionic liquids (ILs) offer a range of advantages over traditional electrolytes including low volatility and high thermal and electrochemical stabilities, and can additionally be made fluorine-free and task-specific. In addition, the transport properties of ILs can be controlled by structural design of chemical functionalities to reduce the ionic interactions and enhance the ion mobilities.

Here we present, an overview of synthesis, physicochemical and electrochemical characterizations of six different families of ILs and their structurally analogous electrolytes based on the aromatic heterocyclic rings, oligoether based aromatic and aliphatic carboxylates, oligoether phosphates and aromatic sulfonyl anions coupled with ntetrabutylphosphonium-, imidazolium-, pyrrolidinium-based and alkali metal cations is presented. These studies are further complemented by NMR diffusometry to investigate the relative anion and anion mobilities and understand the possible interaction mechanisms between the oppositely charged ions within the ILs and the electrolytes, and especially, the influence of Li^+ addition in the IL-based electrolytes.

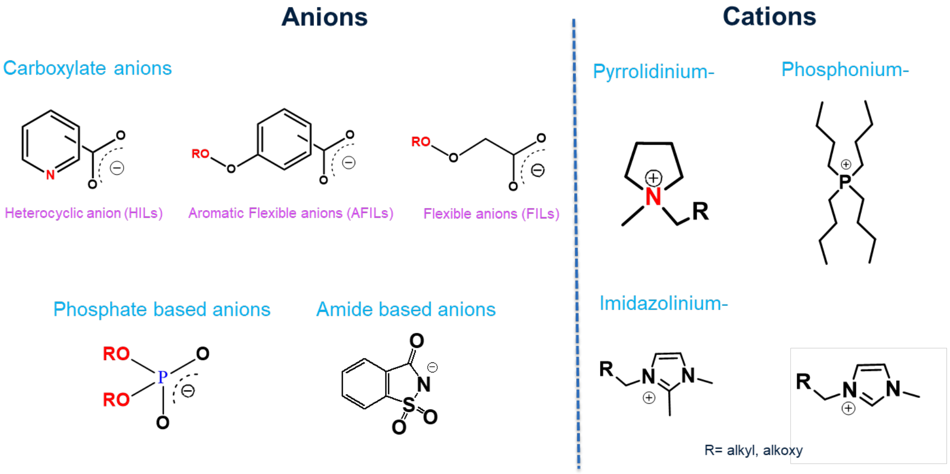

Figure 1. Designed fluorine-free ILs

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Non-Halogenated Functionalised Ionic Liquids

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Non-halogenated ionic materials (IM) are in the research focus both as components of electrolytes in battery applications and as additives to lubricants. Synthesis of ultra-pure (<500 ppm of halides) non-halogenated ionic liquids (ILs) is a challenging task. In addition, more complex impurities, such as transition anionic complexes (TACs) of orthoborate anions, may also pass into the final IL products and change their physico-chemical properties [1] and putatively alter complex bulk structures of ILs [2]. The notable fact is that the most of bis(salicylato)borate anion based IMs reported so far contain salicylic acid and/or the salicylate anion as principal impurities up to 10-20 mol % (as estimated from ^{13}C NMR spectra of these ILs in reported works). Such impurities, which are hydrophobic and rather difficult to get rid of from samples of ionic materials, do significantly alter density, viscosity, thermal stability, electrical conductivity and other physico-chemical properties of the final IM products.

Herein, we report on protocols for the synthesis and purification of sodium salts of the named anions and for metathesis reactions, which secure >98-99 mol % pure bis(salicylato)borate based ionic materials. We prepared a library of sodium salts of methyl- and methyloxy-functionalised bis(salicylato)borate anions and, then, IMs with these anions and tetraalkylphosphonium cations and compared physico-chemical properties of these IMs.

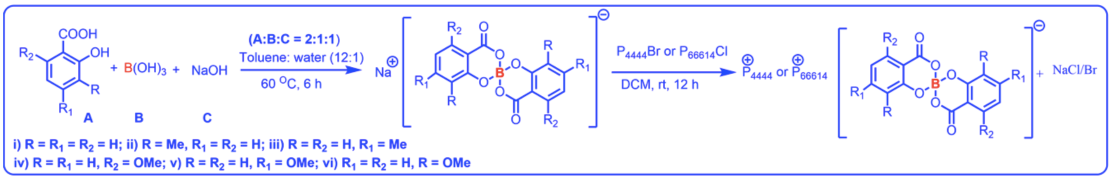

Fig. 1 Reaction schemes for methyl- and methyloxy-functionalised bis(salicylato)borate ILs.

Acknowledgements: The Foundations in memory of J. C. and Seth M. Kempe is gratefully acknowledged for the financial support in the form of a stipend for H.C. (Grant No. JCK-3173). O.N.A. also acknowledges the Swedish Foundation for Strategic Research (project EM16-0013) for the financial support (a part of the salary and costs of chemicals and analyses) and The Kempe Foundations (project numbers JCK-1306 and JCK-1433) and the laboratory fund at LTU for providing grants, from which a Bruker Aeon/Avance III NMR spectrometer at LTU has been purchased.

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Eutectogel formulations for cancer therapy: the codelivery of 5-fluorouracil and ibuprofen

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In cancer therapy, a common strategy based on the association of multiple drugs such as chemotherapeutic and anti-inflammatory agents, has been implemented as the standard first-line treatment of various tumors to improve patients' compliance. Nonetheless, the administration of multiple drugs is frequently challenging, as different pharmacological agents have distinct pharmacokinetic profiles, resulting in an uncoordinated uptake by the tumor cells. The design of an optimal dual-delivery formulation able to both reduce the side effects and enhance treatment efficacy is still challenging. Eutectogels (gels based on eutectic solvents), an emerging class of soft materials, have great potential as controlled drug delivery systems and for biomedical applications [1,2]. Indeed, they are biologically safe and biodegradable materials. The present study involves design, characterization, and drug-release profiles from novel eutectogels to use as controlled dual drug delivery. These easy-to-prepare gels were obtained by gelling DESs consisting of betaine as hydrogen bond acceptor and levulinic acid as hydrogen bond donor combined in different molar ratio [3]. The physico-chemical properties of single gels and gels loaded with selected drugs were determined by rheology and diffusion-NMR spectroscopy. The effect of the gelator percentage and DES components molar ratio is also investigated. In our study, we have chosen two small drugs: *i)* 5-fluorouracil, an anticancer drug, and *ii)* ibuprofen, which has very low water solubility, used to treat pain and inflammation. The eutectogel formulations exhibit variable release rates of the two drugs that depend on the experimental conditions (pH).

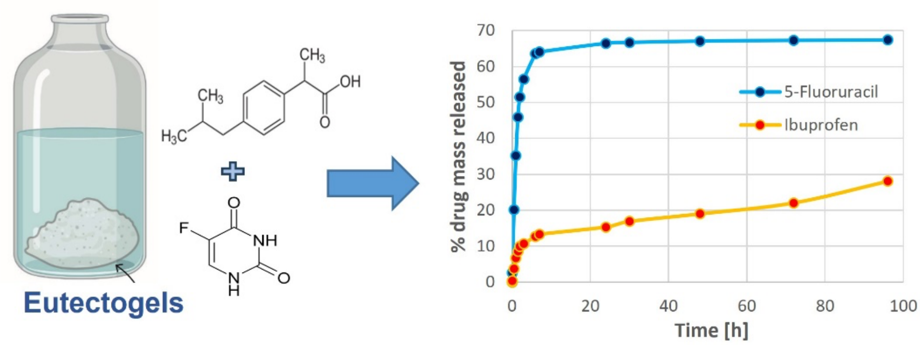

Fig. 1 Sketch of the eutectogel - chemical structure of ibuprofen and 5-fluorouracil - plot of the codelivery profiles.

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Click Chemistry: An Efficient Approach for the Synthesis and application of task-specific ionic liquids.

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Herein, we explore the synthesis and characterization of a novel series of imidazolium ionic liquids (ILs) that originate from the functionalisation of DL-Homocysteine thiolactone hydrochloride. Introducing in the ILs structure thiolactone units enables versatile modification of the imidazolium salts through thiol–alkene/alkyne "click" chemistry. This approach aligns with the principles of Green Chemistry. [1].

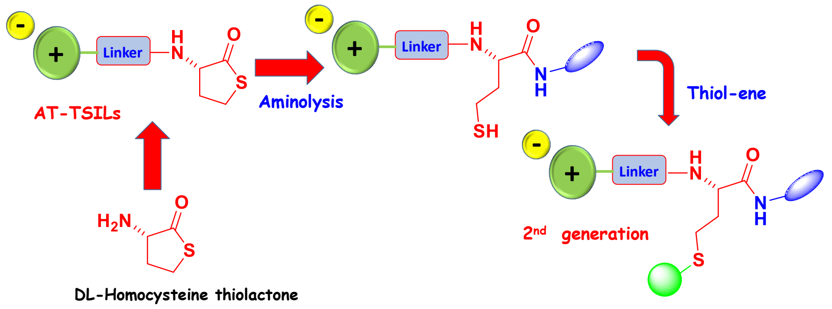

Fig. 1 Synthetic methodology for the preparation of multifunctional Task Specific Ionic Liquids.

The thiolactone ring within FILs-1 undergoes in-situ opening in the presence of amines, leading to the formation of functionalized thiols. These functionalized thiols are subsequently subjected to alkene click reactions, resulting in the production of versatile multifunctional Task Specific Ionic Liquids (TSILs). The remarkable flexibility of this protocol enables the synthesis of a wide array of TSILs by manipulating a limited set of readily available, common intermediates, even at a large scale. Adhering to the general click chemistry approach, different functional groups can be easily incorporated by altering the amine and acrylate structures employed in the synthesis. These ILs have undergone assessment as both homogeneous and heterogeneous systems in various catalytic processes.[2]

Acknowledgements: This work has been partially supported by MICINN-FEDER-AEI 10.13039/501100011033 (PID2021- 124695OB-C22), MCIN/AEI/10.13039/501100011033 and by the European Union Next Generation EU-PRTR (TED2021-129626B-I00 and TED2021-130288B-I00)..

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Development of Poly(ionic liquid)s for Removal and Electrochemical Degradation of Azo Dyes

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Currently, the textile industry uses high amounts of dyes in their processes. Annually, more than 10 000 tons of synthetic dyes are used, and it is estimated that about 10 to 15% remains unused and is discharged into the environment [1-2]. This work focuses on the removal of two anionic azo dyes, used in the textile industry, namely, direct red 80 (DR80) and reactive blue 5 (RB5) in an aqueous solution using a poly(ionic liquid) poly(diallyldimethylammonium) bis(trifluoromethylsulfonyl) imide (PIL) with cationic polymer chain. Extraction efficiencies of 99.3% and 88.3% were obtained for DR80, and of 99.4% and 97.0% for RB5 after 30 minutes, using particle sizes < 71 µm and 0.45-1.00 mm, respectively. The PIL was then subjected to a three-dimensional (3D) Electrochemical Process, as particulate electrode, with the aim of degrading the adsorbed dyes and regenerating the ionic liquid polymer, with a view to its subsequent reuse. In this process, using NaCl as electrolyte, a mixed metal oxide (MMO) anode and a graphite cathode, a degradation of 98.7% for RB5 was achieved, after a few minutes, and a degradation of 99.1% for DR80 was attained, in just over an hour.

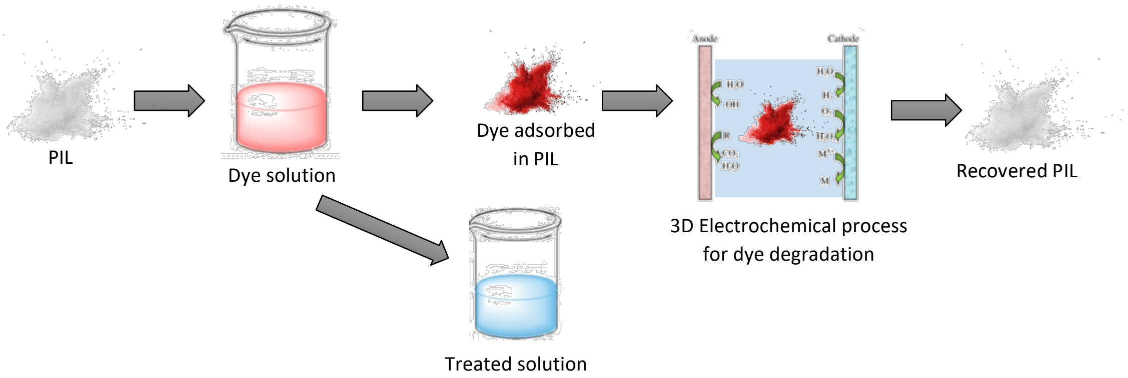

Fig. 1 Schematic of the dye adsorption process on PIL and 3D electrooxidation.

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Efficient Catalytic Hydrogenation of CO_2 derived Compounds over Organometallic Supported Ionic Liquid Phases

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The increase of anthropogenic CO_2 emissions has generated a significant effect in global warming.[1] Several strategies are under development with the aim to decrease this impact, however hydrogenation of CO_2 or derived compounds to produce fine chemicals and fuels have become an important strategy to capture, storage and reuse this gas.[2] In this contribution, we have synthesized several organometallic supported ionic liquid phases (OGA-SILPS) with a green and fast strategy that incorporates Ru with different ligands (**Figure 1a**). Full characterization of the supported catalysts, including XPS, TEM, FTIR and ICP/EA was performed to determine the nature and quantity of the organometallic specie anchored to the SILP as well as its chemical stability (**Figure 1 b**). The efficiency of the catalysts was tested in the hydrogenation of $TBA.HCO_3$ (produced by atmospheric air bubbling of TBA.OH), into $TBA.HCO_2$ (Formate) at relatively mild reaction conditions (**Figure 1 c**). Our results suggest an apparent effect on the type of ligand (and type of metallic precursor) and also on the distribution of them in the SILPS. Apparently, the use of electron-withdrawing group (CO) seems to have a major effect in the catalytic activity in comparison with the one with bis-allyl which its low performance can be associated with electronic and steric effects. In addition, our best catalyst exhibited robustness (up to 6 reuses with no leaching) and showed to be selective in the hydrogenation of another CO_2 derived compounds ($NaHCO_3$, CO_2 pure).

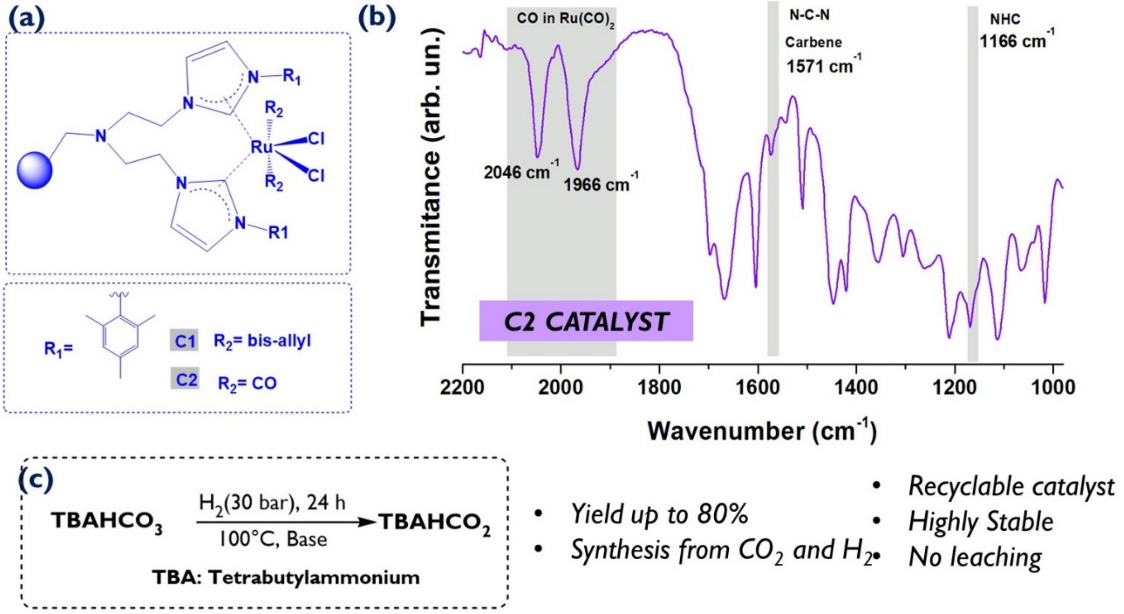

Figure 1. (a) Schematic representation of the synthesized catalysts (b) FTIR spectrum showing some relevant bands and c) typical hydrogenation reaction with some highlights.

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How do drugs dissolve in deep eutectic solvents?

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Deep eutectic solvents (DESs) emerge as a novel class of sustainable solvents prepared as mixtures of hydrogen bond donors, often alcohols, and acceptors, typically salts.[1] The large number of available mixtures allows for tailor-made combinations suitable for diverse applications, notably in extracting bioactive compounds and improving drug solubility.[1,2] The intricacies of DESs, derived from their multi-component nature, present challenges in comprehending their solvation behavior due to complex and varied intermolecular interactions and high viscosity.[1,2] Local environmental effects on the solvation of bioactive solutes in bio-compatible DESs were studied using molecular dynamics simulations. The interactions between DESs and solutes were accurately described using the all-atom, polarizable force field CL&Pol.[3] A detailed molecular-level description and understanding of solvation was facilitated by applying minimum-distance distribution function (MDDF) analysis and the Kirkwood-Buff (KB) theory of solutions that link microscopic information from MDDFs to thermodynamic quantities.[4] We estimate local density variations by computing KB integrals, offering a comprehensive view of solvation mechanisms. These insights provide crucial information for designing DESs specifically optimized for particular solutes as those necessary for novel pharmaceutical applications.[1,2] We studied the dissolution of ibuprofen, a common pharmaceutical ingredient, in biocompatible DESs including betaine and a polyol (glycerol or propylene glycol). Figure 1 illustrates an example that allows for the analysis, at a molecular level, of ibuprofen solvation in a 1:3 betaine:glycerol DES. We found evidence of a hydrogen bond between betaine and the COOH group of Ibuprofen while other interactions between the DES and the solute appear to be non-specific (e.g., dispersive, dipole-dipole) or mediated by other components in the system.

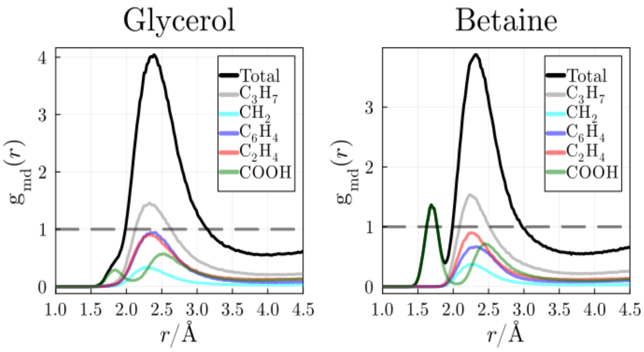

Fig. 1 Decomposition of glycerol (left) and betaine (right) MDDF regarding Ibuprofen chemical moieties.

Acknowledgments: Unicamp, FAPESP, ENS de Lyon, PSMN.

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Water-in-salt solution as leaching media for the recovery of platinum group metals from catalytic converters

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The search for alternative sources of such metals has gained significant attention in recent years to alleviate their growing demand and combat supply risk issues. Due to their economic importance and lack of alternatives in many applications, recovery of platinum group metals (PGMs) from various waste is of particular interest. PGMs are often found in greater concentration in urban residues than in ores whilst the forecasted supply of PGMs is constrained for the foreseeable future. One of the most prominent applications of PGMs is in the production of automotive catalytic converters (ACCs) [1], playing a crucial role in neutralizing pollutants generated through combustion processes. Conversely, the rapid and substantial increase in the number of discarded spent automotive catalytic converters (SACCs) poses both a substantial waste management challenge and a potential secondary source of PGMs. However, the recycling rate of PGM from SACC within the EU reaches only around 50% [2]. Most problematically, the hydrometallurgical extraction of PGMs poses significant challenges as it relies on the use of aggressive and toxic leaching media. Therefore, the quest for alternative leaching media is essential to minimize the environmental impacts and applicability of PGM recycling.

In this work, an alternative leaching step is applied, using a combination of two aluminum salts to dissolve platinum from real SACCs residue. Following a thermal pretreatment step, comminution, and aqueous wash of the sample, the solid-liquid extraction was evaluated using $AlCl_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ as an inorganic substitute to the more aggressive *aqua regia* leachate. Leaching parameters such as the molar ratio between $AlCl_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, water content, temperature, solid to liquid (S/L) ratio and kinetics were systematically optimized. Under the optimised conditions, a platinum leaching efficiency of 91% was achieved with a leaching activation energy of 77.6 $kJ \cdot mol^{-1}$. The leaching media could be reused at least five times with no decrease in the platinum leaching yield, demonstrating the potential of concentrated brines as alternative leaching media for waste valorisation. Finally, the recovery of platinum from co-dissolved impurities was attempted, resulting in a total recovery yield of 81% with a purity of 98%.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). This work was also financially supported by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC).

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Propeline: a green alternative to Ethaline for electrometallurgy of precious metals

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The economical viability of WEEE (Waste from Electrical and Electronic Equipment) recycling is mainly based on the recovery of copper and precious metals. In this context, we aim at developing a green process for the recovery of silver, palladium, and gold from rich printed-circuit boards (cell phones, labtops…). The recovery will be conducted after the necessary stages of non-metallic materials removal and the beneficiation of less precious metals such as copper and nickel, carried out by Terra Nova Development (TND), our industrial partner.

