The 2 Advances on Green Chemistry

BOOK OF ABSTRACTS

Poznan, Poland 16-18 April 2018



Poznan 2018



The 2 Advances on Green Chemistry

BOOK OF ABSTRACTS

Poznan, Poland 16 -18 April 2018



2018

Published by Poznan Science and Technology Park, Adam Mickiewicz University Foundation/ Poznan / Poland.

ISBN: 978-83-950380-0-6



AGC2018 - invitation

Dear Colleagues,

The 2nd Advances in Green Chemistry Conference – AGChem 2018 will be held from 16-19th April 2018 in Poznan Science and Technology Park, Poznan, Poland. First edition of this meeting has finished successfully with over 80 participants from all over the Europe. Even though the EXIL COST Action has finished, it would be a great loss for IL scientific community, if the network that was built by us over the last few years did not remain active.

As during the first edition of our Conference, we would like to especially invite young researchers including MSc Students, PhD Students and Post-docs, as we think this will be a great opportunity for them to share their scientific experience and interact with our IL network.

This will be a great opportunity to see you in Poznan!

PROF. MARCIN SMIGLAK Conference Chairperson

INVITED SPEAKERS

Robin D. ROGERS

525 Solutions, Inc. and The University of Alabama

Luís M. N. B. F. **SANTOS** CIQUP, Department of Chemistry and Biochemistry,University of Porto

Katharina **BICA** (K. Schröder) Institute of Applied Synthetic Chemistry, Vienna University of Technology

Małgorzata SWADŹBA-KWAŚNY

The QUILL Research Centre, School of Chemistry and Chemical Engineering, Queen's University Belfast

ORGANIZING COMMITTEE

The conference is organized by the Materials Synthesis Group of Poznan Science and Technology Park.

Conference Chair: Marcin SMIGLAK

Anna PAWLOWSKA-ZYGAROWICZ Olga STOLARSKA Rafal KUKAWKA Adrian ZAJAC Dawid ZIELINSKI Patrycja CZERWONIEC Jakub HOPPE Andrea SZPECHT Judyta STRAKOWSKA



POZNAN SCIENCE AND TECHNOLOGY PARK Adam Mickiewicz University Foundation

> IONIC LOQUIDS





https://ionicliquidsgroup.weebly.com/

SPONSORS

The organizers would like to thank the following companies for sponsoring this meeting:







We would also like to thank Bartosz Labuhn for the cover design and logo of the Conference.

GENERAL INFORMATION

INTERNET ACCESS

Access to the Internet will be provided by Wireless Lan. Please connect to the SSID: **AGC2018**, password: **AGCCHEM2018**.



GUIDELINES FOR PREPARING POSTER

Posters should be 1.18 m high and 0.84 m wide (Format A0, Portrait). Abstracts will be numbered and listed in the Final Program. The poster boards will be numbered according to the program.

The official sessions for Poster Presentations are:

- Monday, April 16 (17:00-19:00)
- Tuesday, April 17 (17:00-19:00)

Authors are requested to be present in front of the poster during second hour of the official session time.

All poster should be mounted by 1:00 PM on the day of Poster session and should be removed after the Poster session.

The Poster session will take place at the conference venue, nearby the lecture hall. We will provide adhesive tapes for mounting your poster.

GUIDELINES FOR POSTER FLASH TALKS

Flash Talks will be 10 minutes long (7 min. speech + 3 min. discussion).

A presentation file must be prepared similar to the guidelines for the oral talks in the next paragraph.

GUIDELINES FOR PREPARING TALKS

A laptop for Powerpoint presentations will be provided. You must use the provided equipment instead of your own laptop to avoid technical problems. This laptop runs Windows 7 and Office 2010. If you need special software for your presentation (Video Player, etc), please ask in email, if this can be provided.

Speakers are requested to hand in their slides to the slide center two hours before their session. A laptop (identical to the presentation laptop) will be available to check your presentation.

Each Oral Presentation will have a time slot of 20 minutes (17 min. speech + 3 min. discussion).



https://agc2018.syskonf.pl/

SOCIAL PROGRAM

On the Wednesday afternoon, after the lunch we suggest you to participate in one of two, activities we have prepared for you. For the afternoon activities please choose one of two (Participation in the activities with additional costs):

"Imagine Lab" workshop. In Poznan Science and Technology Park operates an interactive/science exhibition (https://wyobraznia.ppnt.poznan.pl/) concerning the explanation of physicochemical phenomenones occurring on our planet. Especially for us, the guides prepared 1h of exciting guided exhibition that will address topics such as optical physics and wave physics. During the second hour of the tour, participants will take part in the workshop concerning air purity and smog ca. 2 h



 "Old Town and Cathedral" excursion – an excursion including sightseeing of Poznan's Old Market Square, Old Town and Cathedral with professional tour guide – ca. 3 h. Meeting place in the front of the City Hall.







Monday

10:00 - 11:00	Registration	
11:00 - 12:00	Robin D. Rogers University of Alabama	Keynote lecture Can Advanced Materials from Renewable Resources Replace Plastics in a Sustainable Society?
12:00 - 12:20	Justyna Cięgotura Poznań Science and Technology Park	Poznan Science and Technology Park – Where business meets science.
12:20 - 12:40	Coffee break	
12:40 - 13:10	Anders Riisager Technical University of Denmark	Oral presentation 1 Pd-catalyzed oxidative carbonylation of aromatic amines with ionic liquids for benign synthesis of ureas
13:10 - 13:30	Radosław Drozd West Pomeranian University of Technology Szczecin	Oral presentation 2 Bacterial nanocellulose as a promising biopolymer for green chemistry - application and modification methods
13:30 - 13:50	Sofia Riaño ^{KU Leuven}	Oral presentation 3 Ionic Liquid-Based Solvent Extraction for the Recovery of Neodymium and Dysprosium from NdFeB Magnets
13:50 - 14:10	Joanna Cybińska Wroclaw Research Centre EIT+	Oral presentation 4 Ionic Liquid in the synthesis of luminescent nanoparticles
14:10 - 15:10		Lunch