The process envisaged is based on electrometallurgy in “Deep eutectic solvents” (DES), a technology that can be considered as green alternative to conventional hydrometallurgy for precious metals recovery. Indeed, DES have a low reactivity and volatility, making them far less noxious to environment than corrosive liquors employed in conventional processes (cyanides, aqua regia). In particular, the DES named Ethaline (choline chloride-ethylene glycol mixture) has been widely used in electrometallurgy, because of its acceptable viscosity and the presence of substantial Cl^- concentration leading to a high solubility of numerous metallic compounds. However, if choline chloride (ChCl) can be considered as a “green” reactant, ethylene glycol (EG) is known to be harmful to men and animals in case of repeated exposure or inhalation periods. Comparable DES with a lower toxic nature than Ethaline can be obtained by replacing EG by other glycols e.g. propylene glycol (PG), widely used in cosmetics and pharmacology, with costs comparable to those of EG: The resulting DES is named Propeline.

We will present the potential of this less known DES in the recovery of precious metals. Because the change in the hydrogen bond donor with PG leads to a modification of the DES bulk properties, the first part of this work deals with the determination of Propeline density, viscosity, conductivity and electrochemical stability, which are properties of interest for electrochemical processes. The influence of water content on these properties was thoroughly investigated. Values of the above property parameters are compared to those obtained with Ethaline as a reference DES. In a second part, we will present the performances of Propeline for the electrochemical leaching of Ag, Pd and Au. The performance of Propeline in leaching was evaluated in ambient atmosphere, i.e. in the presence of water at percent levels. Leaching efficiencies could be studied after thorough development of analytical procedures dedicated to elemental analysis e.g. ICP-EOS in DES. The speciation of leached metals was determined by use of cross-linked analysis, namely UV-vis, and EXAFS/XANES spectroscopic techniques, in both cases with comparison with those in Ethaline. Systems (leached metal species-DES) were then thoroughly studied by electrochemical methods. In particular, diffusion coefficients of the solvated metal species were determined by electrochemical transient and stationary techniques, in the aim of leached metal recovery by electrochemical deposition.

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Exploring the potential of eutectic solvents for the valorization of fish skin

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Gelatin is a versatile and indispensable biomaterial, consisting of a mixture of peptides with heterogeneous molecular weights, and derived from the partial hydrolysis of native collagen. Due to its biocompatibility, biodegradability, and physical properties such as gelling capability, film forming capacity or texture enhancing, gelatin is widely used in food, pharmaceutical or cosmeceutical industries as well as in biomedical and tissue engineering [1].

The primary sources of gelatins are bovine and porcine skins and bones, but in recent years fish by-products are emerging as an alternative due to the absence of religious constraints and their lower health risk [1]. Traditional methods for gelatin extraction typically involve harsh conditions such as high temperatures, acid or alkaline environments, and prolonged processing times, thereby escalating operational costs and compromising the sustainability of the process.

In the current context, industrial practices shift towards more sustainable and eco-friendly alternatives, so it becomes imperative to explore innovative methodologies that address the shortcomings of traditional gelatin extraction techniques. This research explores the potential application of the eutectic solvent constituted by urea and sodium acetate trihydrate (in a molar ratio of 60:40) as an innovative, safe, and sustainable approach to produce gelatin from the skin offcuts of yellowfin tuna obtained after the fish-filleting process.

Once the solid-liquid equilibrium of the system was studied in order to determine the eutectic composition and the minimum working temperature, the solubility of major gelatin-forming amino acids was measured in the mixture. After that, the eutectic was tested as a solvent during the pretreatment of the skin at 35 °C at a solid-to-liquid ratio of 1:3 for 30 min and 3 h. Subsequently, the extraction step was carried out in the same way as in traditional methods, with distilled water at 45 °C.

The product obtained at the end of this process was properly characterized to determine its FT-IR spectrum, amino acid profile, molecular weight distribution, degree of hydrolysis, and thermal and rheological behavior. These analyses showed promising results since they suggested that rheological properties of the gelatin could be tuned just by varying the pretreatment time. Furthermore, yields reached values over 0.30 g of dry gelatin per gram of wet skin, which is notably higher than previous literature results.

Through this research, we aim to contribute to the burgeoning field of sustainable gelatin production by harnessing the untapped potential of fish residues. Our findings hold promise not only for mitigating environmental impacts associated with waste but also for fostering the development of novel, eco-friendly products that align with the principles of a circular and sustainable bioeconomy.

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Formation and Stabilization of Silver Nanoparticles on Thin Films of Symmetric Imidazolium-Based Ionic Liquids

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This study aimed to investigate the sputter deposition of silver nanoparticles (AgNPs) onto films of three symmetric imidazolium-based ionic liquids (ILs) that share the same anion (bis(trifluoromethylsulfonyl)imide) but differ in cation alkyl side chain lengths. The investigated ILs included $[C_7C_7im][NTf_2]$, $[C_8C_8im][NTf_2]$ and $[C_{10}C_{10}im][NTf_2]$. This study extends previous research, where it was concluded that symmetric alkyl side chains of the cationic moieties had better results when these chains were longer (when comparing $[C_2C_2im][NTf_2]$ and $[C_5C_5im][NTf_2]$).[1] Not only the ILs were effective as a media to capture the metal atoms but also as stabilizers during the formation of nanoparticles, as they tend to form small aggregates of uniform sizes.[1-3]

Different conditions were evaluated by modifying the thickness and deposition rate of the IL, as well as the silver deposition time and discharge current. The IL films were obtained in the form of microdroplets through vacuum thermal evaporation. They were deposited onto glass substrates coated with indium tin oxide (ITO). The process of thermal evaporation was conducted by carefully controlling the effusion temperature, deposition rate, and deposition time. The use of Knudsen cells provided a means to achieve precise and reproducible control over the mass flow rate.[4,5] The sputtering process of the metal onto ILs when conducted simultaneously with argon plasma promoted the coalescence of microdroplets of ILs and the incorporation and stabilization of AgNPs in the coalesced IL films. The formation/stabilization of the metal nanoparticles into the IL films was confirmed through high-resolution scanning electron microscopy (SEM) and UV-Vis spectroscopy.

Previous findings demonstrated that both the size and symmetry of the alkyl side chain significantly influenced the formation of droplets on ITO, subsequently impacting the formation and stabilization of AgNPs.[1] In this study, significantly improved results were achieved with ionic liquid films composed of very long alkyl chains attached to the cation. The longer chains promoted the formation and dispersion of AgNPs, which resulted in a higher stabilization even after two weeks of deposition.

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Towards the industrial implementation of cholinium chloride-based aqueous biphasic systems (ABS) – Phase separation hydrodynamics and best biphasic region of operation

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Aqueous biphasic systems (ABS) have been widely studied for extraction and purification of biomolecules. However, the industrial application of these eco-friendly separation platforms relies on effectively scaling and integrating them into current liquid-liquid extraction (LLE) units. Therefore, the phase separation hydrodynamics of three choline chloride ([Ch]Cl)-based ABS comprising polypropylene glycol with an average molecular weight of 400 g/ml (PPG-400), tripotassium hydrogen phosphate (K_3PO_4) and dipotassium hydrogen phosphate (K_2HPO_4) were investigated. The correlation between mixing time (Tm) and phase settling time (Ts) revealed Ts independence from Tm. For polymer/salt ABS, Ts exceeded 6 hours, contrasting with salt/salt ABS where Ts was under 150 seconds, notably decreasing with elevated temperatures. This rapid phase separation in salt/salt systems correlates with the salting-out effect of inorganic salts. Phase density emerged as a critical physicochemical factor in ABS formation. An optimal operating region was identified for [Ch]Cl/salt-based ABS, pivotal for potential industrial biomolecule separation in conventional mixer-settler units.

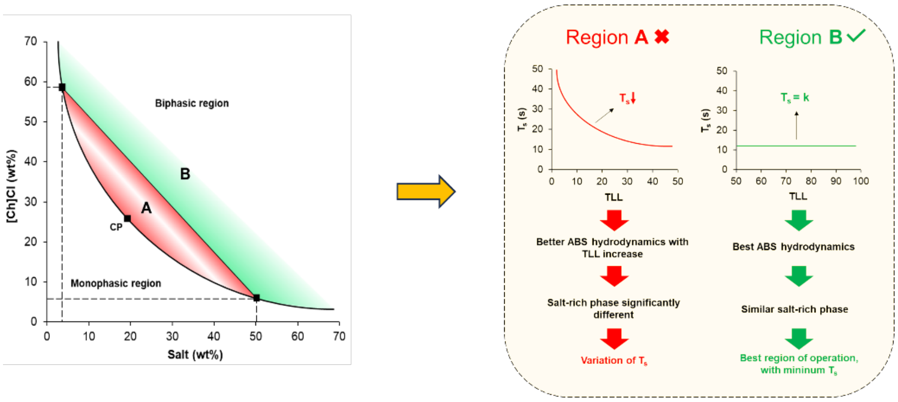

Figure 1. Schematics of the best region of operation for a [Ch]Cl-based salt/salt system.

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Ionic liquids and deep eutectic solvents as alternatives to glycerol for plasticization of starch

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This work focuses on the use and influence of various plasticizers on TPS properties. Glycerol is one of the most common plasticizers used for elaboration of TPS. However, its use in thermoplastic starch has shown several drawbacks such as retrogradation of amylose and glycerol demixtion [1].

To overcome these problems, deep eutectic solvents (DES) and ionic liquids (IL) were studied [2], [3]. Herein, TPS were elaborated by extrusion to ensure destructuration of starch and the homogeneity of the mix. TPS made with DES and IL did not show retrogradation of amylose according to XRD results. Additionally, thanks to dynamic mechanical spectroscopy, DES and IL demonstrated a better plasticizing effect on starch in comparison to glycerol. Mechanical tests have shown that more cohesive TPS could be obtained when using DES and IL as starch plasticizers instead of glycerol.

Finally, the use of starch for elaboration of materials might be controversial because it is used for feeding that is why, the last part of this project targeted on the use of brown algae. Blends with starch and plasticizers, including DES and IL, were processed by extrusion and compared with TPS. Mechanical properties and dynamic mechanical spectroscopy of blends showed that thermomechanical behaviour of blends with brown algae is similar to that of thermoplastic starch.

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Alternative process for the valorisation of microalgal biomass

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The use of microalgae for sustainable development has attracted a great deal of interest in the last few years and is currently a hot topic of research. Indeed, on the one hand microalgae grow in a range of aquatic habitats, including lakes, pounds, rivers, oceans, and even wastewater thus not competing with food and feed crop cultivars for arable land, while on the other, they can tolerate a wide range of harsh conditions such temperatures, salinities, and pH values [1]. These aspects, together with their enormous biodiversity make them a yet not fully exploited option for future renewable material and chemical production. More than 15 thousand novel compounds originated by microalgae have been identified so far [2]. Therefore, through the conscious selection of the most suitable species, it is possible to stress microalgae to produce a product of interest, such as bio-oil by biofixation of CO_2 with the aim of closing the anthropic carbon cycle, or to accumulate a pollutant from the environment, in the context of bioremediation.

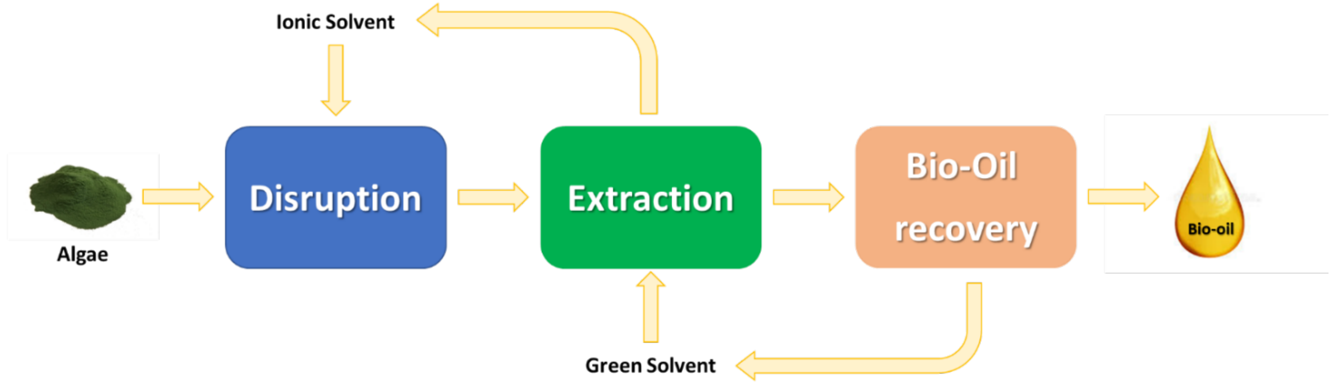

Fig. 1 Schematic representation of the microalgae treatment process

Herein, we report our effort in the treatment of diverse microalgae biomass species by using ionic media for cell disruption. Process parameters such as temperature, treatment time, biomass/ionic solvent ratio have been screened and optimized. Following, an innovative and sustainable extraction process after microalgae cell lysis has also been developed.

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Natural Deep Eutectic Solvents and bio based-Ionic Liquids for the valorisation of agri-food industry wastes

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The agri-food sector annually generates huge amount of waste and by-products, whose disposal causes serious environmental and economic issues. In this scenario, to boost the transition from a linear to a sustainable and circular bio-economy where waste mitigation plays a crucial role, the full exploitation of biomass food waste and its recycle into a new chain of value via the development of sustainable and green processes are of primary importance[1,2].

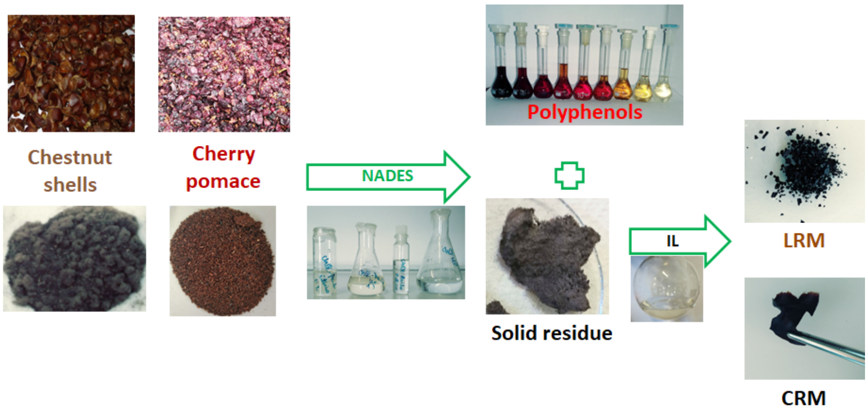

Fig. 1 Schematic valorisation process of agri-food waste.

In this study, natural deep eutectic solvents (NADESs) and bio based-ionic liquids (bio-ILs) have been employed for the valorization of food industry wastes of different nature (Figure 1). Two possible options have been explored, either the comparative analysis of DESs and ILs potential in the same process or their consecutive combined use, thus taking advantage from some complementary ability. More in details, for the first option, DESs and ILs were studied in the removal of lignin from fibers obtained after apple juice preparation. Conversely, for the second option, choline chloride, betaine or L-proline-based DESs were first studied in the extraction of polyphenolic compounds from chestnut waste or cherry pomace, while bio-ILs were employed for the fractionation of the lignocellulosic residue obtained after polyphenols extraction. Cellulose enriched material (CRM) and lignin enriched material (LRM) were obtained, and the nature of the extracted fractions was confirmed by infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA). The possibility to prepare ionogel from some CRMs has also been considered. Finally, the recovery of the NADES and the bio-ILs has also been proven, which make the whole process viable and amenable for large-scale applications.

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O59
Oral Presentation

Influence of Ionic Liquids on the Growth of Organic Semiconductor Films via Vapor Deposition

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The chemical nature, shape, and size of alkyl imidazolium-based ionic liquids (ILs) were investigated for their effects on the growth behavior and morphology of organic semiconductor (OSC) films. The use of IL-assisted vapor deposition can serve as a strategy to enhance the crystallinity of organic films [1].

In this work, two OSCs were examined: carbazole-based TCB and phenylamine-based TDAB. TCB exhibits a molecular structure analogous to TDAB but differs in the additional chemical bonds between the phenyl groups in the carbazolyl unit. This structural variation significantly influences various properties of these OSCs, including the glass-forming ability and thin film morphology [3]. Vapor deposition techniques by thermal evaporation were utilized, with various deposition strategies employed: sequential depositions (IL over OSCs), inverted sequential depositions (OSCs over IL), and simultaneous depositions [1].

TCB, in the absence of IL, exhibited minimal crystallization, while interaction with IL deposited above it resulted in small TCB crystal growth, in the nanometer range. In inverted sequential and simultaneous depositions, TCB crystals displayed significantly larger growth. Prior to IL deposition, TDAB exhibited well-defined pillar-shaped crystals. During sequential depositions, IL did not affect the morphology of the crystalline microstructures of TDAB, with IL accumulating atop them. However, argon plasma treatment induced the collapse of the IL structures, resulting in a thin IL coating on the TDAB pillars. Additionally, in inverted sequential depositions, TDAB crystalline filaments showed a preferential growth inside IL droplets (Fig. 1). Morphological analysis using SEM and crystallinity evaluation through XRD provided insights into film formation dynamics, elucidating the influence of IL on OSC film growth.

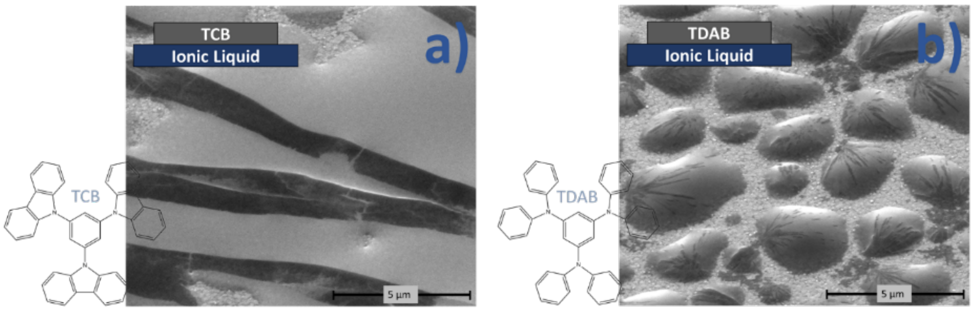

Fig. 1 - SEM micrographs exhibiting OSCs' crystalline growths when deposited over ionic liquids. a) 1,3,5-Tris(N-carbazolyl)benzene (TCB) deposited over [C_8C_1Im][NTf_2] droplets, b) 1,3,5-Tris(diphenylamino)benzene (TDAB) deposited over [C_8C_1Im][NTf_2] droplets.

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Towards the circular economy in the textile industry: using Deep Eutectic Solvents to decolorize wastewaters and cotton

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In the face of escalating climate change and global population growth, the textile industry confronts the dual challenges of depleting water resources and the increasing scarcity of essential materials like garments. Traditionally, the industry has adhered to a linear model, extracting raw materials, transforming them, and introducing the final products into the market. This approach, however, generates significant waste, much of which ends up in landfills due to the inefficiencies in recycling processes, leading to severe environmental consequences.

Recent endeavors strive to propel the textile sector towards a circular, zero-waste economy, with a focus on two key fronts. The first involves innovative approaches to wastewater treatment, utilizing Deep Eutectic Solvents (DESs). These solvents exhibit exceptional efficiency in decolorizing textile wastewaters, particularly in removing dyes, while simultaneously minimizing environmental impact as they derive from sustainable sources.

The second critical aspect addresses fiber recycling, with a special emphasis on cotton. Notably, countries like the USA and the UK collectively produce 15.1 and 1.7 million tons of cotton waste, respectively [1]. Despite their relatively higher recycling rates, averaging around 20%, there remains a pressing need for sustainable methods to enhance cotton recycling. This presentation explores the imperative of developing eco-friendly techniques that effectively remove dyes from cotton, emphasizing the pivotal role of Deep Eutectic Solvents in advancing sustainable practices within the textile industry.

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Rethinking Circularity of Electrified Interfaces for Sustainable Energy Storage Devices

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The integration of circularity principles in the design of energy storage devices (ESD), independently of their configuration, allows for a comprehensive understanding of the environmental implications of developing electrified interfaces supported by more sustainable protocols and technologies [1]. ESDs are vital for addressing the intermittent nature of renewable energy sources since it can store excess energy during periods of low demand and release it when needed, promoting sustainable energy management. Renewable carbon materials, such as biomass-derived carbons, have been investigated as electrodes for high-performance ESD, such as enhancement of energy storage capacity, power delivery, lifespan, environmental impact, and economic considerations [2]. Combining dense ionic fluids such as ionic liquids (IL) with biocarbon's offers high specific surface areas and porosity since ILs facilitate better ion adsorption/desorption at the electrode-electrolyte interface, enhancing charge storage capacity and cycling stability. As a practical example, the glycogen-based carbon material obtained from marine waste (mussel cooking wastewater) presented an S_{BET} surface area of 1526 $m^2\ g^{-1}$ while delivering a specific capacitance of 657 F g^{-1} at 1 A g^{-1} current density and a capacitance retention of 99% after 1000 continuous charge-discharge cycle [2]. The synergy between dense ionic fluids and biocarbon's holds promise for advancing ECD performance while aligning with environmental sustainability and circularity principles.

ESD comprising electrified interfaces with high circularity is crucial in integrating life cycle principles in home energy management systems. By ensuring high circularity in electrified interfaces of batteries/supercapacitors, the entire life cycle of energy storage and consumption can be optimized for sustainability, economic savings, and ecological impact. This approach facilitates the seamless integration of renewable energy systems, such as solar energy with energy storage technologies, to maximize self-consumption and reduce reliance on the traditional electrical grid [3].

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CO_2 Capture and Conversion with Ionic Liquids – Reality or a Dream

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Given the rising cost of CO_2 emissions, there is high demand for new alternatives to standard amine capture technologies. There are a number of publications on carbon capture using ionic liquids, but it is one thing to publish an article and quite another to bring a new breakthrough technology to market.

It is often assumed that ionic liquids are both expensive and not available on a large scale. Together with our partners, we have already shown that CO_2 capture based on ionic liquids also works on a large scale. As part of funded projects, together with our partners, we have now succeeded in converting two pilot systems to a Technology Readiness Level (TRL) of 6. This enabled us to refute this assumption. The remaining question is therefore whether this system makes economic sense.

Fig. 1 TRL 6 CO_2 capture pilot plant.

The advantages of using ILs to capture CO_2 include reducing water consumption and minimizing or eliminating the release of VOCs into the atmosphere. Furthermore, preventing corrosion of system components is an important aspect. However, whether a system can ultimately be used in an economically justifiable manner depends on energy costs being as low as possible. The CO_2 captured in this way can be converted as a raw material in-situ into value-added chemicals such as formate, methanol or synthesis gas using sunlight. In the presence of ILs, the conversion occurs faster, more selectively, which allows the overall cost of the process to be significantly reduced. The payback period for the technology is in the range of 5-10 years.

Part of this work has received funding from the European Union's Horizon 2020 Innovation Action programme under the Grant Agreement No 862192 (SunCoChem)

Ionogels: Advanced Battery technology through semisolid electrolytes with enhanced transport and thermal properties.

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Between the numerous applications of ionic liquids (ILs), the most popular one is in electrochemical technologies (batteries, fuel cells, and CO_2 absorbents) due to their low flammability, low vapour pressure, high ionic conductivities, and wide electrochemical windows. These properties make them ideal for their utilization as electrolytes instead of the commonly used carbonates that are highly inflammable if exposed to abusive, thermal, electrical, or mechanical conditions resulting in catastrophic consequences as fire and/or explosion.

Besides their promising characteristics, ILs can be encapsulated inside porous materials creating semisolid materials called ionogels [1]. The advantage of the ionogels over simply ionic liquids is the preservation of liquid-like characteristics [2] while gaining some of the benefits of solid-like electrolytes such as diminution of spillage during industrial assembly and reduction of lithium dendrite formation.

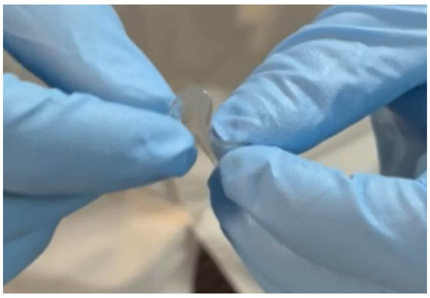

Fig. 1 Ionogel of pure [C_4C_1Pyrr][TFSI]

The IL N-buthyl-N-methylrrolidinium bis (trifluoromethanesulfonyl) imide ([C_4C_1Pyrr][TFSI]) was selected for this work and mixtures with lithium TFSI salt at different concentrations were prepared. Additionally, these mixtures were encapsulated in silica scaffolds using precursors made by ABCR LABORATORIOS company (see Fig. 1). Thermal and transport properties of the ionogels were analysed in this work. Comparison with the corresponding values of liquid mixtures were also accomplished. Finally, a molecular solvent (γ-butyrolactone) was also added to enhance transport properties to liquids and ionogel mixtures.

Acknowledgements: A. Santiago-Alonso, P. Vallet and J. J. Parajó acknowledge GAIN-Xunta de Galicia, FPI program of Ministerio de Ciencia Educación y Universidades and Postdoctoral program I2C- Xunta de Galicia, respectively. This work is financ1iated by MAT2017-89239-C2 (Ministerio de Economía y Competitividad and FEDER program) and GRC ED431C 2016/001 (Xunta de Galicia) programs.

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Designing new eutectic mixtures from waste cooking oils: application to the recovering of critical elements from spent lithium ion batteries

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In the context of a general scarcity of raw materials, the increasing massive production and intensive use of lithium-ion batteries are generating an enormous amount of valuable waste. In recycling industries, the electric discharging and mechanical treatment of spent cathodes and anodes produce a powder (black mass, BM) that usually consists of a mixture of Li, Co, Ni, Mn, F, P, and graphite in varying degrees of oxidation. Therefore, the extraction and selective recovery of the aforementioned elements from BM represent a pivotal target. According to the most recent and promising technologies for BM valorization, their processing with eutectic systems (ESs) has often been presented as innovative, efficient, and sustainable, as many eutectics can be prepared from cheap and low-impact (economically and environmentally) hydrogen bond donors (HBDs) and acceptors (HBAs) [1].

In this context, with the aim of designing a highly sustainable process for the valorization of LCO+NCM (lithium cobalt oxides + nickel manganese oxides) BM, novel eutectic mixtures were designed, prepared, characterized, and tested as an extractant. HBDs and HBAs were obtained from the recycling of waste cooking oils (WCOs) [2], which provided a mixture of triglycerides (containing oleic, linoleic, and linolenic acids), the corresponding free fatty acids (FFAs), and pure glycerol. A Design of Experiments (DoE) approach combined with rheological and spectroscopic (NMR) data allowed the determination of the more effective combinations within these chemicals obtained from waste for BM processing.

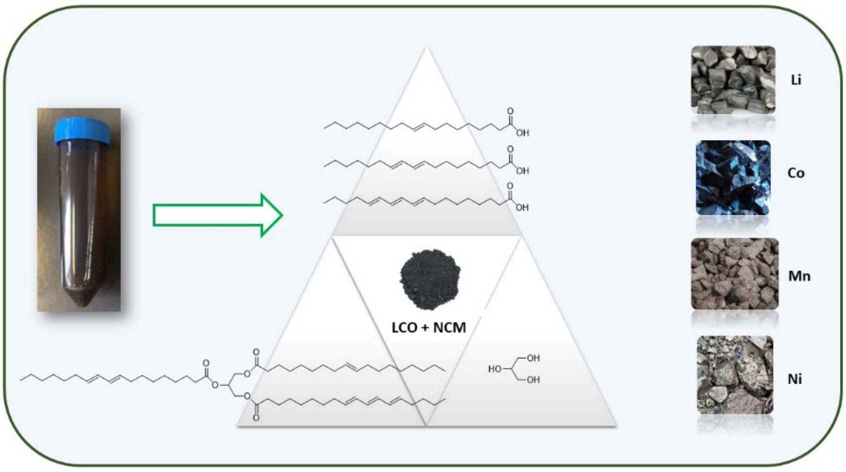

Fig. 1 Representative scheme of the research.

Acknowledgements: Part of this study was carried out within the WORLD Project-RISE EU Horizon 2020 Grant Agreement No. 873005, and within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 – D.D. 1551.11-10-2022, PE00000004).

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Design of eco-friendlier cotton dyeing platforms using deep eutectic solvents and natural dyes

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Textile industry remains as one of the largest wastewater generators in the world, mainly due to the water contaminated with synthetic dyes and other hazardous chemicals after the very inefficient dyeing processes. Recently, deep eutectic solvents (DES) have emerged as innovative solvents for textile dyeing, offering higher environmental friendliness, low vapor pressure, non-volatility, non-flammability, and relatively high thermal and chemical stability. This study explores the combination of cholinium-based and glycerol-based DES with natural dyes to achieve eco-friendlier cotton dyeing processes. The colorimetric and fastness features of the resulting textiles were influenced by the inherent composition and physicochemical properties of the tested DES. The best solvent was selected regarding its dye exhaustion, being further optimized and evaluated regarding its recyclability. At the end, a sustainable and environmentally friendly cotton dyeing platform is proposed, reducing the reliance on harmful chemicals and high energy intensive processes, while minimizing wastewater production in comparison to conventional dyeing processes.

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Understanding the influence of anions on Zn electrochemistry in deep eutectic solvents-water mixtures for Zn-ion capacitors

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Zn ion capacitors are emerging as a fast-growing alternative to other battery/capacitor storage chemistry due to its inherent safety, non-toxicity, ease of handling and recyclability. Although Zn can be electrodeposited from aqueous electrolytes, there are major impediments to overcome for use in Zn capacitors such as formation of dendrites during deposition/stripping process, passivation of Zn electrodes and evaporation of electrolyte. [1-3] In comparison, DES has been shown to be a good medium for the deposition of Zn and has recently shown to be a promising electrolyte for Zn-ion batteries. [4, 5]. However, issues regarding high viscosity and low ionic conductivity needs to be overcome which affects the Zn diffusion process.

Here the performance of formamide-based deep eutectic solvents of Zn salts with different anions (Cl, SO_4, Ac and TfO) electrolyte was investigated. It was observed that anions significantly influence the Zn solvation, electrochemistry, charge storage mechanism and stability of the capacitor. XPS, in-situ Raman spectroelectrochemistry and charge-discharge analyses showed that both chlorine and triflate anions store charge by anion exchange followed by Zn storage in PANI. For acetate and sulphate anions, the storage mechanism is by direct interaction of Zn with PANI. Among the four anions studied, the dual storage mechanism in $ZnCl_2$ and ZnTfO based DES electrolytes resulted in a more stable Zn-polyaniline hybrid capacitor performance. $ZnCl_2$-based DES electrolyte showed the highest storage capacity with an initial capacity of >200 mAh g^{-1}.

Acknowledgements: Calibri 9pt.

Financial support by the EPSRC project EP/W015129/1 is gratefully acknowledged.

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Structural battery electrolytes: effect of composition on the physico-chemical properties

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Structural batteries have emerged as promising composites in the field of Li-ion batteries. They consist of interpenetrated multifunctional components: (*i*) carbon-fibers that enable the intercalation of lithium ions and provide electrical conductivity; (*ii*) a polymer network that transfers mechanical load while confining (*iii*) the liquid electrolyte responsible for ion transport.[1] This unique design enables the storage of electrical energy within load-bearing components of a device or a part of a vehicle. For a good performance, suitable structural battery electrolytes need to be designed that exhibit both high ionic conductivity and stiffness.

In this project, our work focuses on the design and optimization of phase-separated SBEs, where the liquid electrolyte phase is an imidazolium-based protic ionic liquid doped with a lithium salt.[2] The effects of the SBE's composition on thermal properties, charge dynamics, and mechanical strength, as well as on the morphology of the macroscopic samples, have been studied. Our results stress the ability to tune these properties by composition. The SBEs consisting of about 50 wt.% of liquid electrolyte display a good combination of ionic conductivity and storage modulus, with values that allow their use as structural electrolytes in weightless structural batteries of the future.

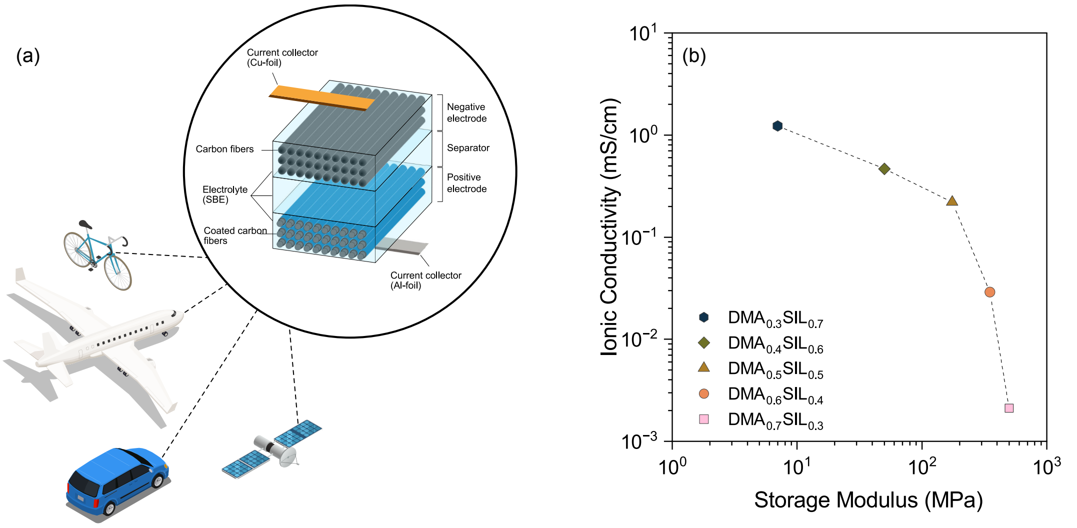

Fig. 1 (a) The structural battery concept and its components, (b) The ionic conductivity versus the storge modulus for SBEs with different composition.

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Optimizing hybrid water-in-salt electrolytes for energy storage

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The transition to a sustainable energy model demands advancements in both capturing energy from various sources (harvesting) and storing it efficiently. These advances led to the proposal of a new "water-in-salt" based electrolyte (WiSE) in 2015 by Suo et al. [1]. This pioneering electrolyte consists in a highly concentrated aqueous electrolyte of LiTFSI whose electrochemical stability window (ESW) was expanded three times from typical aqueous systems. Besides, the free H_2O fraction in these systems is too low, as theses molecules are taking part of the solvation shell of metal ions. As a result, the decomposition of salt anions led to the formation of a protective solid-electrolyte interphase, which prevents the reduction of water and expands the ESW.

The augmentation of kinetic protection within WiSEs necessitates increasing salt concentrations. However, most of these electrolytes currently reside near their saturation limits, impeding further direct additions. One proposed approach to surpass this barrier involves the strategic dilution of WiSEs with organic co-solvents. This dilution fosters the formation of superconcentrated hybrid electrolytes, enabling the incorporation of additional salt while circumventing saturation constraints. Furthermore, this dilution process facilitates the reduction of cation-anion interactions, thereby promoting ionic mobility and ultimately bolstering the kinetic protection afforded by WiSEs.

In this contribution computational results of these hybrid systems formed by adding different cosolvents (including acetonitrile, dimethyl sulfoxide, carbonates, etc.) to the traditional 21 m LiTFSI/H_2O WiSE will be presented. The analysis, conducted through bulk classical molecular dynamic simulations, compares the physicochemical properties of these systems at 298.15 K. By examining various structural and dynamic properties, the study aims to identify key physical factors that contribute to optimal performance. Furthermore, the computational results are validated using experimental data. Finally, recent advancements in these electrolytes when confined between two zeolite templated carbons will be discussed.

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Application of ionic liquids in iron based battery for large scale wind energy and solar energy storage

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Nowadays, intense concern about climate change issue is increasing among policy-makers and stakeholders in many major European economies. In July 2021, European Commission unveiled a set of legislative proposals aimed at achieving carbon neutrality by 2050, while reducing emissions by 55% by 2030 from the 1990 level as an intermediate target. In order to replace fossil fuels, expanding and integrating renewable energy capacity is one of the most crucial actions in these ambitious plans. Energy storage is regarded as a crucial resource to accomplish the sustainability goals for the future energy system given that a significant portion of dispatchable generation capacity based on fossil fuels would be replaced by renewable energy. In order to build a proficient energy supply network in Europe, there is considerable interest in advancing to develop more efficient energy storage technologies. Interestingly, of all energy storage technologies, battery technologies, especially the Li-ion battery has gained great attention in storing energy from renewable energy sources. Li-ion batteries are increasingly being used for energy storage applications due to their versatility, efficiency, and ability to store and release electricity. However, Li-ion based batteries still have many disadvantages, for example, high costs of the raw materials, safety issues, and limited Li resources in the earth. The mineable Li in the earth is only ca. 15 million tons annually nowadays. It is reported that Li can run out in ca. 65 years, indicating a shortage of Li in the near future. The safety issues of Li-ion based batteries are mainly related to fire and explosion risks since the battery is highly active and sensitive to water and oxygen. The organic solvents in Li-ion batteries are flammable and there have been several incidents with exploding Li-ion based batteries reported in the past. Therefore, many researchers try to develop new types of batteries to replace Li-ion based batteries, including sodium (Na) based batteries, and magnesium (Mg) based batteries. However, the costs of Na and Mg based batteries are still high since the cathode material for Na and Mg based batteries is expensive. In addition, flammable organic solvents are still utilized in Na and Mg based batteries. Therefore, there is a similar safety issue for Na and Mg based batteries as there is for Li-ion based batteries.

In our work, ionic liquids (ILs) are utilized as electrolytes to develop a novel low cost and high safety battery: iron-ion battery (Fe-ion battery). Fe is the cheapest metal among all the metallic materials. In addition, there are plenty of mineable Fe in the earth, ca. 230 billion tons. The element abundance of Fe rank No.1 in the universe and No.2 in the earth among the metallic elements. It means that there are plenty of Fe in the nature for the Fe-ion battery fabrication. Therefore, Fe is a cheap metal for new generation battery fabrication. The cost of Fe-ion battery is much lower than the batteries mentioned above. In addition, Fe-ion battery is a kind of extremely safe battery. The ionic liquid electrolyte inside of Fe-ion battery is not flammable, not oxygen or water sensitive, neither. Therefore, there is no explosion risk in Fe-ion battery. Due to the highly safe performance and low cost of Fe-ion battery, we are utilizing Fe-ion battery for large scale wind energy and solar energy storage.

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New Small-Volume Coin Cell for the Measurement of Electrical Conductivity of Ionic Fluids

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This work presents the development and test of a small-volume (140 µL) coin-type cell used in measurements of electrical conductivity of ionic fluids (Figure 1). This cell is part of a measuring apparatus composed by a Precision LCR meter (20 Hz - 500 kHz) from Keysight (model E4980AL, a customized air bath thermal chamber based on Peltier heat/cooling and a dedicated data acquisition & analysis software application. The core of the coin cell is a PEEK block that acts as both the sample container and the electrode spacer. The electrodes are pressed against the core part and the O-rings by two opposing aluminium plates, ensuring the geometry and sealing of the effective measuring compartment. The top and bottom of the cell are connected to a flow line allowing the sample to be introduced by injection. Additionally, this feature makes it possible to apply vacuum and to flow gaseous nitrogen for sample degasification and cell cleaning. The cell constant was experimental verified by measuring the resistance, at different temperatures, of aqueous 0.1 and 0.01 molal KCl solutions [1].

The performance and accuracy of the cell was evaluated by measuring the electrical conductivity of some common ILs, including the NIST recommended reference ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6C_1im][NTf_2]$ [2]. Several types of electrodes were tested: stainless steel AISI 316, stainless steel AISI 316 with titanium nitride (TiN) coating, platinum (Pt), nickel (Ni), titanium (Ti), and Ti with TiN coating. The results were compared with the data previously obtained using a dip-in cell based on a commercial Metrohm conductivity cell (model MTO-6.0908.110).

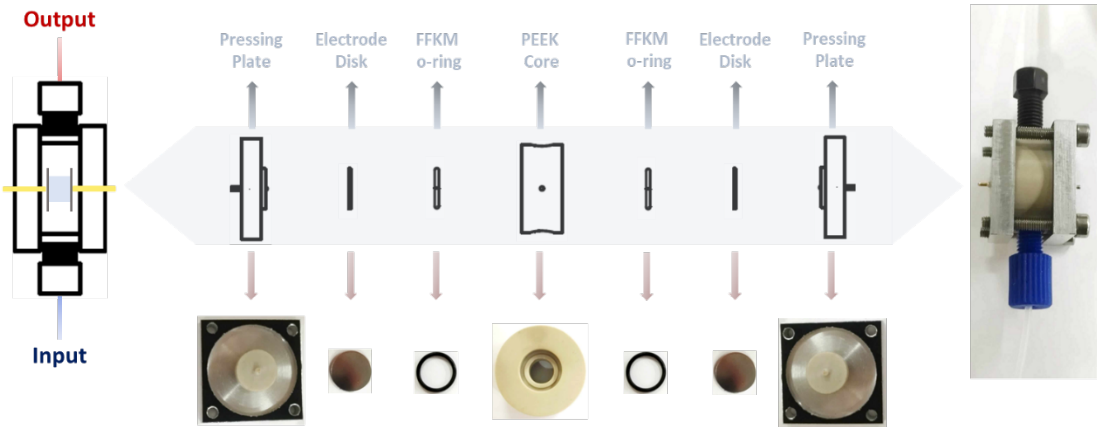

Fig. 1 Assembly scheme and images of the micro coin cell.

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Ionic liquid-Based Electrolytes for next Generation Batteries

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In order to fulfill the requirements of the European Green Deal and the German “Energiewende” the use of renewable energy and, hand in hand with that, the electrification of large parts of daily life is mandatory. Li-ion batteries, although today well-established, have their limitations, especially in terms of safety, because of the use of liquid organic solvent-based electrolytes which usually are both flammable and toxic. Furthermore, the availability and critical supply chains of many materials like Lithium, Manganese and Cobalt pose a risk.

Among the many concepts of post-Li-Ion battery systems metal-air batteries promise one of the highest energy densities.[1] However, they currently also have multiple problems that prevent the use outside of research laboratories.[2]

Ionic liquids are very interesting candidates as electrolytes or additives in such battery system, as their intrinsic properties like negligible vapor pressure high thermal and electrochemical stability make them especially suited in combination with gas-diffusion electrodes. In our conference contribution we would like to discuss the use ionic liquids as electrolytes and additives and their interaction with different gas-diffusion electrodes and the corresponding discharge products both for calcium- and lithium-air systems. In the second part we’d like to give an overview over ionic liquids and novel conductive salts and their interaction with the anode. The main focus shall be put on the SEI formation and stripping/plating behavior on calcium anodes since this is one of the major challenges for calcium-based battery systems.