15:10 - 15:30	Sónia P. M. Ventura University of Aveiro	Oral presentation 5 Extraction of Green fluorescent protein and its purification using centrifugal partition chromatography	
15:30 - 15:50	Łukasz Chrzanowski Poznan University of Technology	Oral presentation 6 Environmental impact of novel ionic liquids – from synthesis to advanced field studies	
15:50 - 16:10	Veronika Zeindlhofer University of Vienna	Oral presentation 7 A shell-resolved analysis of hydrotropic solvation of coffee ingredients in aqueous mixtures of 1- ethyl-3-methylimidazolium acetate	
16:10 - 16:20	Anna Rybińska- Fryca ^{University} of Gdansk	Flash 1 When toxicity is a good thing - case of antibiotic resistant bacteria	
16:20 - 16:30	Jakub Szyling Adam Mickiewicz University in Poznan	Flash 2 Alkynes hydroboration in ionic liquids – green approach to alkenyl boronates	
16:30 - 16:40	Kinga Stefanowska Adam Mickiewicz University in Poznan	Flash 3 Supercritical CO ₂ as an alternative medium for the synthesis of alkenyl silanes	
16:40 - 16:50	Marcin Gano West Pomeranian University of Technology Szczecin	Flash 4 Application new chiral ionic liquids based on (-)- menthol as a solvent in Diels-Alder reaction	
16:50	Poster session +	Get together reception (barbecue)	





Tuesday

09:00 - 10:00	Luís M. N. B. F. Santos University of Porto	Keynote lecture A short history about the understanding of nanostructuration and dual character of lonic Liquids
10:00 - 10:20		Coffee break
10:20 - 10:40	Nebojša Zec Centre for Materials and Coastal Research	Oral presentation 8 Intermolecular interactions in mixtures of ionic liquids and molecular solvents investigated by MD simulations
10:40 - 11:00	Esther Heid University of Vienna	Oral presentation 9 Solvation dynamics in ionic liquids
11:00 - 11:20	Victor Sans University of Nottingham	Oral presentation 10 3D printing devices based on polymerisable ionic liquids: from antimicrobial to photochromic devices
11:20 - 11:40	Spyridon Koutsoukos National Technical University of Athens	Oral presentation 11 Choline Chloride and Tartaric Acid NADES: An Efficient Solvent for the Extraction of Phenolic and Carotenoid Compounds
11:40 - 12:00	Mariam Kholany University of Aveiro	Oral presentation 12 Enantioselective separation of chiral compounds using aqueous biphasic systems
12:00 - 12:20	Coffee break	
12:20 - 12:30	Tribute to prof. Kenneth R. Seddon	
12:30 - 13:00	Rasmus Fehrmann Technical University of Denmark	Oral presentation 13 Gas separation by ionic liquid filters
13:00-13:30	Christian Schröder University of Vienna	Oral presentation 14 How to predict physicochemical properties of ionic liquids from MD simulations
13:30 - 13:50	Marzena Dzida University of Silesia in Katowice	Oral presentation 15 Ionic liquids and IoNanofluids as green media in sustainable heat transfer processes
13:50 - 14:10	Helena Passos University of Aveiro	Oral presentation 16 Ionic liquids as phase forming components of aqueous multiphase systems





14:10 - 15:00	Lunch	
15:00 - 15:40	IoLiT	ec - sponsor presentation
15:40 - 15:50	Patrycja Czerwoniec Adam Mickiewicz University in Poznan	Flash 5 New ionic liquids based on systhemic acquired resistance inducers combined with benzethonium cation
15:50 - 16:00	Paula Ossowicz West Pomeranian University of Technology Szczecin	Flash 6 Evaluation of the antimicrobial and antibiofilm activities of a series cholinium amino acids
16:00 - 16:10	Andrea Szpecht Adam Mickiewicz University in Poznan	Flash 7 Ion chromatography as an excellent tool for ion exchange control in ionic liquids synthesis
16:10 - 16:20	Tomasz Sokolnicki Adam Mickiewicz University in Poznan	Flash 8 Poly(ethylene glycols) and ionic liquids as an alternative media for borylative coupling of vinylboronates with olefins
16:20 - 16:30	Viet Tu Nguyen ^{KU Leuven}	Flash 9 Extraction of Platinum Group Metals from Chloride Leachate of End-of-Life Car Exhaust Catalysts using Undiluted Ionic Liquids
16:30 - 16:40	Ana I.M.C. Lobo Ferreira University of Porto	Flash 10 Volatility Study of [CNPy][NTf ₂] Ionic Liquids
16:40 - 16:50	Ádám Márk Pálvölgyi Vienna University of Technology	Flash 11 Design of chiral ionic liquids for highly selective asymmetric transfer hydrogenation in aqueous medium
16:50 - 19:00	Poster session	
20:00	Dinner	





09:00 - 10:00	Katharina Schröder Vienna University of Technology	Keynote lecture Recent trends in synthesis and catalysis with ionic liquids
10:00 - 10:20	Nerea Rodriguez Rodriguez ^{KU Leuven}	Oral presentation 17 Valorization of industrial tailings using deep- eutectic solvents
10:20 -10:40	Tânia Sintra University of Aveiro	Oral presentation 18 Hydrotropic solubilization of ibuprofen in aqueous solutions of ionic liquids
10:40 - 11:00	Sónia P. M. Ventura University of Aveiro	Oral presentation 19 Aqueous biphasic systems on the multistep purification of cytochrome c PEGylated forms
11:00 - 11:20		Coffee break
11:20 - 11:40	Tomasz Rzemienicki Poznan University of Technology	Oral presentation 20 Synthesis, physicochemical properties and biological activity of double salt herbicidal ionic liquids derived from synthetic auxins
11:40 - 12:00	Xiaohua Li KU Leuven	Oral presentation 21 Trichloride ionic liquids for oxidative dissolution of SmCo magnets
12:00 - 12:20	Inês Vaz University of Porto	Oral presentation 22 The Fluorination Effect on Alcohol-IL anion H- Bond Interaction
12:20 - 12:40	Helena Passos University of Aveiro	Oral presentation 23 Ionic-liquid-based acidic aqueous biphasic systems: a promising alternative in critical metals extraction
12:40 - 13:00	Iuliia V. Voroshylova University of Porto	Oral presentation 24 Influence of the anion on ionic liquids mixtures properties: a molecular dynamics study
13:00 - 13:20	Nicolas Schaeffer University of Aveiro	Oral presentation 25 Sustainable hydrophobic eutectic formulations for the extraction and deposition of metals
13:20 - 13:40	Boyan Iliev IoLiTec Ionic Liquids Technologies GmbH	Oral presentation 26 Ionic Liquids for CO_2 capture and conversion
13:40 - 14:40		Lunch





Thursday

09:00 - 10:00	Gosia Swadźba- Kwaśny Queen's University Belfast	Keynote lecture Lewis acidic ionic liquids, and beyond
10:00 - 10:20	Coffee break	
10:20 - 10:40	Štefan Schlosser Slovak University of Technology	Oral presentation 27 Butyric acid extraction by phosphonium ionic liquid with decanoate anion
10:40 - 11:00	Sónia P. M. Ventura ^{University} of Aveiro	Oral presentation 28 Centrifugal partition chromatography applied on the fractionation of phenolic compounds from lignin depolymerization
11:00 - 11:20	Michał Niemczak Poznan University of Technology	Oral presentation 29 Herbicidal ionic liquids comprising phenoxy acids as effective crop protection agents
11:20 - 11:40	MariamOral presentation 30KholanyViolacein recovery from Yarrowia lipolytic cells with Aqueous Solutions of Surface-Act ionic liquids	
11:40 - 12:00	Krzysztof Rola Wrocław Research Centre EIT+	Oral presentation 31 Polymerizable ionic liquids as green materials for patterning of micro-optical elements
12:00 - 12:20	Olga Lanaridi University of Vienna	Oral presentation 32 Selection and evaluation of ionic liquids for the recovery of platinum group metals from spent autocatalysts
12:20 - 12:40	Closing remarks - Prizes awarding	
12:40 - 13:30	Lunch	





Monday

No	Author	Title
P_001	Leszek Broniarek BBH Biotech Ltd.	The influence of selected choline based DES on growth and survival abilities of Bacillus licheniformis and Kluyveromyces lactis
P_003	Damian Kaczmarek Poznan University of Technology	Ionic liquids with bis-ammonium cation as new feeding deterrents
P_005	Inês Vaz University of Porto	Solvation of alcohols in Ionic Liquids: A pathway for the design of IL-based solvents
P_007	Janusz Nowicki Institute of Heavy Organic Synthesis "Blachownia"	Micellar route of the synthesis of alkyl xylosides - an unexpected effect of amphiphilic imidazolium ionic liquids
P_009	Joanna Feder- Kubis Wrocław University of Science and Technology	Biobased chiral ionic liquids with monoterpene moiety
P_011	Katarzyna Komorowska Wroclaw Research Center EIT+	Ionic Liquids for photonics
P_013	Marcin Gano West Pomeranian University of Technology in Szczecin	Synthesis a new chiral pyrrolidinium organic salt based on terpene alcohol endo-(1S)-borneol
P_015	Monika Karpińska Warsaw University of Technology	Separation of ethylbenzene/styrene systems using ionic liquids in ternary LLE
P_017	Paula Ossowicz West Pomeranian University of Technology in Szczecin	Surface-Active Amino Acid Ionic Liquids





P_019	Anna Pawłowska- Zygarowicz Adam Mickiewicz University in Poznan	Development a new and efficient methods for the synthesis of ionic liquids through the ion exchange reactions carried out in a continuous flow conditions	
P_021	Olga Stolarska Adam Mickiewicz University in Poznan	Solid–liquid equilibria for a pyrrolidinium-based common- cation ternary ionic liquid system, and for a pyridinium- based ternary reciprocal ionic liquid system	
P_023	Rafał Kukawka Adam Mickiewicz University in Poznan	New generation of ionic liquids based on fungicides ion	
P_025	Magdalena Jankowska-Wajda Adam Mickiewicz University in Poznan	Synthesis of new platinum and rhodium complexes on- containing ionic liquids and to determine their structures	
P_029	Adrian Zając Poznan Science and Technology Park	Unsaturated Ionic Liquids in the Synthesis of Ligands for Transition Metal-Based Catalysts	
P_031	Judyta Strakowska Poznan Science and Technology Park	Effect of choline-based deep eutectic solvents on catalytic properties of β -galactosidase from Kluyveromyces lactis	
	Posters with flash talk presentation		
F_001	Anna Rybińska- Fryca University of Gdansk	When toxicity is a good thing - case of antibiotic resistant bacteria	
F_002	Jakub Szyling Adam Mickiewicz University in Poznan	Alkynes hydroboration in ionic liquids – green approach to alkenyl boronates	
F_003	Kinga Stefanowska Adam Mickiewicz University in Poznan	Supercritical CO_2 as an alternative medium for the synthesis of alkenyl silanes	
F_004	Marcin Gano West Pomeranian University of Technology in Szczecin	Application new chiral ionic liquids based on (-)-menthol as a solvent in Diels-Alder reaction	





Tuesday

No	Author	Title
P_002	Aitor Sainz Martinez Vienna University of Technology	Continuous conversion of carbon dioxide to propylene carbonate using supported ionic liquids
P_004	Daria Czuryszkiewicz Poznan University of Technology	Ionic liquids with tryptophanate anion
P_006	Jakub Szyling Adam Mickiewicz University in Poznan	Hydroboration in poly(ethylene glycols) – green approach to alkenyl boronates
P_008	Julia Woch Institute of Heavy Organic Synthesis "Blachownia"	Paraffin based emulsions as impregnates for food packaging
P_010	Joanna Feder- Kubis Wrocław University of Science and Technology	Task-specific ionic liquids containing natural occurring bicyclic terpene derivative as effective template for mesoporous silica nanoparticles
P_012	Kinga Stefanowska Adam Mickiewicz University in Poznan	Synthesis of alkenyl-substituted silsesquioxanes and spherosilicates by hydrosilylation reaction in conventional and non-conventional solvents
P_014	Maria Bairaktari National Technical University of Athens	Green approaches towards the synthesis of quinazolinone derivatives
P_016	Nádia Figueiredo University of Porto	Theoretical study of the addition of solvents to ionic liquids
P_018	Tomasz Sokolnicki Adam Mickiewicz University in Poznan	Catalytic hydroboration of 1,3-diynes in traditional and green solvents
P_020	Anna Pawłowska- Zygarowicz Adam Mickiewicz University in Poznan	New methods of carrying out chemical reactions with the use of flow reactors