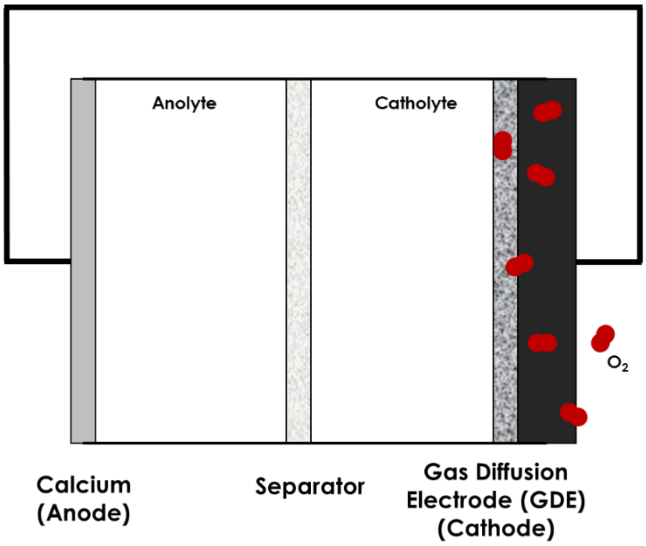

Fig 1. Schematic of a metal-oxygen battery

In summary, in our contribution we will give some insight how we design ionic liquids for metal-air batteries for the different requirements of the anolyte and catholyte.

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Poster Contributions

SEED4GREEN - A seed for the green transition. Tailoring Deep Eutectic Solvents for 5-Hydroxymethylfurfural (HMF) transformation.

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Aiming towards sustainability, biomasses are the ideal, virtually endless supply of suitable precursors for chemistry. Attractive candidates as synthons are small molecules from (poly)saccharides. Among them, 5-hydroxymethylfurfural (HMF) has a prominent role, as its diverse functional groups enable a large repertoire of chemical transformations.

The green fingerprint of HMF chemistry can be boosted by developing HMF transformations in sustainable solvents such as Deep Eutectic Solvents (DESs).

SEED4GREEN fits, with a dual objective, the EU central theme of a rapid green transition:

i) exploration of the chemical space of the HMF/DES pair, ii) networking and consolidating the collaborations in the DES field to achieve the first paradigms of HMF chemistry in DES.

The project architecture encompasses two pillars:

A) **HMF reactions in DES**: model reactions - oxidation, reduction, reductive amination and Diels-Alder (DA) reaction will be studied in view of the preparation of low-value substrates of interest for high-volume applications and high-value compounds for low-volume fine chemicals.

B) **HMF solvation in DES**. The intermolecular interactions in selected systems will be studied with a broad spectrum of methods (NMR, FTIR and Raman spectroscopies, X-ray scattering, MD and ab initio calculations) upon changing DES nature, third component (e.g. water) and temperature.

The delivery of a full recognition of opportunities and limitations of the DES-HMF partnership will represent a cornerstone approach for future application-oriented solvent system analysis.

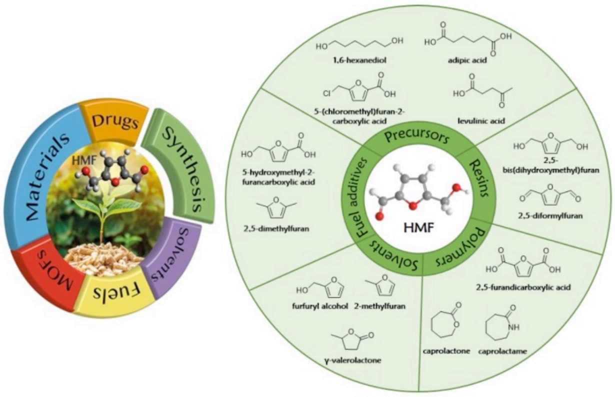

Fig. 1 HMF – a promising bio-based platform chemical

Acknowledgements: The SEED4GREEN project has been funded by European Union – Next Generation EU in the framework of the PRIN 2022 (project SEED4GREEN - Code 20223W4RT9).

Biomass-Derived Fluorine-Free Ionic Liquid Electrolytes: Synthesis and Energy Storage Application

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For safer energy storage systems, it is essential to develop non-flammable and fluorine-free electrolytes with a high thermal stability, high electrochemical stability, robust ionic conductivity as well as low toxicity.[1–4] Here we present synthesis, characterization, and electrochemical performance of a novel class of fluorine-free ionic liquids (ILs). These novel ILs demonstrated impressive physical and electrochemical properties such as wide electrochemical window, high thermal stability, better ionic conductivity as well as low glass transition temperatures. A variation in the cation chemical structure has significantly influenced the transport and electrochemical properties of these ILs over a wide temperature range. As expected, the ionic conductivity and ion diffusivity increased with increasing temperature. This study further demonstrated the use of these fluorine-free ILs as high temperature and broad potential window supercapacitor electrolytes.

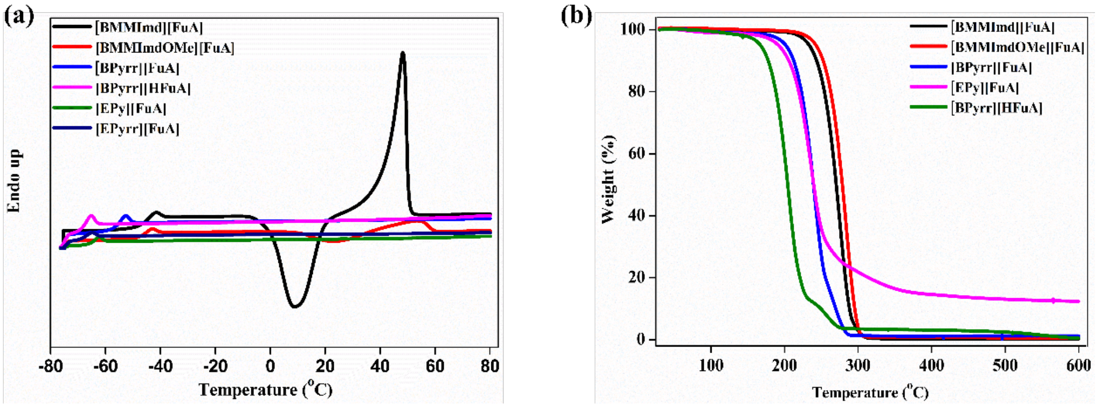

Fig. 1 (a) DSC curves and (B) TGA thermograms of the synthesized biomass-derive fluorine-free ILs.

Acknowledgements: The financial support from the European Union is gratefully acknowledged.

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Hydrolysis of polyurethane foam wastes using ionic liquid-superbase catalytic systems

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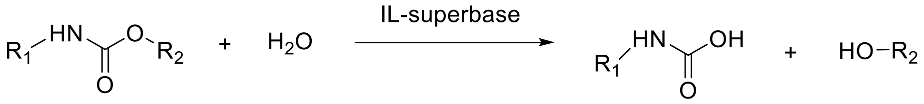
The fossil origin of over 98% of today's produced polymers and the prevalent disposal method through incineration play a substantial role in contributing to CO_2 emissions throughout the life cycle.[1] Addressing these challenges and minimizing the environmental impact of polymer waste needs the development of novel chemical and biochemical conversions for efficient recovery and recycling. According to Plastics Europe (2022), Europe produced 57.2 Mt of plastics in 2021 and generated 29.5 Mt of plastic waste in 2020. It is estimated that 65% of this plastic waste was landfilled or incinerated and only 35% was sent to recycling.[2] Polyurethane (PU) have a yearly production tonnage of 18.6 MMT/year. As a result of the absence of reuse procedures, a large amount of PU foam wastes from mattress has been thrown out by simple landfilling with dramatical impact on the environment. However, the current strategies towards a fully circular plastic economy are not yet economically viable [3]. Thus, novel chemical re/upcycling strategies to depolymerize PU into valuable monomers to re-synthesize the same plastic or to convert it into a different material are foreseen.[4]

It has been described that the combination of the ionic liquid technology,[5] and (bio)catalysis, has been shown as a suitable approach to carry out the easy and green depolymerization of PUF wastes (<100 °C, 1 bar, 6 h),[6] opposite to the classical glycolysis in reaction media based on a large excess in glycols, which occurs under harsh operation conditions (180-250 °C, and pressures up to 50 bar), and long reaction times (24-48 h). We present here the use of ionic liquid-superbase combination technologies for the depolymerization of polyurethane foam wastes under mild conditions.



Scheme 1: Hydrolysis reaction of polyurethane.

Acknowledgements: This work was partially supported by MICINN-FEDER-AEI 10.13039/501100011033 (PID2021-124695OB-C21/C22) and MICINN –European Union Next Generation EU-PRTR (TED2021-129626B-C21/C22)

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A theoretical study of low concentration per- and polyfluoroalkyl substances (PFAS) remediation from wastewater by novel hydrophobic deep eutectic solvents (HDES) extraction agents

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In this study, we focus on hydrophobic deep eutectic solvents (HDES) and investigate their potential for per- and polyfluoroalkyl substances (PFAS) remediation from wastewater through a nanoscopic approach using quantum chemistry and classical molecular dynamics simulations. Specifically, we study the properties of two selected widely used long-chain PFAS, Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), solutions in water with a novel HDES obtained by 1:1 M mixing ratio of cineole (CIN) and linoleic acid (LNA). Our results show that the strong affinity of PFAS substances for CIN and LNA molecules forming the HDES is accompanied by a disruption of interactions between PFAS and water molecules, confirming the HDES capability for PFAS removal from aqueous environments. The liquid structures are characterized by strong hydrogen bonding in the PFAS hydroxyl groups with the oxygen atoms in CIN and the carbonyl groups in LNA. Our study provides a molecular-level understanding of the PFAS extraction mechanism and suggests that the use of HDES solvents with low toxicity as extraction agents for PFAS remediation from wastewater could be a proper solution to design novel PFAS treatment materials suitable for liquid extraction.

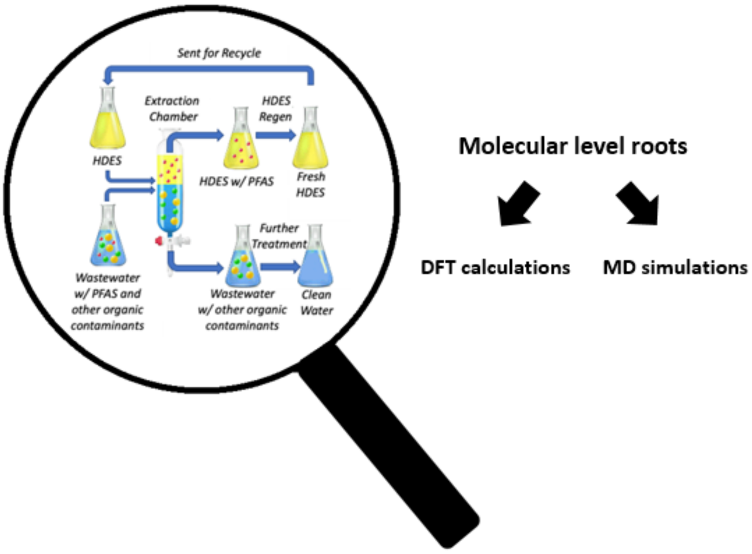

Fig. 1 Illustration of PFAS extraction from wastewater via novel HDES.

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Deep eutectic solvents and extraction of bioactive compounds

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There is great interest in various extraction/separation methods to treat plant materials for bioactive compounds. This search has always been challenging because of increasingly strict control requirements for solvent residues in the final products and a growing interest in environmentally friendliness of the process. Special attention in this field is on eutectic solvents from natural (natural DES - NADES) and pharmaceutical products (therapeutic DES - THEDES). This combination of eutectic solvent components has enormous chemical diversity, sustainability, biodegradability, and pharmaceutically acceptable toxicity profile. Also, there are already some examples where this type of solvents can overcome difficulties related to recover the target compounds from the extracted mixture, usually hindered due to solvent low vapor pressure [1].

Therapeutic deep eutectic systems are defined as eutectic systems in which at least one of the individual components is an active pharmaceutical ingredient or a eutectic system in which the active pharmaceutical ingredient is dissolved. Great attention is devoted to terpenes, among others, which can be combined with non-steroidal anti-inflammatory drugs [2]. Under consideration are *Dipsacus fullonum L*. plants, that have shown great antioxidant and antimicrobial activities, as well as effectiveness against several cancer strains and a source of *anti-Borrelia* compounds [3]. DESs have been shown to be effective solvents for extracting bioactive compounds, with yields several times higher than traditional organic solvent extracts depending on the group of analytes. This improved extraction efficiency could be attributed to DESs enhancing the permeability of active components through barriers in plant and their better solubility in DES. From the other side, this property of DES could be used to transport the drug through biological barriers and improve the bioavailability of drug.

The aim of our study is to understand the interactions that take place between DES components and extracted/solubilised compounds.

Acknowledgements: Tallinn University of Technology - R&D project SS22004; Estonian Centre of Analytical Chemistry- TT4; Estonian Research Council- Grant PRG1784.

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Insight into the thermal and structural properties of oxalatoborate-based ionic liquids

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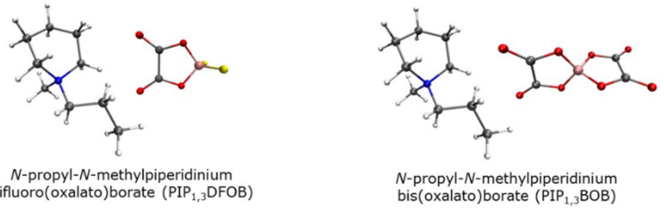
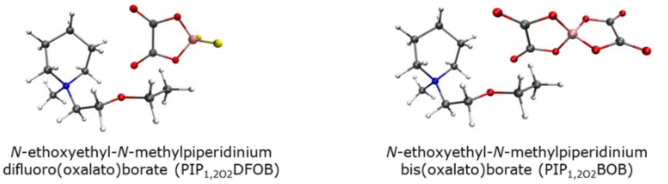
Ionic liquids (ILs) are normally defined as compounds completely composed of ions with melting point below 100 °C and have attracted considerable attention due to their inherent safety and adjustability. In the field of battery technology, they are frequently proposed as substitutes or additives to conventional electrolytes to enhance stability and introduce novel functionalities [1]. Particularly, ILs containing (oxalate)borate anions, exemplified by bis(oxalate)borate (BOB) and difluoro(oxalate)borate (DFOB), have recently emerged as potential additives to carbonate-based electrolytes. Despite these advancements, there is a scarcity of studies correlating the experimental properties of (oxalate)borate-based ILs with their molecular structure [2]. Consequently, here we propose a structural study of four ILs: N-ethoxyethyl-N-methylpiperidinium bis(oxalate)borate (PIP$_{1,2O2}$BOB), N-ethoxyethyl-N-methylpiperidinium difluoro(oxalate)borate (PIP$_{1,2O2}$DFOB), N-propyl-N-methylpiperidinium bis(oxalate)borate (PIP$_{1,3}$BOB), and N-propyl-N-methylpiperidinium difluoro(oxalate)borate (PIP$_{1,3}$DFOB), with the aim of correlate their structural properties with their thermal behaviour. The molecular structures of the studied ILS are reported in Fig. 1.



N-propyl-*N*-methylpiperidinium difluoro(oxalato)borate (PIP$_{1,3}$DFOB)

N-propyl-*N*-methylpiperidinium bis(oxalato)borate (PIP$_{1,3}$BOB)



N-ethoxyethyl-*N*-methylpiperidinium difluoro(oxalato)borate (PIP$_{1,2O2}$DFOB)

N-ethoxyethyl-*N*-methylpiperidinium bis(oxalato)borate (PIP$_{1,2O2}$BOB)

Fig. 1 Cation and anion structures of the four studied ILs.

Differential scanning calorimetry was employed to examine the thermal behavior of the systems. Subsequently, a computational approach combining molecular dynamics simulations and density functional theory calculations was employed. The simulations indicated an increase in the degree of freedom of the cation's lateral chain when an ether oxygen atom was present. In addition, when comparing PIP$_{1,2O2}$DFOB and PIP$_{1,2O2}$BOB, a significant anion-anion interaction was observed in the former due to charge delocalization induced by fluorine atoms. The stronger anion-anion interaction correlated well with a weaker cation-anion interaction and reduced segregation.

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Probing the acidity level of ionic liquids: implementation of the Hammett acidity functions in Raman spectroscopy

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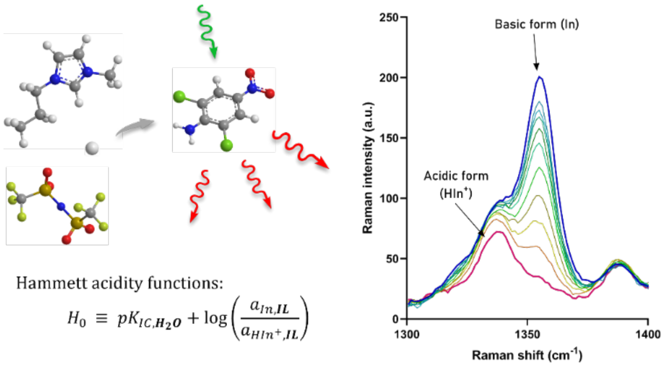
Ionic liquids (ILs) possess outstanding properties, such as specific solvation abilities and a super-acidic feature, explaining their use as solvents for acid-catalysed reactions, for instance.[1] In that context, determining the levels of acidity accessible in ILs is essential to better apprehend their use as super-acidic media for novel chemical processes. The fundamental level of acidity achievable in ILs is related to the solvation properties of the solvent on the proton. However, data on solvation energies for protons in non-aqueous solvents, and ILs especially, are still missing, since the solvation energy of protons in such solvents can only be determined experimentally through extra-thermodynamic hypotheses. [2] One of the methods relying on such hypotheses is the Hammett acidity function, based on the protonation equilibrium of nitroanilines, monitored by UV-visible spectroscopy (UVS).[3] However, the transfer of the Hammett method from molecular solvents, as originally proposed, to ILs might not be straightforward due to the possible interactions between the nitroanilines and the ions of the ILs (π-staking) as well as the suggested non-dissociating behaviour of ILs. In this work, we implemented, for the first time, the determination of the Hammett acidity function using Raman spectroscopy (RS). Using RS instead of UVS would enable the use of new, non-coloured, more spherical and non-aromatic pH-reporters, better meeting the fundamental hypothesis of Hammett. In this work, the level of acidity of three 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs (alkyl = ethyl, butyl, octyl) was determined, to study the influence of the alkyl chain length on the acidity of the solvents, either by UVS and RS to confirm the appropriate implementation of the Hammett acidity function in RS. Since RS has a lower sensitivity than UVS, the influence of the pH-reporter concentration on the observed acidity level (hence the solvation energy) was also assessed. Finally, other constituting cations were selected to study the influence of specific interactions between the IL and the pH-probe: the 1-Butyl-1-methylpyrrolidinium and 1-*tert*-butyl-3-methylimidazolium cations were chosen to study the consequence of aromaticity and steric hindrance on the acidity, respectively.



Hammett acidity functions:

$$H_0 \equiv pK_{IC,\boldsymbol{H_2O}} + \log\left(\frac{a_{In,\boldsymbol{IL}}}{a_{HIn^+,\boldsymbol{IL}}}\right)$$

Fig 1**.** Left: Scheme of the protonation of 2,6-dichloro-4-nitraniline (IC) in the 1-butyl-3-methylimidazolium bistriflimide ionic liquid (IL) measured by Raman spectroscopy, and equation of the Hammett acidity functions. Right: Evolution of the 1300-1400 cm^{-1} Raman spectrum of the IC with increasing amounts of bistriflimidic acid in the same IL.

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Modeling fragmentation of non-covalent molecular clusters in soft-ionisation mass spectrometry of deep eutectic solvents

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Computational modeling of mass spectrometry (MS) experiments gives us insight into the information unavailable from the experiments such as the structure of initial precursor ion after desolvation and the fragmentation energy of the parent and daughter ions. The contemporary universe of computational models for MS can be categorized into two modes based on their treatment of the experimental data: Top-down approach of training dissociation metrics on the available library of metabolomic and proteomic data to annotate and predict the MS processes; Bottom-up approach of statistical fragmentation of molecular entities using the quantum chemical thermochemistry and molecular dynamics simulations.

The analysis of non-covalent molecular clusters observed in soft-ionization MS (SI-MS) techniques cannot utilize either of the above approaches as the systems are too large to be simulated quantum chemically, and a reference library of MS data and breaking curves for non-covalent clusters similar to the data libraries of protein MS does not yet exist.

In this work, we are proposing an approach to bridge the gap between the two above computational models. Our integrated approach preserves the first-principles nature of a statistical simulation of fragmentation with the potential scale-up to the chemical systems of sizes of dozens of non-covalently held molecules (supramolecules). Our model integrates the CREST software suite[1] for conformer sampling and thermochemistry calculations, with the M_3C fragmentation simulation algorithm[2]. A similarity metric is used to compare the simulated and experimental breaking curves, and combinatorial sampling of precursor ions produce the best candidates for the structure of the precursor ion in the SI-MS experiments of the choline chloride-urea deep eutectic solvent (reline) (figure 1).

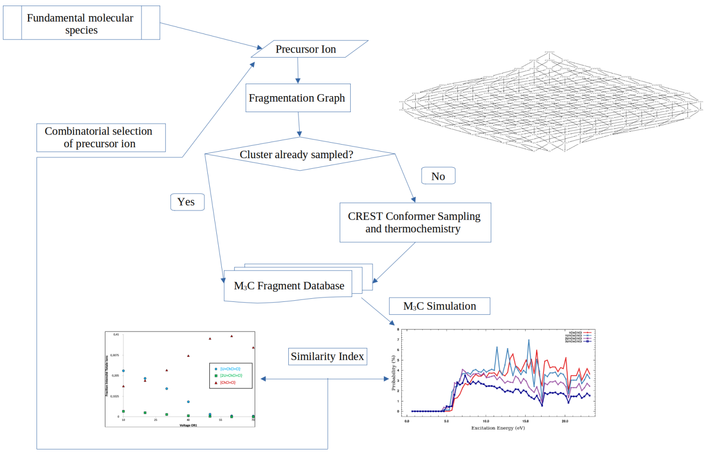

Fig. 1 Work flow of the integrated suite for simulation of fragmentation process of molecular clusters in soft-ionization mass spectrometry.