P_022	Olga Stolarska Adam Mickiewicz University in Poznan	Eutectic mixtures of ionic liquids - determination of the eutectic point and analysis of the relationship between the structure of ions and the properties of obtained eutectic mixtures
P_024	Rafał Kukawka Adam Mickiewicz University in Poznan	Supported Ionic Liquid Catalysts as efficient tool for hydrosilylation reaction
P_026	Patrycja Czerwoniec Adam Mickiewicz University in Poznan	New ionic liquids based on systemic acquired resistance inducers combined with phytotoxicity reducing cholinium cation
P_028	Adrian Zając Poznan Science and Technology Park	Synthesis and Characterization of Polymerizable Ionic Liquids as Precursors of Nanoscale Polymeric Structures
P_030	Jakub Hoppe Adam Mickiewicz University in Poznan	Physical properties of DES based on choline cation with various HBD
Posters with flash talk presentation		
F_005	Patrycja Czerwoniec Adam Mickiewicz University in Poznan	New ionic liquids based on systhemic acquired resistance inducers combined with benzethonium cation
F_006	Paula Ossowicz West Pomeranian University of Technology in Szczecin	Evaluation of the antimicrobial and antibiofilm activities of a series cholinium amino acids
F_007	Andrea Szpecht Adam Mickiewicz University in Poznan	Ion chromatography as an excellent tool for ion exchange control in ionic liquids synthesis
F_008	Tomasz Sokolnicki Adam Mickiewicz University in Poznan	Poly(ethylene glycols) and ionic liquids as an alternative media for borylative coupling of vinylboronates with olefins
F_009	Viet Tu Nguyen KU Leuven	Extraction of Platinum Group Metals from Chloride Leachate of End-of-Life Car Exhaust Catalysts using Undiluted Ionic Liquids
F_010	Ana I.M.C. Lobo Ferreira University of Porto	Volatility Study of [CNPy][NTf ₂] Ionic Liquids
F_011	Ádám Márk Pálvölgyi Vienna University of Technology	Design of chiral ionic liquids for highly selective asymmetric transfer hydrogenation in aqueous medium

ABSTRACTS

Can Advanced Materials from Renewable Resources Replace Plastics in a Sustainable Society?

Robin D. Rogers

525 Solutions, Inc. and The University of Alabama P. O. Box 2206, Tuscaloosa, AL 35403 E-mail: rdrogers@ua.edu

Humanity has always relied on Nature for survival, but today we take oil as a feedstock and use it to produce chemicals to suit any purpose, from fuels and medicines to plastics. By reducing our reliance on Nature, we have forgotten our respect of Nature in the process. The world is now covered in oil in the form of non-biodegradable synthetic plastics which mar our landscapes and threaten our oceans. By 2050 there is predicted to be more plastic in the ocean than fish. At the same time, plastics represent a \$654 billion market worldwide and are ubiquitous in modern life. Simply eliminating synthetic plastic use with no viable alternatives would be almost impossible and catastrophic from both a social and economic point of view.

Chemists make new chemicals and that has led to the development of a chemical industry that knows how to sell these chemicals. The more chemicals we make, the more the industry seeks new and better markets to sell them into. New, more sustainable technologies have been forced into the business of 'replacements' and must follow the same commercialization pathways as the old technologies they are trying to replace. The unsustainable practices, however, have often had decades or more head start and thus the economics to replace them are often insurmountable without government or policy intervention. The technologies to directly replace synthetic plastics with renewable biopolymers from plants and animals are there, but the consistencies of supply and economies of scale to make them competitive are not.



Figure reproduced from Rogers, R. D. "Eliminating the need for chemistry," C&E News 2015, 93, 42–43 Credit: Steven Kelly/C&EN/Shutterstock.

With a plethora of abundant natural and renewable resources (in terms of both quantity and diversity), from water purification - to cosmetics - to medical applications, the quality of human life can greatly benefit (and improve at the same time) from new, innovative technologies using building blocks obtained directly from plants and animals. With this mission in mind, we are exploring the entire range of the "biorefinery concept," from dissolution, and conversion of plant and animal resources into value added chemicals and extraction of essential oils or vital chemicals, to isolation of pure biopolymers and production of new biomaterials from them. Because we can directly dissolve Nature's raw materials, we can shape them, functionalize them, blend them, and use other non-chemistry means to produce advanced functional materials. These new, innovative materials represent new market opportunities which we will develop and promote.

A short story about the understanding of nanostructuration and dual character of ionic liquids

Luís M. N. B. F. Santos

CIQUP, Department of Chemistry and Biochemistry, University of Porto, Porto, Portugal E-mail: lbelchiorsantos@gmail.com

The first part of this lecture I will present a brief description of the strengths and weaknesses of my academic and scientific career, as well as, a critically analysis of the adopted strategy to keep my self-motivation and driving force to work in science.

In the second part, I will present a short overview of our recent achievements concerning the molecular understanding of the nanostructuration and dual character of ionic fluids.[1-3] Ionic fluids and in special ionic liquids, form nanoaggregates constituted by anions and cations giving rise to a polar network and nonpolar domains. In some recent publication [4] we were able to give additional support to the molecular interpretation of nanostructuration. Further studies allowed us to unravel the role of IL nanostructuration and acidity on the preferential interactions established between the alcohol and the IL,[4] the speciation and cohesive energy of protic ionic liquids, [5] as well as, the description and interpretation of thin films and microdroplets of ILs deposited by physical vapor method onto different surfaces.[6]

The dual character and level of nanostructuration in the ILs is dependent of the alkyl chain size, cation and anion nature and affects their physical chemistry properties, functionalities and applicability.

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, for the financial support to Project UID/QUI/0081/2013 and FCUP-CIQ-UP-NORTE-07-0124-FEDER-000065.

- [1]Rocha, M.A.A.; Lima, C.F.R.A.C.; Gomes, L.R.; Schröder, B.; Coutinho, J.A.P.; Marrucho, I.M.; Esperança, J.M.S.S.; Rebelo, L.P.N.; Shimizu, K.; Canongia Lopes, J.N.; Santos, L.M.N.B.F. *Journal of Physical Chemistry B*, **2011**, *115*, 10919-10926.
- [2]Almeida, H.F.D.; Freire, M.G.; Fernandes, A.M.; Lopes-da-Silva, J.A.; Morgado, P.; Shimizu, K.; Filipe, E.J.M.; Lopes, J.N.C.; Santos, L.M.N.B.F.; Coutinho, J.A.P. Langmuir, 2014, 30, 6408-6418.
- [3]Lopes, J.N.A.C; Pádua, A.A.H. Journal of Physical Chemistry B, 2006, 110, 3330-3335.
- [4]Vaz, I.C.M.; Bhattacharjee, A.; Rocha, M.A.A.; Coutinho, J.A.P.; Bastosa, M.; Santos, L.M.N.B.F. Phys. Chem. Chem. Phys., 2016, 18, 19267-19275.
- [5] Rodrigues, A.S.M.C.; Lima, C.F.R.A.C.; Coutinho, J.A.P.; Santos, L.M.N.B.F. *Phys. Chem. Chem. Phys.*, **2017**, *19*, 5326-5332.
- [6]Costa, J.C.S.; Coelho, A.F.S.M.G.; Mendes, A.; Santos, L.M.N.B.F. *Applied Surface Science*, **2018**, 428, 242-249.

Recent trends in synthesis and catalysis with ionic liquids

Katharina Bica (K. Schröder)

Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, 1060 Vienna, Austria E-mail: katharina.schroeder@tuwien.ac.at

Despite remarkable developments in ionic liquid technologies with a diverse application range considerable less progress has been made in their preparation. Until today, most hydrophobic prepared in a two-step process involving the initial alkylation of an amine or phosphine followed by subsequent metathesis to exchange the anion, a strategy which has been described in seminal books and reviews on ionic liquids in synthesis already in the late 1990s and since then remained almost unaltered [1].

While this state-of-the art procedure is working in high yields, a number of critical aspects limits its utility for the large-scale production of hydrophobic ionic liquids. The alarmingly large discrepancies (physico-)chemical properties of ionic liquids can be traced to halide and metal contamination of the hydrophobic ionic liquid, together with variations in its water content [2]. Yet, the specifications needed for many new technological applications require metal- and halide free ionic liquids without trace contamination of inorganic salts.



In here, we discuss problems associated with synthesis in and of ionic liquids and revisit the classic synthesis of hydrophobic ionic liquids, aiming for a fast and halide-free approach that eliminates the need of anion metathesis [2]. Critical aspects of a novel and atom efficient synthesis of ionic liquids, but also of their application in biphasic catalysis will be discussed and advantages of continuous flow based processes will be highlighted.

- [1] T. Welton and P. Wasserscheid, Ionic Liquids in Synthesis, VCH-Wiley, Weinheim, 2002.
- [2] K. Bica, M. Schön, P. Gärtner and M. D. Mihovilovic, Method for producing ionic liquids containing bis(trifluoromethanesulfonyl)imide anions, PCT Int. Appl. (2017), WO 2017112972 A1 20170706.

Lewis acidic ionic liquids, and beyond

<u>Małgorzata Swadźba-Kwaśny</u>^{1*}, James M. Hogg¹, Lucy Brown¹, Sesime Coffie¹, Rachel Whiteside¹, Fergal Coleman¹, Julien Estager₁, John D. Holbrey¹, Peter Nockemann¹, Karolina Matuszek², Anna Chrobok²

¹ The QUILL Research Centre, School of Chemistry and Chemical Engineering, Queen's University Belfast, BT7 3LH Belfast, Northern Ireland, UK

² Department of Chemical Organic Technology and Petrochemistry, Silesian University of

Technology, Krzywoustego 4, 44-100 Gliwice, Poland

E-mail: m.swadzba-kwasny@qub.ac.uk

Lewis acidic ionic liquids and their applications in catalysis have been studied for decades[1], with several processes implemented on the industrial scale[2]. Despite the breadth of investigated reactions, structural diversity of Lewis acidic ionic liquids had been rather limited, with most examples combining a 'spectator' organic cation (quaternary ammonium or phosphonium) with anions of a general formula $[M_x X_y]^-$, where $M = e.g. Al^{III}$, Zn^{II} , Ga^{III} or Fe^{III} , and X = Cl or Br.¹ There are several major drawbacks to this design, predominantly: (i) cation is the cost-incurring component, but has little contribution to chemical reactivity, and (ii) Lewis acidity is associated with an electron-rich species (anion), which in fact may impair the acidity strength.

Alternative systems developed by our group, such as liquid coordination complexes [3] and ionic liquids with Lewis acidic cations [4], will be presented. Our approach to developing such Lewis acidic liquids will be outlined, and discussed as a part of a broader trend in the field of ionic liquids, where ionic liquid systems are expanded beyond purely ionic components, in order to achieve enhanced performance and cost efficiency. This was recently labelled as "the 4th evolution of ionic liquids" by MacFarlane and co-workers [5], following on from "the 3rd evolution of ionic liquids", proposed in 2008 by Rogers and co-workers [6]. Through addition of molecular components, new families of liquid materials are generated. They deviate from the orthodox definition of ionic liquids, but the philosophy behind their design is firmly rooted in several decades of research in the ionic liquid community. In the triumph of practicality over semantics, it is feasible to develop advanced functional liquids, with superior performance and cost-efficiency compared to "classical" ionic liquids.