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Supported ionic liquids for efficient thermal energy storage

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Recently, ionic liquids (ILs) have shown potential as phase change materials (PCMs) for thermal energy storage (TES) [1]. ILs have some very useful properties for PCMs – they are generally thermally stable, non-volatile, and non-flammable. Thermal properties such as heat of fusion, specific heat capacity and thermal conductivity of ILs are some important parameters to characterize their TES performance.

Our studies on the thermal properties of amine and carboxylic acid based protic ionic liquids (PILs) have shown that the thermal stability of, for example, acetate PILs, as analysed by thermogravimetric analysis (TGA) combined with differential scanning calorimetry (DSC), limits the useful temperature range for using this class of ILs as TES materials. However, there are still several potential ammonium and carboxylate based PILs that have shown the potential of this type of compounds to be applied as TES materials.

The liquid state of ILs at room temperature is considered an advantage of ILs as solvents. However, for practical use of materials for TES, the melting temperature of the IL must be matched to the temperature of the heat source, and the IL is usually in the solid state at room temperature [2]. The desired result – a shape stable PCM – can be achieved by impregnating ILs into porous materials – aerogels. This combination of aerogels and ILs allows the PCM to maintain a stable shape in response to temperature changes and reduces PCMs leakage. Proper selection of aerogel material (e.g. carbon or silica) allows the phase change temperature of the IL to be matched to the working temperature range of the TES.

In this work, we study the performance of some amine and carboxylic acid based PILs impregnated in porous aerogels. The performance of these PILs in this heterogeneous system is characterised using thermal analysis (TGA and DSC) techniques.

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Evaluation of cellulosic ionogels for energy storage devices

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Ionogels are defined as polymeric networks swollen by an ionic liquid (IL). These materials have attracted attention in the manufacturing of electronic devices thanks to a combination of good mechanical properties with high ionic conductivity and electrochemical stability [1].

Cellulose, the most abundant renewable material on earth, is a promising sustainable alternative to traditional petroleum-based polymers. When dissolved in certain ILs it can form a 3D network that gives rise to soft-solid, jelly like ionogels. The use of cellulose as matrix offers good mechanical properties, low cost, biodegradability and biocompatibility [1].

In this work, ionogels using different cellulose derivatives (avicel cellulose, wood kraft cellulose, methyl cellulose, and cellulose acetate) at concentrations ranging from 0.5 to 3 wt% and the IL 1-ethyl-3-methylimidazolium dimethyl phosphate ([Emim][DMP]) have been formulated and characterized as potential electrolytes aimed for their use in supercapacitors.

Thermal properties of the ionogels were evaluated by TGA and DSC, showing water loss above 60 ºC. Rheological analysis found soft-gel behaviour, with dynamic storage modulus to the dynamic loss modulus ratios (G'/G'') ranging from 4,0 to 7,5, except for the cellulose acetate formulations, which precipitated during the gelation process. Impedance and conductivity of the samples have been determined through electrochemical impedance spectroscopy tests (PEIS), showing conductivities in the range of 10-25 mS/cm, an order of magnitude bigger than the pure ILs. Supercapacitors employing the ionogels as electrolytes sandwiched between active carbon electrodes supported on aluminium foil as current collector were assembled and tested on a potentiostat. Tests included linear sweep voltammetry (LSV) to check electrochemical window, cyclic voltammetry (CV) to measure the capacitance and galvanostatic charge-discharge (GCD) to evaluate the cycling performance of the devices. Furthermore, some of the formulated ionogels showed self-healing behaviour and 3-D printability, having enormous potential to be used in novel electronic devices.

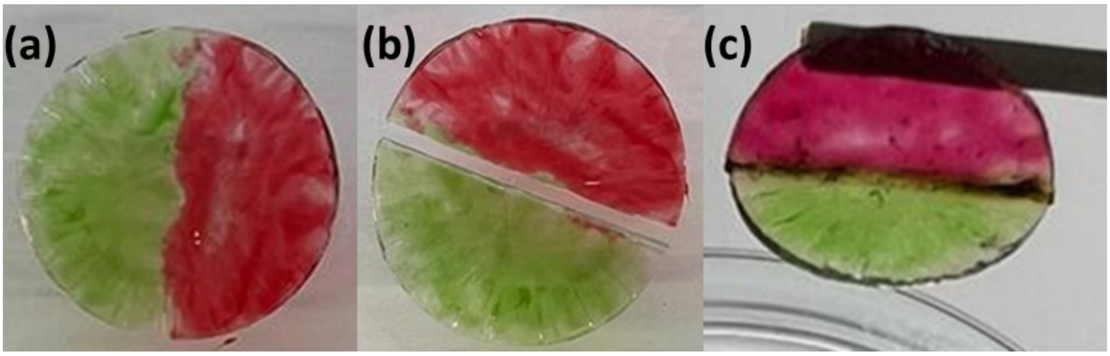

Fig. 1 Demonstration of the self-healing ability of the ionogeles prepared in this work. An ionogel sample was colored superficially (a) it was then damaged/halved (b) and finally healed by a heating process (c).

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Green approach for the synthesis of new biosourced ionic liquids and influence of water as a co-solvent on their physicochemical properties for biomass derivatization

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Lignin, the second most abundant biopolymer after cellulose, is a heteropolymer composed of three monomers [1] which represents a great interest for the chemical industry. Its complex structure is a hindrance to its valorization. Despite this, the valorization of lignin is an issue for scientists and industries. It is therefore a real challenge to find a way to valorize it. Indeed for a few years, studies on the dissolution and the treatment of lignin have been developed. Scientists have used different ionic liquids (ILs) or deep eutectic solvents as solvents such as the cation imidazolium modified by methyl, ethyl, allyl, butyl, hexyl or benzyl groups [1]. However, these petroleum-based ILs are very cyto- and eco-toxic [2], so other biobased and less ecotoxic ionic liquids have been used for lignin dissolution [3]. Linked to sustainable development as well as to the availability of raw materials of petrochemical origin and to the naturalness desired by consumers, the term "biosourced" appears more and more.

This presentation will address a green approach for the synthesis of ILs qualified as biosourced (monocatenar or bolaform systems) from specific agro-resources according to several principles of green chemistry. As these solvents could be used to solubilize lignocellulosic biomass and/or to extract bioactive compounds, their physicochemical characteristics such as density, speed of sound and heat capacity have been determined. The synthesis and the characterization by NMR, IR and elemental analysis are realized in France and the physico-chemical part in Czech Republic. Preliminary results concerning this last point will be also presented.

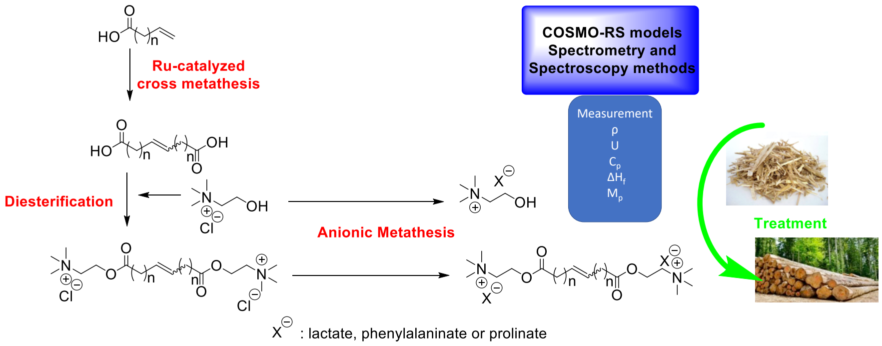

Fig. 1 Illustration of the different step of this work

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Synthesis and biological evaluation of the new derivatives of kazcaine

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Synthesis of new derivatives of kazcaine was performed in order to obtain several new substances with highly effective pharmacophores. The obtained substances were studied for different biological activity. The range of synthesized derivatives with lower toxicity and higher effectiveness than the basic substance kazcaine had been found [1-4].

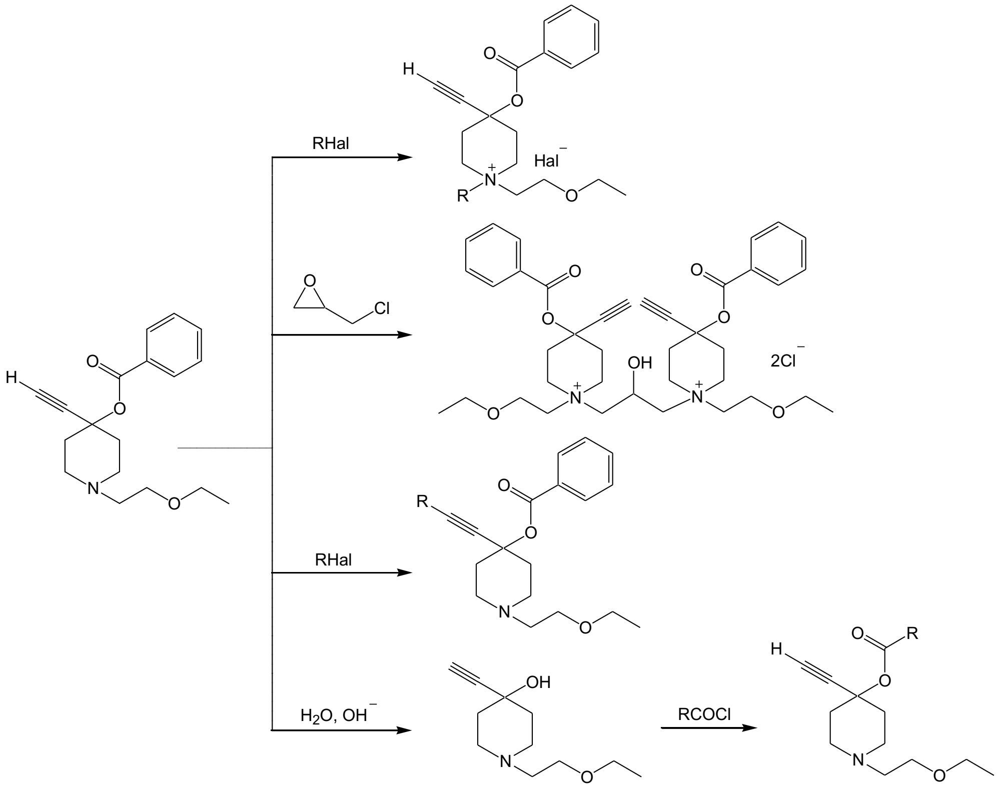

Fig. 1 Methods for the synthesis of kazcaine derivatives

The biological activity studied: myelostimulating activity, antidiabetic activity, local anaesthetic and antioxidant activity.

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Novel Ionic Liquids: Lubricants for Space and Electrolytes for Supercapacitors

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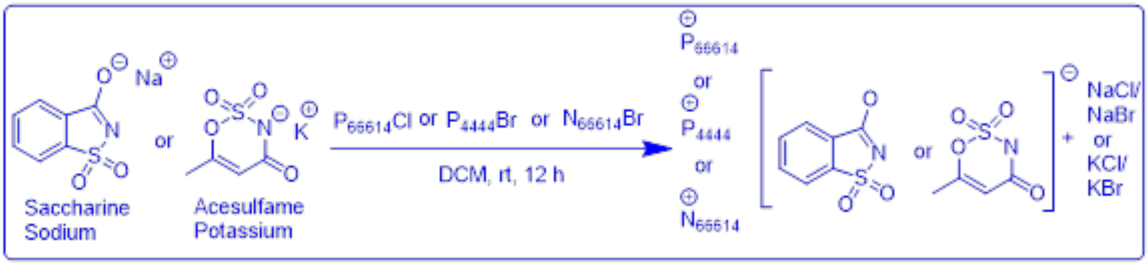
Ionic liquids (ILs) are organic salts, which are liquids with low melting points (m.p <100 oC). Several applications of ILs viz organic synthesis, catalysis, electrochemistry, biomass conversion, friction modifier, lubricants, batteries, solar cells, supercapacitors, CO2 capture, medicines, used as recyclable solvents for a variety of chemical reactions, separation processes as active pharmaceutical ingredients, as alternatives to traditional organic diluents, and solvent extraction of metal ions all are well documented. Potassium acesulfame and saccharine are widely used sweeteners to replace sugar in soft drinks, ice cream, yogurt, ketchup, etc. Although, only three research groups have documented the synthetic procedures of ILs with acesulfame and saccharine anions,[1-3] there are so far no reports on the use of these ILs in electrolytes for supercapacitors. Tetraalkylphosphonium ILs with the saccharine anion were recently reported in tribology.[3] However, ILs with acesulfame as lubricants or additives to lubricants were yet not been explored. To address the latter, we have prepared, purified and characterised non-halogenated tetraalkylphosphonium and tetraalkylammonium ILs with acesulfame and saccharine anions. The named non-halogenated ILs were successfully prepared with >99% purity. The synthetic procedure is shown below. Investigation of physico-chemical and tribological properties of these novel non-halogenated ILs will be reported elsewhere.



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The Foundations in memory of J. C. and Seth M. Kempe is gratefully acknowledged for the financial support in the form of a stipend for H.C. (Grant No. JCK-3173). O.N.A. also acknowledges the Swedish Foundation for Strategic Research (project EM16-0013) for the financial support (a part of the salary and costs of chemicals and analyses) and The Kempe Foundations (project numbers JCK-1306 and JCK-1433) and the laboratory fund at LTU for providing grants, from which a Bruker Aeon/Avance III NMR spectrometer at LTU has been purchased.

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Extraction of Ag (I) from acidic media by CYPHOS® IL 104 involving reverse micelle

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The imidazolium based ionic liquids (ILs) are the most used as diluents in extraction system, while the phosphonium based ILs, among which Trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) and Trihexyl (tetradecyl)phosphonium bis-(2,4,4-rimethylpentyl)phosphinate (Cyphos® IL 104) are the most popular, can both be applied as solvents and extractants.[1] In most cases, an ion exchange extraction mechanism has been reported, but a major knowledge about the interactions involved, for instance, between ILs and the involved species during the extraction (water, anions, metal ions) is required to better understand the extraction equilibria.[2]

The distribution of Ag(I) between acidic aqueous phase (HNO_3) and organic phases, composed of Cyphos® IL 104 diluted in kerosene or kerosene/1-decanol, has been studied. In order to elucidate the interactions in solution and the chemical equilibria responsible for Ag(I) extraction by Cyphos® IL 104, ionic conductivity, dynamic viscosity, and interfacial tension measurements, determination of water and nitric acid extraction were performed, and the organic phases were characterized by infrared spectroscopy (ATR-FTIR). Ag(I) is extracted by Cyphos® IL 104 with high affinity, even under slightly acidic conditions (close to 100% at pH 5). An atypical extraction equilibrium was demonstrated. The change in the physicochemical properties as a function of Cyphos® IL 104 concentration permits to deduce the formation of reverse micelles or aggregates in organic phases at the critical micellar concentration CMC = 0.001 mol L^{-1}. The ATR-FTIR characterization allowed to better understand the extraction mechanisms of Ag(I) by Cyphos® IL 104. A thorough analysis of these data indicates a similar mechanism to solvation, and the reverse micelles (or agglomerates) are involved in Ag(I) extraction.

Acknowledgements: This work was supported by Consejo Nacional de Ciencia y Tecnología, CONACYT (CB 259,307 project), ECOS-NORD (M17P03 project), and ECOS-ANUIES-CONACYT (291271 project), and PhD scholarship number 367,900 / 246366.

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Hydrothermal synthesis of the potassium fluoroscandates

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The formation of complex K-Sc-F compounds was considered in a number of works, since scandium compounds have a high potential to be used for, e.g. fuel cells, phosphors or lasers [1-3]. The preparation of potassium fluoroscandates of various compositions has been studied in this work. According to the literature [4], four compounds can be formed in the KF–ScF_3 system: $KScF_4$, KSc_2F_7, K_3ScF_6 and $K_5Sc_3F_{14}$. In the present work, we were able to synthesize the K-Sc-F compounds using mild hydrothermal synthesis (Teflon lined stainless steel autoclaves; up to 200°C) according to the steps shown in Fig. 1. Crystal structure and cell parameters of the prepared fluoroscandates were determined using X-ray powder diffraction.

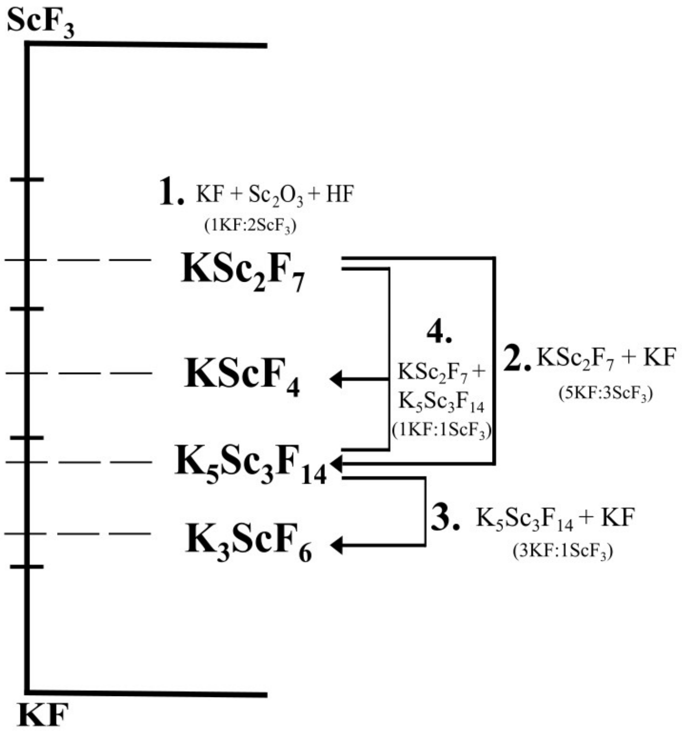

Fig. 1 Scheme of the steps of hydrothermal synthesis

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Chemo-enzymatic approaches for carbon dioxide capture and transformation to cyclic carbonate esters for Non-Isocyanate Polyurethane synthesis.

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Carbon dioxide (CO_2) is considered as the main reason for globalwarming. However, it is abundant, cheap and non-toxic, and its specific molecular structure makes it an important C1 feedstock for the polymer industry. Mono- and di-glycerol carbonate molecules are useful monomers for the production of bio-based non-isocyanate polyurethane (NIPUs) with a wide range of chemical properties.[1]

By using the IL technology, a sustainable approach for the chemo-enzymatic synthesis of bis(cyclic carbonate) esters from CO2, glycidol and organic anhydrides under solvent-free conditions has been demonstrated. By this clean approach, useful precursors for the synthesis of Non-Isocyanate Polyurethanes (NIPUs) [4], are obtained. The process involves two consecutive catalytic steps, taking the advantage of the resulting synergic effects by combining both ionic liquid (ILs) and biocatalyst technologies. In a first step, lipase-catalysed the transesterification and/or esterification of different diacyl donors (e.g. glutaric anhydride, succinic anhydride, dimethyl succinate, etc.) with glycidol in solvent-free systems under mild reaction conditions (70 °C, 6h), producing the corresponding diglycidyl esters up to 100% conversion.

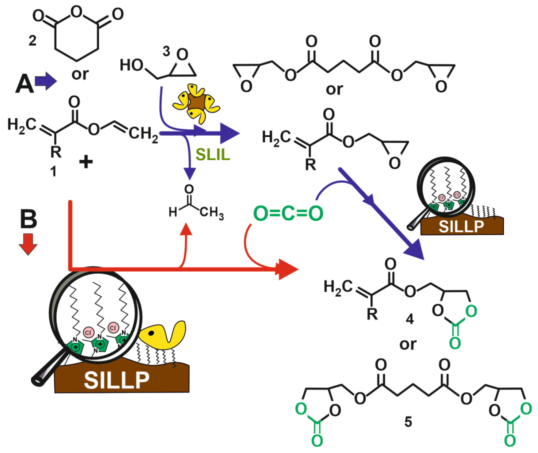

Fig 1. Chemo-enzymatic synthesis of bis(cyclic carbonate) esters from CO2, glycidol and organic anhydrides under solvent-free conditions.

Acknowledgements
This work was partially supported by MICINN-FEDER-AEI 10.13039/501100011033 (PID2021- 124695OB-C21/C22 and PDC2022-133313-C21/C22), MICINN –European Union Next Generation EU-PRTR (TED2021-129626B-C21/C22) and SENECA (21884/PI/22) for financial support. J. D. is fellow of the “Maria Zambrano program” at the University of Murcia (Spain).

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From Supramolecular differences to Bioactive properties: Highly modular Ionic Liquids based on Amino Acids

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The development of new bioactive agents for the treatment of various diseases is a challenge that the pharmaceutical industry must achieve without compromising the safety and efficacy of drugs. In this context, ionic liquids are of great interest mainly due to two factors. First of all, their structure is highly modular, allowing great structural diversity. This diversity can be used to adjust its physicochemical properties depending on the needs required in a given application, and second its biocompatibility and high solubility capacity.[1] In the work presented here, a family of new imidazolium salts derived from a broad spectrum of amino acids have been synthesized and studied.[2] Its "in vitro" bioactivity has been studied against two strains of cancer cells (A-549 and HT-29) at different pHs. Furthermore, its selectivity has been evaluated using healthy human kidney cells (HEK-293) as control.[3] Add to this, the aggregation behavior of these compounds has been studied in order to determine if the compounds formed self-assembled aggregates at their bioactive concentrations. Finally, the potential of some molecules to alter the integrity of liposome-based "synthetic cells" (POPC) has been evaluated.

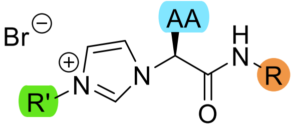

Figure 1. General structure of the ionic liquids.

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Investigating the Eutectic Mixtures formed by Choline Chloride and Hydroxyphenol Isomers

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Deep Eutectic Solvents (DESs) are mixtures formed by a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), having a melting point significantly lower than the ideally predicted one for the eutectic composition. DESs exhibit negligible vapor pressure, non-flammability, high conductivity, high solvation capabilities, and low toxicity, making them safer and more sustainable solvents compared to the most common organic ones [1]. Besides these advantages, DESs are also "designing" solvents: this means that it is possible to produce ad hoc media for a specific purpose by changing one of the components or introducing new substituents into an existing one. Several DESs found in the literature contain choline chloride as HBA and an enormous variety of chemical species acting as HBDs, thus leading to diverse characteristics and physical properties. In this work, we aim to demonstrate how structural modifications in the HBD component can induce serious changes in the thermal properties of these systems, which are ultimately correlated to the interactions occurring in solution at atomistic level. To this purpose, we decided to study three archetypical systems formed by choline chloride with isomers of the hydroxyphenol component, where the two hydroxyl groups are respectively in ortho- (catechol), meta- (resorcinol), and para-positions (hydroquinone) (Figure 1). To do so, we performed differential scanning calorimetry (DSC) measurements on mixtures formed between these components at various molar ratios to unveil the thermal behaviour of these systems. Infrared spectra have been recorded and the inspection of the O-H stretching region allowed to retrieve information about the formation of the hydrogen-bond network. Molecular dynamics simulations have been carried out because they provide a detailed picture about the microscopic interactions among the components. This multidisciplinary approach allowed us to unveil the structure-property relationship in these systems, and the obtained results will be fruitful as a starting point for the synthesis and the development of novel DESs for different purposes.

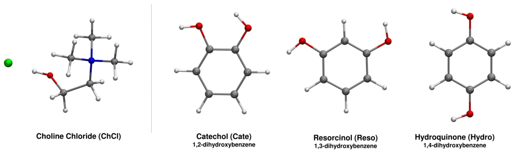

Fig. 1 Molecular structure of the pristine components employed in this work

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Complexation in Ionic Liquid Electrolytes Probed by Multinuclear NMR Diffusometry

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Ionic liquid-based battery electrolytes typically consist of either lithium or sodium salts. The presence of metal ions is expected to increase ionic conductivity of the electrolytes. However, pulsed-field-gradient (PFG) nuclear magnetic resonance (NMR) technique has demonstrated that the diffusivity of metallic ions (Li^+ or Na^+) is usually much slower than the much bulkier organic cation and anion [1]. Even mobility of the organic ions is also decreased in the presence of Li^+ or Na^+. Generally, this is explained by the complexation occurring in the electrolyte, which is induced by Li^+ or Na^+ ions. Understanding the structure, composition and dynamics of such complexes is of interest in the field of energy storage. Multinuclear ^1H, ^{11}B, ^{31}P and ^7Li PFG NMR has demonstrated that the formed complexes include part of organic cation and anion. Dynamic parameters of the complexes determined from ^1H NMR are quite informative. This is particularly important for the systems with sodium salts, where strong quadrupolar interaction do not allow to directly measure diffusivity of the Na^+ ion.

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Extraction properties of 1-butyl-3-methylimidazolium ionic liquids in the process of butadiene separation from C_4 fraction

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1,3-Butadiene is a fundamental raw material in the petrochemical industry, playing a crucial role in the synthesis of synthetic rubber, resins, and various organic chemicals, including tetramethylene sulfone and tetrahydrofuran. Typically, 1,3-butadiene is derived from the by-products of naphtha vapor cracking. This process yields C_4 components like n-butene, iso-butene, n-butane, and iso-butane alongside 1,3-butadiene. The similar boiling points, molecular sizes, and physical properties of C_4 hydrocarbons, especially diolefins and mono-olefins, present a difficulty in separation. At present, the separation of 1,3-butadiene from other C_4 hydrocarbons is mainly carried out by extractive distillation in industry. [1] This work is focused on the search for alternative solvents – ionic liquids – for the separation of butadiene from the C_4 fraction.

The research involved determining activity coefficients at infinite dilution for 1,3-butadiene, 1-butene, butane, and isobutene in a series of ionic liquids with the 1-butyl-3-methylimidazolium cation and varying anions at different temperatures using the inverse gas chromatography method [2]. Based on the obtained results, selectivity and efficiency coefficients were determined for the separation of n-butane/1,3-butadiene, 1-butene/1,3-butadiene, and isobutene/1,3-butadiene. The 1-butyl-3-methylimidazolium thiocyanate reveals the highest selectivity value from chosen ILs in mentioned above separation problems. Unfortunately, the highest selectivity of [BMIM][SCN] is accompanied by the lowest capacity. Optimal selectivity and capacity coefficients for separation 1,3-butadiene from C_4 fraction were obtained for bis(1-butyl-3-methylimidazolium) tetrathiocyanatocobaltate.

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Deterpenation of citrus essential oil by extraction with a biocompatible ionic liquid

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The processing of citrus fruits in food industries for the production of juices, jams, etc. generates copious amounts of waste. Interestingly, this waste contains a large number of bioactive compounds, and a popular valorisation option is their recovery in the form of essential oil, which is a product that offers a varied range of applications. However, in the citrus essential oils typically obtained, only a small percentage of their compositions corresponds to oxygenated compounds, which is the fraction mainly responsible for the appealing organoleptic properties of the product. The remaining fraction (usually >90 %) consists of various terpenes and sesquiterpenes, considered as non-active contributors in the context of the applications of interest of these essential oils. Moreover, the presence of this terpenic fraction may cause problems of stability of the essential oil, limiting its shelf life. Thus, an effective deterpenation of the crude essential oil will lead to a series of benefits, from economic savings in terms of transportation/handling to a better quality of the product itself. Unfortunately, none of the separation methods essayed to date is free of relevant issues that should be overcome in order to obtain the desired deterpenated oil in a satisfactory manner. Among the most important techniques for essential oil deterpenation, solvent extraction is one of the most directly applicable methods in the citrus sector. However, the traditionally tested molecular solvents exhibit a poor thermodynamic performance, along with other issues related to their intrinsic organic nature. In this regard, we tested ionic liquids in the past years as a potentially more efficient and sustainable alternative, and these non-volatile solvents showed good potential for the targeted separation [1,2]. Nevertheless, little attention was paid to the biocompatibility of these ionic liquids, which contained imidazolium- or pyridinium-based cations. In a step further, now we present here our preliminary results for the deterpenation of citrus essential oil with a biocompatible ionic liquid: (2-hydroxyethyl)trimethylammonium 2-hydroxypropanoate, or choline lactate. The citrus essential oil has been modelled as a mixture of limonene and linalool, as the most representative compounds of the oxygenated and terpenic fractions, and the study of the liquid-liquid equilibrium of the ternary system constituted by limonene + linalool + choline lactate has been conducted. Based on the suitable thermodynamic correlation of the experimental tie-lines, the extractive capacity of choline lactate for the essential oil deterpenation process in an extraction column has been explored with a process simulation software, evaluating the influence of parameters such as the number of equilibrium stages and the solvent-to-feed ratio.

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Efficient reversible production of hydrogen with CO_2 in a catalytic system employing Ru-PNP complexes and ionic liquids.

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Hydrogen can be used as an energy carrier for renewable energy to overcome the deficiency of its intrinsically intermittent supply. However, the lack of a safe, efficient, convenient, and low-cost storage and transportation method for hydrogen limits its application. In this regard formic acid (FA), which can reversibly be converted into hydrogen and carbon dioxide through catalysis, has significant potential for practical application as a Liquid Organic Hydrogen Carrier (LOHCs). [1,2]

In this work, high catalytic activities of Ru-PNP complexes in ionic liquids (IL) were obtained for the reversible hydrogenation of CO_2 and dehydrogenation of FA under exceedingly mild conditions (Figure 1). The catalytic system promotes CO_2 activation already at 25°C leading to >90% FA yield, without sacrificial additives and volatile solvents. Regarding the dehydrogenation process, only CO_2 and H_2 are obtained by just increasing the temperature under non-inert conditions, without any CO formation in the gas stream, nor organic residues. These results demonstrate the potential of the Ru-PNP/IL system as LOHC battery, LOHC H_2 releaser, and hydrogenative CO_2 converter.[3]

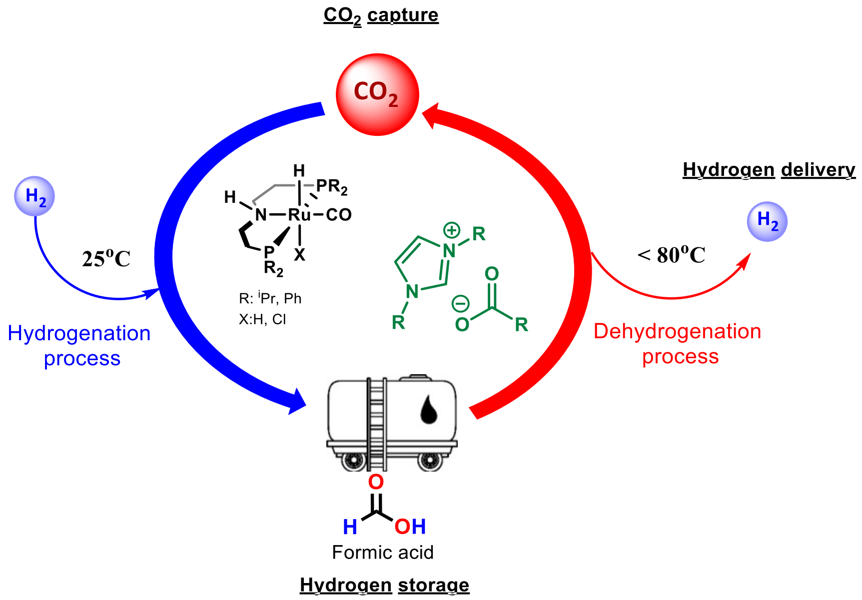

Fig. 1 Catalytic system of hydrogenation and dehydrogenation of FA

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Structural and Dynamic Properties in Ionic Liquids Ternary Mixtures with Water as Solvent, a Computational Study

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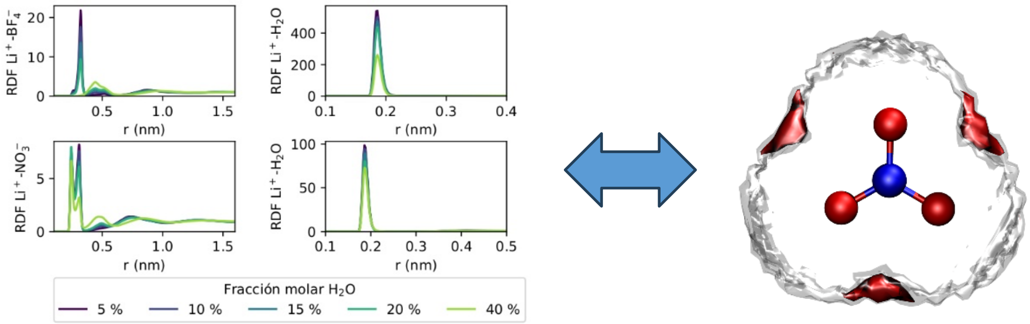
The need to carry out a global decarbonization of the economy is one of the major problems of the century. A technology that is emerging strongly is electrochemical storage in the form of batteries. Ionic liquids (ILs) are proposed as promising candidates to act as a medium in which metallic ions are transported, given their properties such as their wide electrochemical window or their extremely low vapor pressure, which provide the necessary stability for this task. In this context, we will present a computational study through molecular dynamics of some of the most important structural and dynamic properties of two ternary mixtures in bulk. These mixtures will be composed of an ionic liquid, a lithium salt, and water as the molecular solvent. The ILs employed are EAN (protic) and EMIMBF4 (aprotic); extensively studied in the literature ([1]). On the other hand, lithium salts are the most commonly used for introducing ILs as electrolytes in batteries ([2]). However, the use of water as a solvent in this type of systems is novel. On one hand, aqueous electrolytes are one of the main candidates to be used as safe, low-cost, and environmentally friendly batteries. But, due to the low electrochemical stability of free water, while increasing the solvent concentration is useful for increasing the conductivity of the mixture, it hinders the development of reliable aqueous batteries ([3]). The protic and aprotic nature of the ILs used will lead to notable differences in structural and dynamic properties, which will be shown in detail.



Acknowledgements: The financial support of the Spanish Ministry of Science and Innovation (PID2021-126148NA-I00 funded by MCIN/AEI/10.13039/501100011033/FEDER, UE) is gratefully acknowledged. Moreover, this work was funded by the Xunta de Galicia (GRC ED431C 2020/10). H.M.C. thanks the USC for his “Convocatoria de Recualificación do Sistema Universitario Español-Margarita Salas” postdoctoral grant under the “Plan d Recuperación Transformación” program funded by the Spanish Ministry of Universities with European Union’s NextGenerationEU funds.

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Pharmaceutical Active Ionic Liquid Behavior in Natural Deep Eutectic Solvents: Insights into Solvent Composition Effects

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The study focuses on the interactions between a newly synthesized pharmaceutically active ionic liquid (API) called benzocainium ibuprofenate and natural deep eutectic solvents (NADES) menthol and decanoic acid mixtures. The mixtures were prepared in different molar ratios of 1:1, 1:2, and 2:1. The ionic liquid consists of benzocaine, a drug used for local anesthesia, and ibuprofen, a nonsteroidal anti-inflammatory drug. On the other hand, menthol is known for its pain relief properties, while decanoic acid works as an antibacterial and anti-inflammatory agent.

The first step involved synthesizing the ionic liquid and confirming its structure using advanced techniques such as infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy and differential scanning calorimetry (DSC, Figure 1). Afterward, deep eutectic mixtures of menthol and decanoic acid were prepared in the molar ratios of 1:1, 1:2, and 2:1. The structure of these mixtures was confirmed using DSC.

The study then measured the densities, speeds of sound, and viscosities of the investigated ionic liquid in NADES as a solvent in a temperature range of T = (293.15 to 318.15) K at different IL molalities. The research analyzed the interactions between the ionic liquid benzocainium ibuprofenate and the menthol:decanoic acid mixtures. Furthermore, it explored the influence of temperature and composition of the mixture on viscosity, speed of sound, and density. The study also examined the structure-making/breaking properties of the ionic liquid and its impact on the ordering of the solvent molecules.

Overall, the study provides a detailed understanding of the properties and behavior of the ionic liquid benzocainium ibuprofenate and the menthol:decanoic acid mixtures in different molar ratios. The results of the study can potentially be applied in various fields such as pharmaceuticals, chemistry, and material science.

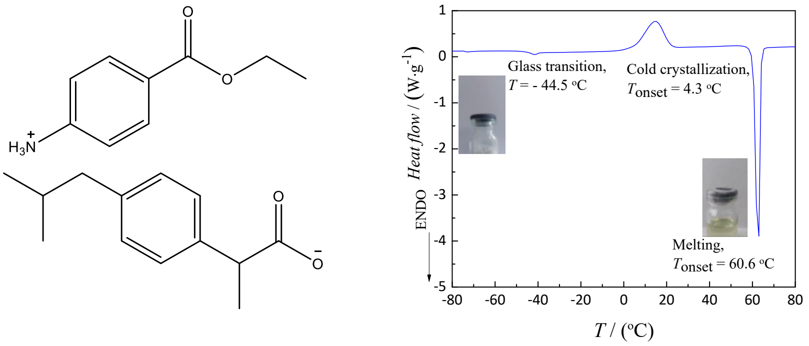

Fig. 1 Structure and DSC curve of benzocainium ibuprofenate ionic liquid.

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Formation of the ternary fluorides from the molten salts and by means of the mild hydrothermal synthesis

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Fluorides are well known for their various industrial applications. Many research projects are focused on the optical properties of these compounds and their rare-earths doped forms [1,2].

Molten salt systems $(LiF–NaF)_{eut}–n\{NdF_3,SmF_3,GdF_3\}$ have been investigated in order to perform the systematic study and search for new complex fluorides suitable for the design of materials with peculiar properties. Except LiF and NaF, hexagonal $Na_{1.5}Nd_{1.5}F_6$, $Na_{1.5}Sm_{1.5}F_6$, $Na_{1.5}Gd_{1.5}F_6$ (space group P-6) [3] and tetragonal $LiGdF_4$ ($I4_1/a$) [4] compounds have been detected in the spontaneously cooled samples. In addition, mild hydrothermal synthesis (ethylenediaminetetraacetic acid (EDTA) and polyethylene glycol (PEG) assisted [5,6]) was applied for the preparation of compounds with components ratio of 1:1:4 in the following systems: {Li–Cs}–{La,Nd,Sm,Gd,Er,Yb}–F. Reactions were carried out in solutions placed in the Teflon-lined stainless steel autoclaves under autogenous pressure. It should be noted that the results of the experiments under such conditions are influenced by the ratio of the components (usually, it defers from the stoichiometry of the planned compounds), time, temperature, solvent, and pH of the solutions.

Obtained samples have been characterised by means of X-ray powder diffraction (XRPD), differential scanning calorimetry (DSC) and energy dispersive X-ray spectroscopy (EDXS). In contrast to the spontaneously cooled samples, ternary phases with fluorite-related structure quite often could be detected after the hydrothermal synthesis.

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Critical evaluation of volume properties of the zirconium-based fluorides melts MF-K_2ZrF_6 (M = Li, Na, and K).

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MF-K_2ZrF_6 (M = Li, Na, and K) melts are very important systems in metallurgy applications. Based on the experimentally measured data of density (determined by the Archimedean method) molar volumes, partial molar volumes and the excess molar volumes were calculated. Partial molar volumes of K_2ZrF_6 were obtained by using two different approaches - simple polynomial regression analysis and multicomponent polynomial regression in the form of the Redlich-Kister equation[1]. The excess molar volume possesses negative values throughout the entire concentration range for all three investigated systems. These negative values of the excess partial molar volumes of K_2ZrF_6 are similar in the case of the LiF and NaF and are slightly suppressed in the KF system. The excess partial molar volume of K_2ZF_6 in KF shows smaller overall volume contraction that adopts 60% of volume contraction in LiF or NaF systems

Systems MF-K_2ZrF_6 (M = Li, Na and K) were converted to ZrF_4 coordinate and compared with the literature data. The partial molar volumes of ZrF_4 of the systems MF-ZrF_4 (M = Li, Na and K) are also significantly different in KF system in contrast to LiF and NaF systems.

Acknowledgements: This work was supported by the Slovak Research and Development Agency under contract No. APVV-19-0270 and by the Slovak Grant Agency, grant no. VEGA 2/0083/24

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Viscosity modelling of pure molten salts and their binary mixtures utilized in heat transfer and storage applications

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Abstract

Concentrated solar power (CSP) plants are widely recognized as renewable technologies which have a significant role in clean electricity generation [1]. Thermal energy storage (TES) is utilized as a beneficial tool to integrate the renewable energies and electricity generation. In recent years, molten salts have received much attention of research due to their specific properties in a wide range of applications and has emerged as promising candidates as heat transfer fluids (HTFs) in heat transport and storage applications. Therefore, noticeable efforts have been taken to develop an available database for transport properties of molten salts, e.g. the viscosity, because viscosity of molten salts plays a crucial role in determining the optimal operational conditions, including equipment design and pumping costs. Extensive research has been conducted using various experimental and theoretical techniques to study this property. Due to the high temperature or the presence of some hazardous species, running experiments in the entire temperature and compositional range is complicated if not impossible. Therefore, the presence of an accurate viscosity model could facilitate the molten salt's viscosity data development [2, 3]. This work focuses on both the temperature and composition dependence of viscosity of pure alkali and alkaline earth nitrates, chlorides, carbonates and their mixtures using an Arrhenius-like model based on the associate species calculated from the thermodynamic database. This model was originally developed for oxide-based systems [4] and is now adapted to salt systems. It is noteworthy to mention that a good agreement for the temperature dependence of viscosity has been achieved for all the unary molten salts. However, an excess viscosity induced by composition, i.e. due to the formation of possible large clusters, is required for some binary salt systems. Nevertheless, more experimental viscosity data is still necessary, as well as the evaluation of the validity of literature data, especially digitalized from existing equations.

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Role of hydrogen bonding donor and anion in choline based eutectic media structural organization

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Choline-based salts are among the most commonly used for formulation of deep eutectic solvents (DES), reline (choline chloride:urea=1:2) being the most well-known DES[1]. Typically, these salts are mixed with hydrogen bonding donor species, such as urea, to lead to type III DES[2]. Accordingly, the bulk structural landscape in such DES, e.g. reline, is characterized by an extended network of hydrogen bonding (HB) interactions, leading to the 'alphabet soup' of different kinds of HBs[3]. Therein, however, also dispersive interaction play a distinct role in determining the equilibrium structure, thus making morphology the result of a delicate balance between different interactions.

Aiming at assessing this complexity, we report the results of both experimental and computational investigations of four different liquid mixtures based on the choline cation paired either with chloride or acetate anions and with either urea or water as HB donor (HBD) species, at ratio salt:HBD 1:2. These samples are liquid above 30°C and have been characterized experimentally with different techniques, including X-ray scattering[4–6]. These systems have been explored by means of ab initio Molecular Dynamics simulations at 350 K , to ensure enhanced fluidity of samples, over unusually long simulations times (typically several hundreds of psec). These highly realistic simulations have been carefully interrogated to extract atomistic details on the structural correlations and the role played by salt anion and HBD species.

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Towards the use of 1-ethyl-3-methylimidazolium propionate in fish waste valorisation: solubilities

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The fishing industry generates a large amount of waste, which causes serious environmental problems if not properly managed. In order to optimise resources more efficiently, there has been a great interest in the use of fish waste as a material to generate added-valued products [1]. Among them is collagen, which is a structural protein present in fish bones, scales, skin and tissues. This protein and its hydrolysates are of great interest in the pharmaceutical, cosmetic and material industries.