- [1] Estager, J.; Holbrey, J. D.; Swadźba-Kwaśny, M.; Chem. Soc. Rev., 2014, 43, 847-886.
- [2] Brown, L.C.; Hogg, J.M.; Swadzba-Kwasny, M.; Top. Curr. Chem., 2017, 375, 1-40.
- [3]Coleman, F.; Srinivasan, G.; Swadźba-Kwaśny, M.; Angew. Chem. Int. Ed. Engl., 2013, 52, 12582-12586.
- [4]Coffie, S.; Hogg, J.M.; Cailler, L.; Ferrer-Ugalde, A.; Murphy, R.W.; Holbrey, J.D.; Coleman, F.; Swadźba-Kwaśny, M.; Angew. Chem. Int. Ed., 2015, 54, 14970-14973.
- [5]MacFarlane, D.R.; Chong, A.L.; Forsyth, M.; Kar, M.; Vijayaraghavan, R.; Somers, A.; Pringle, J.M.; Faraday Discuss., 2017, 206, 9-15.
- [6]Hough, W.L.; Smiglak, M.; Rodriguez, H.; Swatloski, R.P.; Spear, S.K.; Daly, D.T.;. Pernak, J.; Grisel, J.E.; Carliss, R.D.; Soutullo, M.D.; Davis, J.J.H.; Rogers, R.D.; *New J. Chem.*, **2007**, *31*, 1429-1436.

Pd-catalyzed oxidative carbonylation of aromatic amines with ionic liquids for benign synthesis of ureas

Anders Riisager¹, Nanette Zahrtmann^{1,2}, Cyril Godard², Carmen Claver², Eduardo J. García-Suárez¹

¹Department of Chemistry, Centre for Catalysis and Sustainable Chemistry, Technical University of Denmark, Kgs. Lyngby, Denmark

²Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Tarragona, Spain E-mail: ar@kemi.dtu.dk

Ureas are indispensable compounds commonly found in the structures of a large number of biologically active compounds, and are also widely used as agrochemicals, dyes, antioxidants and HIV inhibitors as well as key intermediates in organic synthesis [1]. Ureas can be prepared via the oxidative carbonylation of amines in the presence of a Pd-complex catalyst, usually at high pressure and temperature and under an explosive CO/O_2 gas mixture making the overall system unsafe [2]. Accordingly, it is desirable to develop an active catalytic system applicable for the oxidative carbonylation of amines under milder reaction conditions.

Ionic liquids (ILs) are reported to have beneficial effects in many homogeneously catalyzed reactions [3]. Furthermore, the use of ILs in liquid–liquid biphasic reactions makes in many cases processes greener than when using traditional organic solvents, due to associated advantages such as, e.g. low vapor pressure, good thermal stability and tunable solubility and coordination properties [4]. In addition, such systems provide good separation of reaction products and catalyst recovery.



Figure 1. Pd-catalyzed oxidative carbonylation of aniline to diphenylurea with IL

In this work, we present a new efficient, robust and versatile Pd-complex/IL catalytic biphasic system for the oxidative carbonylation of aromatic amines under mild reaction conditions (Figure 1) [5]. Reaction parameters, including oxidant agent, pressure, temperature, catalyst and IL loading were optimized resulting in a catalytic system which operates under mild conditions, is fully recyclable, is 100% selective and has activity two orders of magnitude higher than previously reported systems [6].

- [1] Díaz, D.J.; Darko, A.K.; McElwee-White, L., Eur. J. Org. Chem., 2007, 27, 4453-4465.
- [2]Zheng, S.-Z.; Peng, X.-G.; Liu, J.-M.; Sun, V.; Xia, C.-G., Chin. J. Chem., 2007, 25, 1065-1068.
- [3] Supported Ionic Liquids: Fundamentals and Applications, R. Fehrmann, A. Riisager, M. Haumann, Wiley-VCH, **2014**.
- [4] Haumann, M.; Riisager, A., Chem. Rev., 2008, 108, 1474-1497.
- [5] N. Zahrtmann, C. Claver, C. Godard, A. Riisager, E. J. Garcia-Suarez, *ChemCatChem*, DOI: 10.1002/cctc.201800004.
- [6] Chen, B.; Chuang, S.S.C., Green Chem., 2003, 5, 484-489.

Bacterial nanocellulose as a promising biopolymer for green chemistry - application and modification methods

Radosław Drozd¹, Magdalena Szymańska¹, Rafał Rakoczy², Karol Fijałkowski¹

¹Faculty of Biotechnology and Animal Husbandry, Department of Immunology, Microbiology and Physiological Chemistry, West Pomeranian University of Technology al. Piastów 45, 70-311 Szczecin, Poland
²Institute of Chemical Engineering and Environmental Protection Processes, Department of Chemical Engineering, West Pomeranian University of Technology, al. Piastów 42, 71-065 Szczecin, Poland E-mail: rdrozd@zut.edu.pl

Bacterial nanocellulose (BNC) is a natural biopolymer synthesized by *Komagataeibacter xylinus*. Due to its unique properties such as high mechanical strength, great capacity for water absorption high crystallinity and low level of impurities is considered a promising material for industrial application. Production of this biopolymer with the use of the bacterial cultures does not require time-consuming and cost-intensive technology, which makes the manufacturing of bacterial cellulose more environmentally friendly. Despite its many advantages, the BNC is often modified to increase its applicability. The properties of bacterial nanocellulose can be changed during the *K. xylinus* culturing by modification the media composition by various carbon source, additives such as hetero or homo oligosaccharides, that can be incorporated to BNC structure on this way. The bacterial nanocellulose is also often functionalized by addition of specific chemical groups (NH2, COOH etc.) able to react with proteins or active substances for it immobilization. Apart this most conventional methods a new approach as exposition to external electromagnetic field resulted in significant change of water properties the bacterial nanocellulose. In this short review we will present a review of actual methods and new field of applications of bacterial nanocellulose.

This work was funded by National Centre for Research and Development in Poland (Grant no. LIDER/011/221/L-5/13/NCBR/2014).

- [1] Drozd, R.; Rakoczy, R.; Wasak, A.; Junka, A.; Fijałkowski, K., Int. J. Biol. Macromol., 2018, 108, 462-470.
- [2] Drozd, R.; Rakoczy, R.; Konopacki, M.; Frąckowiak, A.; Fijałkowski, K., *Carbohydr Polym.*, **2017**, *161*, 208-218.
- [3] Fijałkowski, K.; Żywicka, A.; Drozd, R.; Junka, A.F.; Peitler, D.; Kordas, M.; Konopacki, M.; Szymczyk, P.; Rakoczy, R., *Electromagn Biol Med.*, **2017**, *36*, 192-201.

Ionic Liquid-Based Solvent Extraction for the Recovery of Neodymium and Dysprosium from NdFeB Magnets

Sofía Riaño¹ and Koen Binnemans¹

¹KU Leuven, Department of Chemistry, Celestijnenlaan 200F, 3001 Heverlee, Belgium E-mail: sofia.riano@kuleuven.be

In contrast to the increasing rare earth elements (REEs) demand, their supply is currently experiencing a shortage. The recycling of REEs from resin-bonded and sintered NdFeB magnets through solvent extraction is a promising alternative to overcome this situation while reducing the impact of mining and the balance problem [1]. Recycling allows the recovery of REEs that are minor constituents in the ores but are at the same time high in demand by the market (e.g. dysprosium) [2]. Ionic liquids (ILs) are organic salts which consist entirely of ions. They represent a greener and safer alternative to conventional solvents used in solvent extraction due to their chemical stability, negligible vapor pressure and low flammability [3].

A solvent extraction system based on the combination of [C101][SCN] and Cyanex® 923 was investigated for the separation of Nd(III) and Dy(III) from chloride media. The addition of Cyanex® 923 to the ionic liquid brings four main advantages: 1) it enhances the distribution ratios 2) it decreases the viscosity of the organic phase, therefore it improves the mass transfer, 3) it increases the loading capacity of the ionic liquid and 4) it improves the phase disengagement. Stripping of Dy(III) from the organic phase was easily achieved with water. This route highlights the potential of ionic liquids in solvent extraction for the recovery of highly demanded rare earths from NdFeB magnets. (Fig. 1)



Figure 1. Simplified flow sheet for the extraction from chloride aqueous solutions

This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 720838 (NEOHIRE project).

- [1] Riano, S.; Binnemans, K. Green Chemistry, 2017, 17, 2931-2942.
- [2] Vander Hoogerstraete, T.; Wellens, S.; Verachtert, K.; Binnemans, K. Green Chemistry, 2013, 15, 919-927.
- [3] Binnemans, K.; Jones, P.T.; Acker, K.; Blanpain, B.; Mishra, B.; Apelian, D. *The Journal of The Minerals, Metals & Materials Society*, **2013**, *65*, 846-848.

Ionic Liquid in the synthesis of luminescent nanoparticles

Joanna Cybińska^{1,2}, Anja-Verena Mudring³

 ¹Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, 50-383 Wroclaw, Poland
 ²WCB EIT+, Wroclaw, Stablowicka 147, 54-066 Poland
 ³Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrhenius väg 16 C, 106 91 Stockholm, Sweden E-mail: joanna.cybinska@chem.uni.wroc.pl

Technological progress stimulates research on the materials with luminescent properties, which are increasingly finding new applications from medical diagnosis by lighting techniques and solar convectors [1]. These applications increase the requirements for materials, thus not only their chemical, mechanical or spectroscopic properties are important, but also the grain size or morphology [2,3]. Because of the small grains size, nanomaterials possess physicochemical properties, which make them significantly different from bulk counterparts or crystals. In nanocrystalites, quantum effects can play an important role and have effect on changes in the refractive index, electron-phonon interaction, multi-phonon relaxation or nonlinear processes [3]. Commonly used methods to obtaining phosphors are solid-state, hydrothermal, Pechini or sol-gel synthesis. However, they usually lead to a product with many imperfections (inhomogeneity, large grain size, fluorescence quenching defects).

In our research we applied the Ionic Liquids based method to obtain pure and highly luminescent $LnPO_4$ and LnF_3 materials using lanthanide ions as emission center. For both types of the nanomaterials ionic liquids were used as reactant, reaction media and in-situ stabilizer of the synthetized nanoparticles. Changing in the anionic or cationic part of ILs influence the materials morphology and particles size thus the spectroscopic properties of the material can be tuned. The low temperature process allows also for better control of the quality of the obtained materials.



Fig. 1. The SEM micrographs and emission spectra of LnPO4 obtained using synthesis in ionic liquids.

Partial financial support from the National Science Center within the Grant Opus UMO-2015/19/B/ST8/02761 is grateful acknowledged.

- [1] Jüstel, T.; Nikol, H.; Ronda, C., Angew. Chem. Int. Ed., 1998, 37, 3084-3103.
- [2] Ozin; G.A.; Arsenault; A.C.; Cardematiri, L.: Nanochemistry A Chemical Approach to Nanomaterials, RSC Publishing, Oxford, **2009**.
- [3] Feldmann, C.; Goesmann, H., Angew. Chem. Int. Ed., 2010, 49, 1362 1395.

Extraction of Green fluorescent protein and its purification using centrifugal partition chromatography

Sónia P.M. Ventura¹, Bruna P. Soares¹, Margarida Martins¹, João H. P. M. Santos¹, Mafalda R. Almeida¹, Mara G. Freire¹, Jorge F. B. Pereira², João A. P. Coutinho¹

¹CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal ²Department of Bioprocesses and Biotechnology, School of Pharmaceuticals Sciences, UNESP – Universidade Estadual Paulista, 14800-903, Araraquara, SP, Brazil E-mail: spventura@ua.pt

The green fluorescent protein (GFP) is a biomolecule used in many biological approaches namely as gene marker, requiring high purity levels. GFP is usually recovered from recombinant *Escherichia coli* strains that are induced to produce the target biomolecule intracellularly. After cell disruption for GFP release [1], a purification step is required. Aqueous biphasic systems (ABS) have emerged as an interesting alternative purification platform, since they are cost-effective and easily scaled-up. Actually, the centrifugal partition chromatography (CPC) can enhance the resolution of the separations and convert liquid-liquid extractions based on ABS into processes scalable to large flow rates. In this sense, this work proposes the continuous purification of GFP by applying ABS formed by polyethylene glycol, sodium polyacrylate and sodium sulfate as electrolyte. After the selection of the technique. In the end, an integrated process to purify GFP was developed and the reuse of the main phase formers implemented to be used in new cycles of purification.

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. The authors are also grateful to FCT by the financial support considering the Project "Optimization and Scale-up of Novel Ionic Liquid-based Purification Processes for Recombinant Green Fluorescent Protein produced by Escherichia coli", process number FAPESP 2014/19793-3. The authors also thank FCT for the doctoral grants SFRH/BD/122220/2016 and SFRH/BD/102915/2014 of M. Martins and J.H.P.M. Santos, respectively. S.P.M. Ventura acknowledges for the IF contract IF/00402/2015. J.F.B. Pereira acknowledges financial support from FAPESP through the project 2014/16424-7. M.G.F. acknowledges ERC for the grant ERC-2013-StG-337753.