Ionic liquids (ILs) consisting of 1,3-dialkylimidazolium cations paired with anions possessing high hydrogen-bond basicity have been shown to be effective in the pretreatment of lignocellulosic biomass [2]. This type of anions is associated with the weakening of the hydrogen-bonding network of the biopolymer. One of those ILs is 1-ethyl-3-methilimidazolium propionate, $[C_2C_1im][CH_3CH_2COO]$, which is therefore an interesting alternative to facilitate the extraction of collagen from fish skin.

In this work, as a preliminary step before exploring collagen extraction from fish waste using this IL, the solubility of key amino acids that constitute collagen was determined in the pure IL and its mixtures with water. Selected amino acids were: glycine, β-alanine, L-proline, trans-4-hydroxy-L-proline, L-arginine, L-glutamic acid, and L-aspartic acid.

Solubility was measured using jacketed glass cells where the IL, or its mixture with water, was placed. An Ultratherm-200 P Selecta bath was used to circulate water for temperature control. The amino acid was added in excess to the amount required for saturation at the working temperature (ranging from 298.15K to 328.15K), stirred for 24h and let to settle for 12h. A sample of the supernatant phase was withdrawn with a syringe and filtered to ensure removal of any possible non-dissolved amino acid particles. Finally, the composition of the sample was determined via the density measurement. Previously, calibration curves were prepared for each amino acid and solvent. To determine solubilities, the equilibrium samples were diluted with the same mass of solvent to obtain the composition, later re-calculated according to the dilution, using the corresponding calibration curve.

The van't Hoff model was successfully used to correlate the experimental data and calculate the apparent dissolution properties.

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Gas dehumidification using supported nicotine based ionic liquid membranes

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Gas dehumidification using membranes is a promising technology and has many advantages over other water vapor removal methods including simple installation, ease of operation and low process cost [1]. Although hydrophilic polymers exhibit strong permeation properties, they face issues like swelling and plasticization [2]. For this reason, actual separation factors are orders of magnitude lower than the ideal selectivities [2]. Enhancing polymeric membrane properties can involve integrating ionic liquids (ILs) to form supported liquid membranes.

In this work, nicotine based ILs were investigated for gas dehumidification. After preparation, the chemical structure of ILs was confirmed with NMR and FTIR spectroscopy. Viscosity, short-term thermal stability and glass transition temperature were also investigated. Membranes were prepared by drop-casting nicotine-based ILs onto a circular hydrophobic PVDF substrate. Gas and water vapor permeability and selectivity measurements were conducted using the Wicke-Kallenbach method.

In single gas permeation experiments, the lengthening of the alkyl chain led to (a) an increase of gas permeabilities attributed to IL viscosity decrease and (b) a decrease of water vapor permeability due to IL hydrophobicity increase. However, the presence of ether groups in the alkyl chain had a positive effect on water vapor permeation properties. Permeation properties under mixed gas conditions were unaltered compared to those of single gas permeation experiments and water vapor/gas performance was the highest relative to other reported SILMs with TFSI⁻ as counter anion (Fig. 1).

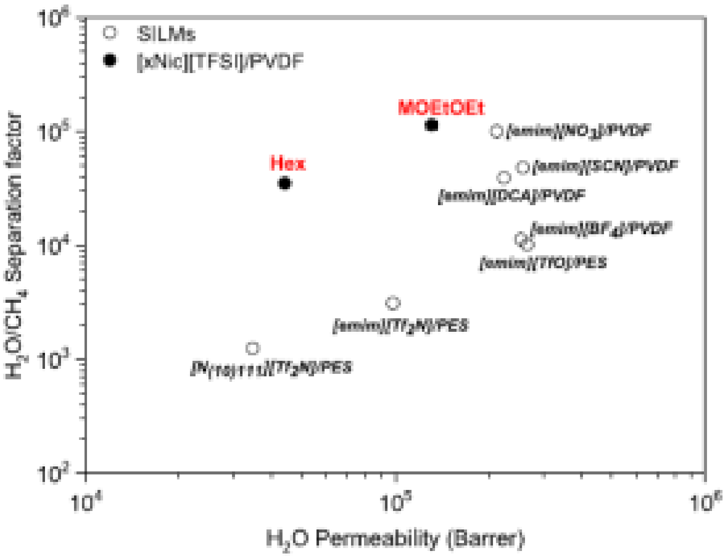

Fig. 1. H_2O/CH_4 separation factor of supported nicotine-based IL membranes as a function of H_2O permeability compared with other SILMs.

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P31
Poster Presentation

Tribological Behavior of Hybrid Nanolubricants for Internal Combustion Engines

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In this study, the improvement in SAE 10W-40 engine oil tribological performance after the addition of magnesium oxide (MgO) nanoadditives and two different phosphonium-based ionic liquids (ILs) was investigated. The tribological properties, friction coefficients and wear parameters, of the formulated oil modified with 0.01 wt.% MgO and 1 wt.% ILs compared with the neat 10W-40 oil were performed and analyzed using a ball-on-three-pins tribometer and a 3D optical profilometer, respectively. Further analysis on the worn surface was carried out by Raman spectroscopy and SEM microscopy illustrating the formation of the protective IL and MgO tribo-films as hybrid additives. In friction tests with sliding steel-steel tribo-pairs, IL3-based hybrid nanolubricant decreased the friction coefficient and wear volume by 7% and 59%, respectively, in comparison with the neat SAE 10W-40, while the one based on IL1 only achieved a reduction of these parameters by 6% and 39%, respectively, as can be seen in Figure 1. Thus, the tribological characterization also revealed that the MgO and IL3 addition has a positive synergy over the commercial lubricant, adequately meeting the requirements for their use in internal combustion engines.

In summary, this study has shown that the addition of ionic liquids to MgO nanoparticles can improve the stability and lubrication behavior of MgO nanolubricant and encourages more investigations on using nanoparticle additives with green solvents such as ionic liquids to protect the environment as well as prolong the lifetime of machinery.

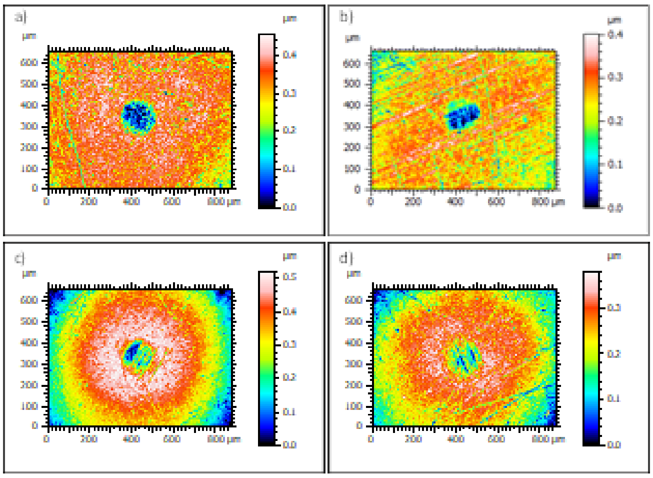

Fig. 1. Surface topography of worn scars in lubricated pins for the a) 10W-40 oil, b) MgO nanolubricant, c) IL1-based nanolubricant, and d) IL3-based nanolubricant.

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Development of a molten salt electrorefining process suited for the recycling of HALEU fuel production scraps

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High Performance Research Reactors (HPRRs) are vital instruments in materials research, nuclear physics and nuclear medicine. Their high neutron flux irradiation capabilities were historically obtained by the use of highly enriched uranium (HEU) fuel. In light of non-proliferation there is a strong drive to convert existing HPRRs to High Assay LEU (HALEU) with U-235 enrichments below 20 % and provide HALEU fuel solutions for future HPRRs. The majority of fuel types under development are UMo and U_3Si_2 metallic alloys. Innovative manufacturing techniques are being used to fabricate these fuels, but there is a need to develop recycling techniques to recover the significant amount of production scraps.

A suitable method to support the recycling of HALEU fuel can be found in pyroprocessing. This is a combination of electrochemical operations in high temperature molten chloride media. Deployed as a batch process, it can be designed with a small footprint and has the possibility to provide low waste amounts. There is limited literature data available, therefore, the goal of this work is the research on recycling of U_3Si_2 and UMo fuel types by pyrochemical techniques. Very limited information on the recycling of UMo has been published [2] while on the U_3Si_2 case, no experimental work has been performed to our knowledge. Since both fuels are metallic, the proposed separation process is electrorefining in LiCl-KCl eutectic molten salt. This process consists of an oxidation of U at the anode, which is then transported through the electrolyte to the cathode, where it is reduced as metallic uranium dendrites [1]. A High Temperature Electrochemical Cell has been designed and modified to perform the electrorefining experiments at 450 °C. Alloy feed materials, UMo and U_3Si_2 are prepared by an arc melting method and characterized with SEM-EDS. Separation factors for U, Mo and Si are calculated and overall cathode impurities are determined by ICP-MS.

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Synergies of a polyoxometalate-ionic liquid hybrid with a phosphonium ionic liquid as transmission fluid additives for electric vehicles

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Electric Vehicles (EVs) offer a compelling solution to counter the negative impact caused by internal combustion engines (ICEs) in the transportation sector. Whether powered by batteries, fuel cells, or full cell hybrid systems, the efficient operation of EVs requires the use of new components and energy infrastructure, leading to additional costs associated with manufacturing and maintenance. Furthermore, the mechanical components of EVs experience increased speeds, heavier loads, higher temperatures, and electrical currents [1]. It is important to note that these conditions can cause component wear over time.

Nanomaterials and ionic liquids (ILs) as additives for lubricants have been widely investigated, demonstrating excellent tribological properties [2,3]. However, limited research has been carried out in tribology for EVs, and it is crucial to analyze how these additives can be used to develop transmission fluid for electric integrated drive-units which fulfill the demands of low viscosity, and electrical conductivities with excellent antiwear and antifriction capabilities [4].

Polyoxometalates (POMs) are metal-oxygen nanoclusters, typically of vanadium, molybdenum or tungsten, with tunable size and structure. Furthermore, as anionic species, POMs are accompanied by counter-cations that can also be carefully selected to provide new properties to the resulting salt [5]. Therefore, combination of highly tunable as IL cations and POMs result interesting as nanoadditives for lubrication in EVs.

In this work, the effect on the tribological properties and the electrical conductivities of three hybrid nanomaterials of $[X]_3[PW_{12}O_{40}]$ (where [X] refers to different IL cations) and an IL, $[P_{6,6,6,14}]$[DEHP], as additives for two low viscosities oils (a polyalphaolefin and an ester) is presented.

Acknowledgements: This research is supported by Xunta de Galicia (ED431C 2020/10) and by MCIN/AEI/10.13039/501100011033 through the PID2020-112846RB-C22 project. It is also supported through PID2021-127341OB-I00 for M.d.C.G.-L, FPU20/01072 for L.V.-A. and IJC2020-044369-I for J.M.V.-F.

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Electroreductive transformations of biomass derived compounds in green solvents

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Electrosynthesis is promising pathway for decarbonization of the chemical industry, as it enables replacement of redox agents with electricity, which can be generated from renewable sources. Electrosynthetic transformations are advantageous compared to other processes as high product selectivity can be achieved at ambient conditions. One challenge of organic electrosynthesis is the poor conductive properties of the required organic solvents. It is typically mitigated by the addition of large amounts of supporting electrolyte salts, effectively resulting in increased waste generation [1]. Green solvents such as room temperature ionic liquids (RTILs) and deep eutectic solvents (DESs) represent a promising alternative electrolyte, as they are conducting, non-volatile and recyclable. Combined with their large electrochemical window, tunability and ability to solubilize organics, these alternative solvents are ideal for electrosynthetic applications [2,3].

Another unique ability of DESs and RTIL is their ability to dissolve whole biomass or biomass components. Therefore, they are attractive solvents for several biorefinery processes including pretreatment, fractionation, and catalytic conversion [4,5]. Selective reductive transformations are key in biomass valorization to yield precursors for fuels and chemicals. Thus, in this work, we present an electrosynthetic protocol for C-O activation and reductive transformation of biomass derived compounds, utilizing green solvents as electrolytes and reaction medium.

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Synergistic effects of functionalized WS_2 and SiO_2 nanoparticles and a phosphonium ionic liquid as hybrid additives of low viscosity lubricants

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Now, the industry needs developed lubricants to enhance the energy efficiency and sustainability. This need is also vital for electric vehicles (EVs) as near 60% of the provided energy to an EV is used to overcome friction [1]. To reach these needs, it is primary to add additives to base oils [2]. Therefore, the study of nanomaterials as additives could support the development of a new group of low-viscosity lubricants exclusively designed to the requirements of electric transmissions. This research studies the antifriction and antiwear synergies between a phosphonium ionic liquid (IL) and f-WS_2 and f-SiO_2 nanoparticles (NPs) as additives of a polyalfaolefin low viscosity base oil (PAO6). For this aim, mass concentrations of 0.1 wt% of nanoadditives and 1% of IL was chose to prepare the nanolubricants. Pure sliding and rolling/sliding tribological tests were carried out at 120 ºC, achieving great friction reductions in comparison with the PAO6 base oil, particularly for the double hybrid nanolubricant (PAO6 + 1 wt% IL + 0.1 wt% f-WS_2 + 0.1 wt% f-SiO_2). Regarding the wear generated, the best antiwear performance was also achieved for the double hybrid nanolubricant (width reduction around 50% and worn area decrease of 85%). Besides, through Raman microscopy and roughness study of the worn surfaces, it can be suggested that the lubrication mechanism of doubled hybrid nanolubricants could be supported by the adsorbed tribofilm (IL and f-WS_2) and the mending effects (f-WS_2 and f-SiO_2).

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Ionic liquids based breath gas analysis technology for disease screening and diagnosis

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Early-stage disease screening and diagnosis is important and crucial for patient identification as well as disease treatment for both human being and animals. However, current disease screening and diagnosis tests are normally invasive diagnostic tests, for example using blood or part of body tissues. Therefore, patient would not like do the disease screening and diagnosis tests often, which limits the discover of fatal disease in early-stage, for example cancer diseases, cardiovascular diseases (ischemic heart disease, stroke), respiratory diseases (chronic obstructive pulmonary disease, lower respiratory tract infections) and neonatal diseases.

In recent years, breath analysis is paid attention to by many researchers due to its promising non-invasive diagnosis techniques, which detects gas-analytes such as exhaled volatile organic compounds (VOCs) and inorganic gases that are considered to be important biomarkers for various disease types. However, detective sensitivity of the current breath analysis technology to disease screening and diagnosis is not high. In order to increase detective sensitivity of breath analysis techniques, in this work ionic liquid based breath analysis technology is developed. VOCs and inorganic gasses from breath gas has high solubility in ionic liquids. Ionic liquid can absorb and concentrate VOCs and inorganic gases biomarkers. Therefore, the absorbed biomarkers in ionic liquid from VOCs and inorganic gases can reach the detective level of instrument even though biomarkers concentration in breath gas is low. Ionic liquids (ILs) are types of salts. Many ILs are liquid at room temperature. ILs have many advantageous properties: (1) Low vapor pressure, high thermal and chemical stability. The properties are excellent to utilize as electrolyte. Low vapor pressure, high thermal and chemical stability electrolyte can produce high safety battery. (2) Low melting point. Many ILs are liquid at temperatures as low as -60 ^{o}C and can be utilized in cold climate areas; (3) Phase behavior of ILs can be controlled by polarity modulation; (4) Favorable solubility in inorganic and organic chemicals; (5) Chemical and functional groups can be designed to form task-specific ILs. ILs are green solvents, and are widely utilized in CO_2 capture and storage, catalysis, nano science, biotechnology, cellulose science, extraction and separation process, and petroleum science.

In this work, we develop brand new ionic liquids based breath analysis technology for disease screening and diagnosis. Lung cancer is among the diseases that have been considered for biomarker detection by breath analysis researchers. Therefore, in this work, breath gases from lung cancer patients will be investigated by ionic liquids based breath analysis technology to identify disease-specific biomarkers of lung cancer at early stages. This technology will benefit people’s healthcare in the whole world due to lung cancer is the first fatal disease among males and the second fatal disease among females.

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Anomalous transport in Ionic Liquid Mixtures, Theoretical and Computational Modeling

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Recent works in the literature report an anomalous behavior of the ionic transport for ethylammonium nitrate mixtures with DMSO as cosolvent [1]. This behavior does not fit into the current theoretical frameworks, like the *random-alloy model* [2], that do not take into account the energetics of the hydrogen bond network that appear in most protic ionic liquids. In this communication we will show an extension of the *random alloy* model that consider the energetics between the ionic liquid and the molecular cosolvent. This modification will be backed by both experimental and computational results.

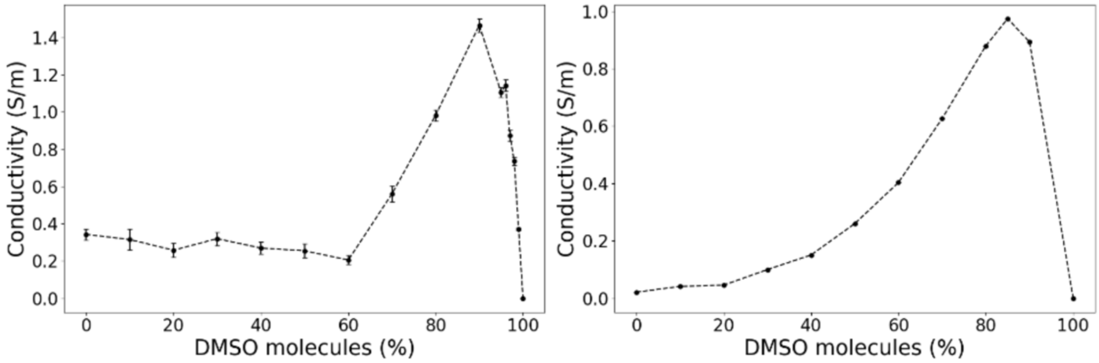

Fig. 1 Anomalous transport (left) versus the usual behavior of the ionic conductivity in ionic liquids mixtures.

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Enhancing thermal and electrochemical stability of lithium-ion battery electrolytes

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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 LIBs are exposed to mechanical or thermal abuse conditions. These safety issues are intrinsically related to 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. Starting from rather "facile" electrolyte modifications by replacing the organic 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 potential optimal electrolytes for lithium-ion batteries that can combine low flammability, good thermal stability and high electrical conductivity.

In this work the 0.5 M solution of LiTFSI salt in ionic liquid 1,3-diethylimidazolium *bis*(trifluoromethylsulfonyl)imide, (C_2C_2imTFSI), was tested as electrolyte for LIBs by using robust anatase TiO_2 nanotube arrays (NTAs) electrode and in parallel the same electrolyte with functionalized additive 1-methyl-3-sulfonatebutylimidazole. That additive is sulfonate-containing zwitterion, which prevents decomposition of electrolyte. Through that, the additive addition is contributing to that the voltage decreases less with the number of cycles. The galvanostatic (GS) testing was performed at room temperature, at current rate 3C (Figure 1). Capacity of TiO_2 NTAs is due to both bulk and surface storage of Li^+-ion, and significantly increases with addition of sulfonate-containing zwitterion (additive). GS experiments demonstrated excellent capacity retention with improved Coulombic efficiency during final cycling at current rate ~3 C.

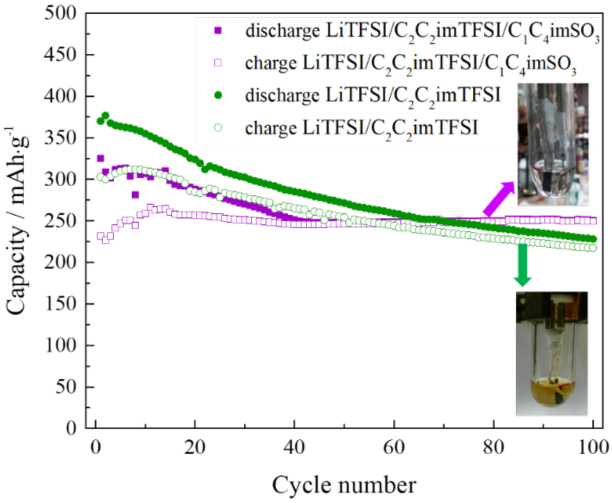

Fig. 1 Comparison of galvanostatic discharge/charge performance of anatase TiO_2 NTAs in: LiTFSI/C_2C_2imTFSI electrolyte and LiTFSI/C_2C_2imTFSI/C_1C_4imSO$_3$ electrolyte.

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Acetate ionic liquids to obtain hydrolyzed collagen from tuna skin

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In the last few years, the concept of marine by-products as residues has completely changed as they contain numerous valuable compounds such as amino acids, bioactive peptides, fatty acids, collagen, hydroxyapatite, etc. Hydrolyzed collagen consists of a group of peptides with low molecular weight with interesting applications in food, pharmaceutical, and cosmetic industries [1]. However, the methods of production involve thermal treatments (high energy requirements), acidic or alkaline extraction (with significant environmental impacts) or enzymatic hydrolysis (long treatment and high cost). In a previous work [2], the solubility of collagen-forming amino acids in 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium acetate ionic liquids (ILs) was determined, and the first was selected due to the higher solubilities achieved. So, in this work [C_2mim][OAc] was chosen to favor the extraction of hydrolyzed collagen from tuna skin.

The methodology for the extraction consists of two stages, a first maceration through agitation (30 rpm) of the skin with the IL or its aqueous solution, and a subsequent extraction with water. The variables to carry out the first stage (maceration time, temperature, skin/solvent ratio, and IL/water ratio) were optimized through a design of experiments, resulting in optimal conditions of t=12.5 min, T=11.8 °C, skin/solvent ratio=2.8, and the use of pure ionic liquid as the most suitable maceration fluid for skin treatment. In the extraction stage, the usual conditions in the industry were used (agitation at 30 rpm, 50 °C, and a skin/water ratio of 3/1). From the resulting aqueous solution, on the one hand the hydrolyzed collagen was precipitated with acetone and dried (50 °C, 72h) for its characterization (yield, FT-IR spectroscopy, SDS-Page, amino acids profile, degree of hydrolysis, molecular weight distribution, DSC and TGA). On the other hand, the aqueous solution was cooled to obtain a gel whose rheological properties were characterized.

The proposed method allowed obtaining a gelatin of high quality without the drawbacks of the traditional methods.

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Structurally Flexible Fluorine-Free Ionic Liquid-Based Electrolytes for High-Temperature Supercapacitors

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The electrochemical and charge storage performance of a fluorine-free structurally flexible hybrid pyrrolidinium-based ionic liquid electrolyte (HILE) in a symmetric graphite-based supercapacitor is thoroughly investigated. The HILE revealed thermal decomposition at 270 °C, a glass transition (T_g) temperature of −73 °C, and ionic conductivity of 0.16 mS cm^{-1} at 30 °C [1]. The chemical and electrochemical properties are investigated using a systematic variable temperature ^{1}H and ^{31}P NMR spectroscopy and diffusometry, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD). The supercapacitor demonstrated a notable specific capacitance of 186 F g^{-1} at a scan rate of 1 mV s^{-1} and a specific capacitance of 122 F g^{-1} at a current density of 0.5 A g^{-1}. The maximum energy density of 48.8 Wh kg^{-1}, a power density of 450 W kg^{-1} at a current density of 0.5 A g^{-1}, and a potential window of 4V were obtained. Altogether, this study demonstrate that the new HILE can be used in symmetric graphite-based supercapacitors over a wide potential window of 4 V and a temperature range from −20 to 90 °C (Fig. 1).

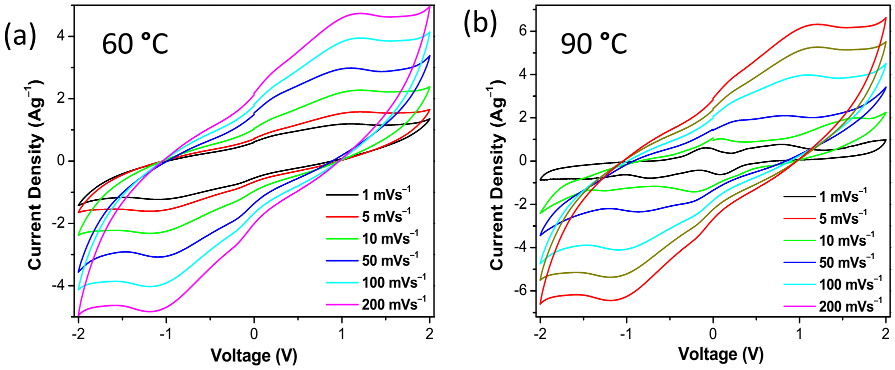

Fig. 1 CV plots at different scan rates and different temperatures.

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Menthol/Thymol DES based eutectogels as drug delivery systems

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Physically crosslinked gels are formed due to non-covalent interactions, such as hydrogen bond, electrostatic forces and van der Waals interactions. There has been growing attention in designing drug delivery systems based on physical gels as the gelation process often occurs under mild conditions and in absence of chemical crosslinking agents. As materials, Deep Eutectic Solvents (DESs) are an emerging class of sustainable materials formed by two or more components linked by a strong hydrogen bonding network and used in different applications [1]. The use of DESs as drug delivery systems is related to the possibility of developing gel-basedDESs “eutectogels” able to deliver the loaded drugs in a controlledway [2].Here we present the synthesis and characterization of supramolecular gels based on DESs and dissolve some active pharmaceutical ingredients in them at different concentrations. The final goal is to study 1) the dynamics of a drug at the microscopic level mainly exploiting 1H High-Resolution Magic Angle Spinning (HR-MAS) NMR technique and 2) the macroscopic release behaviour of the drug from eutectogels at different experimental conditions. Gels prepared arebased on nonionic type V DESs consisting of thymol as hydrogen bond donor and menthol as hydrogenbond acceptor. In our study, we have choosen ethosuximide a water-soluble anticonvulsant drug as a model drug. Experimental data clearly indicate that molecular mobility in gel systems is not influenced by concentration changes and is always lower than the diffusion observed in aqueous solution.

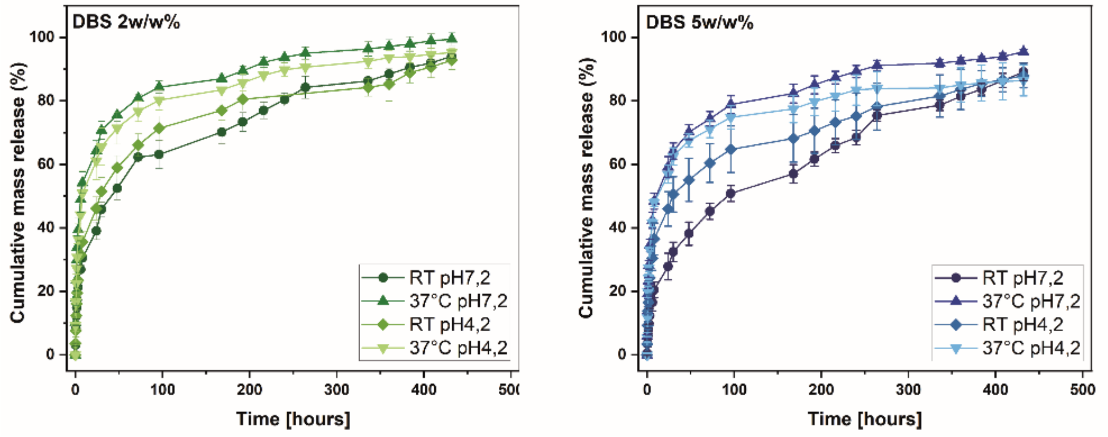

Fig. 1 - Cumulative mass release curves of ethosuximide from eutectogels with 2w/w% (green) and 5w/w% (blue) of gelator at different conditions.

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Thiolactone Chemistry in Action: Creating Task-Specific Hybrid Systems of Functionalized Polymeric Ionic Liquids and Metallic Nanoparticles for Superior Bioactivity

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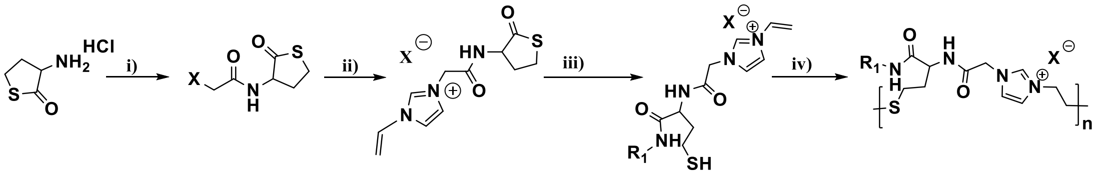
Ionic liquids (ILs) have a highly adaptable structure, which allows for the customization of their physicochemical properties for diverse applications. [1] Their bioactivity is intimately related to this structure. Polymeric ionic liquids (PILs), evolved from ILs, show potential in enhancing these properties. This study details the synthesis of PILs through click chemistry, employing amino-thiolactone. This method is noted for its simplicity and flexibility. [2] The process includes the synthesis of the alkyl-imidazolium salt of amino-thiolactone, followed by its ring-opening via aminolysis, and culminating in thiol-ene photopolymerization to produce a variety of PILs. This synthesis method is scalable and allows for the creation of a wide range of PILs using common intermediates. [3]



Scheme 1. Synthesis (i) Bromoacetyl bromide, K_2CO_3, CH_2Cl_2, 1 h, r.t., 60–65%; (ii) ACN, 1-vinylimidazole, 16 h, 45ºC, 80–85%; (iii) 3-(Dimethylamino)-1-propylamine/H_2O, 24 h, r.t.; (iv) Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LPA), 0.5 h, r.t.

To enhance the bioactivity of PILs against more resistant bacterial strains, this study presents the synthesis of multicomponent systems. The underlying hypothesis is that a combination of various PILs with at least one additional component, such as nanoparticles (e.g., Silver - AgNPs, Gold - AuNPs, Palladium - PdNPs), could boost their efficacy. The research involves using synthesized PILs in the formation and stabilization of Ag-, Au- and PdNPs, leading to the development of nanoparticle-PIL (NP@PIL) hybrid systems. This process involved using different molar ratios of metal/polymer, with the metal rapidly reduced to nanoparticles by adding the corresponding metal solution to a $NaBH_4$ solution containing the polymer. The formation of NPs is manifested by an immediate colour change in the solution. Leading to the production of nanoparticles with an average diameter of around 5 nm.

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Thermodynamics of alkylsilane-based ILs with different anions

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The insertion of silicon atoms on the alkyl chain of ionic liquids (SiILs) has been revealed to reduce the viscosity of this kind of substances[1]. It has also been shown that the viscosity decrease can be of different magnitudes for different anions [1,2]. In this work we aimed to study and understand the impact that different anions have on the thermodynamic properties of ILs composed by the [(SiCSiC)C$_1$im] cation. The structures of the cation and the different studied anions are presented in Figure 1.

The studied properties include the glass transition, melting point, thermal decomposition, heat capacity, and volatility. The phase behavior of the ILs was studied by differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) was used to investigate the thermal decomposition of the ILs. The heat capacity was studied through two different techniques: differential scanning microcalorimetry (in the temperature range from T = 283 K to T = 333 K), and a high-precision drop microcalorimeter (at the temperature of T = 298.15 K). The volatility of the ILs was studied by Knudsen effusion apparatus coupled with quartz crystal microbalance (KEQCM).

Glass transition was obtained for all ILs. [N(CN)$_2$] and [C(CN)$_3$]-based ILs were found to have significantly lower thermal stabilities than the other studied ILs. [B(CN)$_4$] and [OTf]-based ILs revealed lower volatility than the [NTf$_2$] based IL. The differences in heat capacity of alkylsilane-based ILs composed of different anions are identical to those found for conventional *n*-alkyl-based ILs.

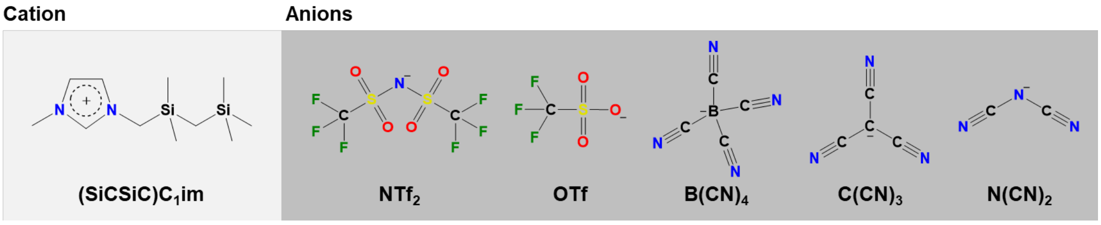

Fig. 1 Structures of cation and anions of the studied SiILs.

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Ionic liquid based bio-battery: A self-powered and charged free battery

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In light of global energy concerns and environmental challenges, the quest for sustainable green energy technologies has become paramount. In our laboratory, we've introduced a new-generation, self-powered battery that requires no charging. This battery uses algae in a culture solution as an electrolyte, with either a nickel sheet or graphite serving as the cathode and an aluminum sheet as the anode. Remarkably, this innovative battery can operate continuously for months on end without the need for recharging. To understand the factors influencing performance, we assessed various electrode materials (Al, Ni, Graphite), light conditions (darkness and natural light), and different electrode spacings for their effects on open circuit voltage (OCV) readings. Additionally, we connected Bio-photovoltaics (BPVs) of identical size in both series and parallel configurations to evaluate their performance. Our analysis of cell voltage and current, as measured by our acquisition system, revealed that light conditions significantly influence the voltage of this microbial photovoltaic algae battery. Indeed, experimental results underscored that the algae battery's performance varied markedly between light and dark conditions. During the daytime, the battery produces electrons from the photosynthesis of algae; these electrons are then captured by the electrode material, generating an electric current that keeps an LED consistently illuminated. At night, the battery utilizes the energy not consumed during the day's photosynthesis to continue producing electricity. This ability makes algae batteries a beacon for energy conservation and environmental protection. Our research underscores the potential to harness bio-energy from photosynthesis more efficiently and offers valuable insights into expanding the practical applications of biologically self-powered batteries that don't require charging.

Biological power supply that encompass the necessary features have yet to be developed. This is largely due to the inherent challenges in designing miniaturized units that not only preserve their contained energy prior to use but are also readily activated to deliver the desired energy output. This work introduces an innovative BPV system that successfully powered an LED: a commonly used low-power electronic light source-for over three months at room temperature and under ambient lighting conditions. During photosynthesis under light conditions, NIVA-CHL163 consumes carbon dioxide and water, producing oxygen and other organic compounds. In the absence of light, the glycogen stored within the microalgae is utilized. As a result, NIVA-CHL163 microbial batteries function similarly to Microbial fuel cells (MFCs) under both dark and light conditions. Integrating power generation with local algae can diminish the strain on the existing electrical infrastructure, realizing true carbon neutrality and eliminating combustion emissions. This approach offers distinct advantages in addressing energy production challenges, particularly as it can act as a decentralized power source for rural regions without electricity access.

In addition, in order to make the algae battery have better performance, ionic liquid was selected and used in algae battery as a part of electrolyte. By adding ionic liquid to the system, electron transfer driving force was enhanced without affecting the activity of algae. The output power density of microbial photovoltaic cells had a signally performance improvement compared with the original algae battery.

Reference: Yuli Kou, Yuchao Li, Jide Wang and Yansong Zhao. A new generation self-powered and charged free battery : Bio-photovoltaic (BPV) cells. 2024 (*under review*)

Ionic Liquids in Separation of Sulfur Compounds from LPG

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The mathematical model LSSVM [1] (*Least Squares Support Vector Machine*) based on group contribution method and linear solvation-energy relationship (LSER) descriptors was used to calculate the selectivity coefficients of ionic liquids in the separation problem of removal of sulfur compounds from LPG (*Liquefied Petroleum Gas*). The selectivities were calculated based on infinite dilution activity coefficients obtained from the calculations. The selectivity coefficients as function of temperature in alkanes/mercaptans (propane, butane and ethanethiol, propanethiol, butanethiol, H_2S) were determined for about 30 000 ionic liquids, including hypothetical and described in the literature. The influence of the functional groups in the cation, alkyl chain length in the cation substituent, cation and anion structure were examined on the selectivity.

Obtained results were checked experimentally for selected ionic liquids. The selectivities were calculated from the experimental infinite dilution activity coefficients. To check the influence of functional groups on the selectivity three ionic liquids with common dicyanamide, $[DCA]^-$ anion were selected, namely: 1-ethyl-3-methyl-3*H*-imidazol-1-ium dicyanamide, 3-(2-hydroxyethyl)-1-methyl-3*H*-imidazol-1-ium dicyanamide and 3-allyl-1-methyl-3*H*-imidazol-1-ium dicyanamide. Additionally another two ionic liquids were selected: 1,3-dimethyl-3*H*-imidazol-1-ium dimethyl phosphate and tris(2-hydroxyethyl)methylammonium methyl sulfate. In general, experimental results were higher compared to the results obtained from the calculations, especially for ionic liquids with hydroxyl substituents.

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Deep Eutectic Solvent for recycling of valuable metals from spent lithium-ion battery cathodes

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The substantial increase in spent lithium-ion batteries (SLIB) has resulted in serious environmental impacts that require attention and appropriate intervention. In this study, we designed a DES composed of ethylene glycol (EG) and hydroxylamine hydrochloride ($NH_2OH\cdot HCl$) with appropriate acidity, remarkable reductive property and strong coordination capability for the efficient one-step leaching of cobalt ions and lithium ions from $LiCoO_2$ (LCO). Following leaching at a modest temperature of 80 °C for 8 hours, the solubility of $LiCoO_2$ reaches an 83.3 mg g^{-1} (much higher than previous works), accompanied by remarkably high leaching efficiencies of up to 99.7% for lithium and 88.0% for recovery of cobalt. Notably, this approach significantly enhances the solubility of the $LiCoO_2$ while upholding leaching efficiency. Importantly, this study achieves a one-step separation of lithium and cobalt, avoiding metal co-precipitation and simplifying the separation procedure. Furthermore, the residual components within the system can be reclaimed and recycled. This work provides an efficient and sustainable route for the recovery of precious metals from lithium-ion batteries, characterized by its cost-effectiveness and straightforward processing.

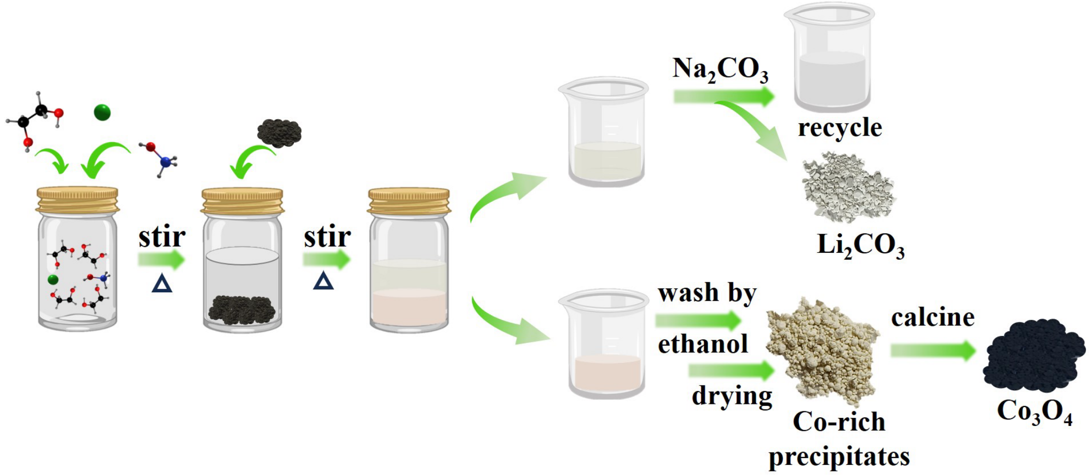

Fig. 1 Overview of the process for the recovery of value metals by dissolution from $LiCoO_2$.

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Integration of experimental techniques and molecular simulations. A multi-scale approach of [EMIM][BF4] + [EMIM][EtSO4] mixture.

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Our research focuses on exploring the properties and nanostructure of the double salt – ionic liquid system 1-ethyl-3-methylimidazolium with bistriflimide and ethylsulfate ([EMIM][BF4] and [EMIM][EtSO4]), through experimental techniques, molecular simulations, and other multi-scale approaches. Ionic liquids (ILs) have gained significant attention in recent decades. What makes ILs so unique is their exclusively composed ions structure and remain in liquid state at room temperature. The properties of ILs can be customized combining cations and anions with different characteristics, allowing them to adapt to specific requirements (*Tailor made solvents*). Double salts ionic liquids (DSILs) are a specific type of IL that contains more than one cation or anion, resulting in distinct physicochemical properties compared to their individual salt components. Some criticism has been considered on the possible large-scale application of ILs, citing issues such as toxicity and poor biodegradability [1, 2].

All the properties of pure ILs and binary mixture in the full composition range were measured as a function of temperature between 283.15 to 313.15 K. Experimental data was considered for the calculation of excess molar volume (V^E) and mixing viscosity (Δη). V^E are slightly and positive in all composition range (Fig. 1a). V^E for imidazolium-based mixtures may be linked to the free volume created by the alkyl chain, although deviations are very low, so it could be inferred that the effect of free space rearrangement upon mixing with negligible disruption in the established intermolecular forces. Mixtures shows a negative non-negligible Δη (Fig. 1b). Negative values are usually assigned to factors such as fewer surfaces available for friction [3], or mainly to the weakening of intermolecular forces between molecules [4]. The distribution of anions around the [EMIM] cation is analyzed via Spatial Distribution Functions (SDFs), Fig. 1c. SDFs indicate that both anions are mainly placed around the C(1) site of [EMIM] and non-negligible distributions are also produced around the C(2) sites, corresponding to the interaction between neighbor anion – cation clusters. It is notable that both anions show an analogous distribution around the cation, maintained in the whole composition range.

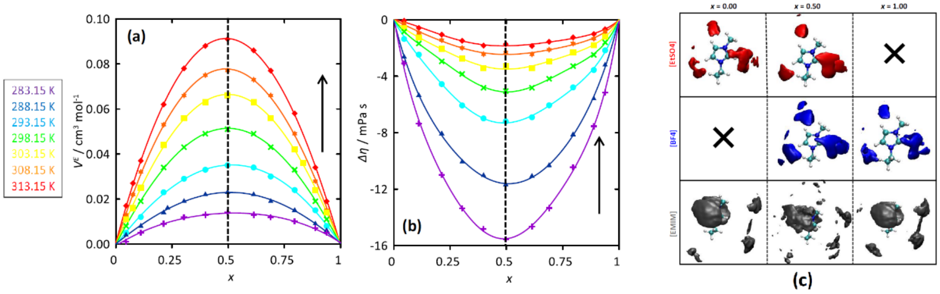

Fig. 1. (a) Excess molar volume (V^E) and (b) mixing viscosity (Δη) for x [EMIM][BF4] + (1-x) [EMIM][EtSO4] (x stands for mole fraction) as a function of temperature. (c) SDF around central [EMIM] cation for the reported molecules from MD simulations at 303 K and 1 bar.

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