References:

[1]Martins, M.; Chien Wei, O.; Neves, M.C.; Pereira, J.F.B.; Coutinho, J.A.P.; Ventura, S.P.M., J. Chem. Tech. Biotech., 2018, DOI: 10.1002/jctb.5596.

Environmental impact of novel ionic liquids – from synthesis to advanced field studies

Łukasz Chrzanowski¹, Tadeusz Praczyk², Juliusz Pernak¹

¹Poznan University of Technology, Department of Chemical Technology and Engineering, 60-965 Poznan, Poland ²Institute of Plant Protection – National Research Institute, Poznan 60-318, Poland

E-mail: lukasz.chrzanowski@put.poznan.pl

Recent advances in the field of ionic liquids set new standards in terms of their synthesis and broadens the range of their possible applications. The possibility to include commercially relevant herbicides into the structure of ionic liquids opens up novel solutions for the agricultural sector. This process eliminates the major disadvantages of classic herbicidal formulations (unintended transport via vapours and the necessity to include adjuvants). Nevertheless, the direct introduction of such compounds into the environment results in the need for the development of strict and novel procedures for evaluation of their environmental impact. This issue directly relates to the assessment of biodegradability as well as toxicity of such compounds, taking into account the complexity of terrestrial matrices and the diversity of microbial populations which proliferate in agricultural fields. In this case, the classic methods which rely on the use of activated sludge microorganisms may be used as initial indicators, however their ability to reflect actual environmental conditions is limited.

This presentation provides a comprehensive summary of a 5-year research conducted on novel herbicidal ILs (HILs). Several HILs will be presented with respect to their efficiency against common weed species in both greenhouse and field studies. Additionally, evaluation of their biodegradability as well as toxicity towards a wide range of organisms will be discussed. To assess the actual biodegradability of the studied compounds, experiments conducted with C¹³ labelled HILs in both aquatic and soil system were performed. Moreover, Next-Generation Sequencing studies were conducted in order to investigate the influence of HILs on the structure of autochthonic soil bacterial community during field studies.

A shell-resolved analysis of hydrotropic solvation of coffee ingredients in aqueous mixtures of 1-ethyl-3-methylimidazolium acetate

Veronika Zeindlhofer¹, Magdalena Berger, Othmar Steinhauser¹ and Christian Schröder

¹Department of Computational Biological Chemistry, Faculty of Chemistry, University of Vienna, Austria

E-mail: veronika@mdy.univie.ac.at

Although aqueous ionic liquids have been successfully applied in biomass extraction for quite a few years, their general ability to enhance the solubility of small organic molecules in water has only been unraveled recently [1]. Co-solvents increasing the solubility of hydrophobic molecules in water are commonly referred to as "Hydrotropes" and have a wide range of possible applications such as in the formulation of drugs, cosmetics and cleaning agents and can be used in purification technology.

To investigate mechanisms of hydrotropy in ionic liquids, classical molecular dynamics simulation is a valuable tool since it allows analysis of solvent structure around a solute at a molecular level. However, structural analysis is often conducted under the assumption of spherical solvation shells, which is problematic especially for many small aromatic solutes due to their high anisotropy. Consequently, one requires a spatial decomposition method that accounts for solute anisotropy, such as Voronoi tessellation. It enables a fully shell-resolved analysis of preferential solvation, solvent orientation and dielectric properties even for anisotropic solutes and thus helps to determine whether classical theories of hydrotropy are applicable in the case of aqueous ionic liquids or if new explanations are required [2].

For this work, we chose a selection of small aromatic compounds present in coffee as model solutes to study their hydrotropic solvation in aqueous mixtures of the ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]) with classical molecular dynamics simulation. We show that Voronoi tessellation is crucial for these solutes and test possible hydrotropy mechanisms for [EMIM][OAc].

- Cláudio, A.F.M.; Neves, M.C.; Shimizu, K.; Canongia Lopes, J.N.; Freire, M.G.; Coutinho, J.A.P. *Green Chem.*, 2015, 17, 3948–3963.
- [2] Zeindlhofer, V.; Khlan, D.; Bica, K.; Schröder, C. RSC Adv., 2017, 7, 3495–3504.

Intermolecular interactions in mixtures of ionic liquids and molecular solvents investigated by MD simulations

<u>Nebojša Zec¹</u>, Abdenacer Idrissi², Slobodan Gadžurić³, Milan Vraneš³

¹German Engineering Materials Science Centre (GEMS) at Heinz Maier-Leibnitz Zentrum (MLZ) Helmholtz-Zentrum Geesthacht GmbH, Lichtenbergstr. 1, 85747 Garching bei München, Germany ²University of Lille, Science and Technology, LASIR (UMR CNRS A8516), Bât. C5, Cité Scientifique, 59655 Villeneuve d'Ascq Cedex, France

³Faculty of Science, Department of Chemistry, Biochemistry and Environmental Protection,

University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

Email: nebojsa.zec@hzg.de

Molecular dynamics simulations were applied to quantify the intermolecular interactions in pure molecular solvents (γ -butyrolactone, γ -valerolactone, propylene carbonate) and their binary mixtures with imidazolium based ionic liquids. Hydrogen bond, dipole-dipole and stacking interactions are the main interactions in these systems. The hydrogen bond interactions were quantified by calculating appropriate atom distances and angle between them. The first one is distance between hydrogen on C² carbon of imidazole ring and carbonyl oxygen of molecular solvent, while the second one is distance between C² carbon and the same carbonyl oxygen. In the case of a linear hydrogen bond and then a strong one, the C²…O distance will be equal to the sum of C²- H² bond and the intermolecular H²…O distances, while in the case of a bent hydrogen bonding, with a given θ angle, the C²…O distance is shorter. We calculated these distances using the nearest neighbor approach.

In order to study the orientational aspects, we calculated several combined angular and distance distributions where the angles are defined in Figure 1 while the distance is that between a reference center of the ring and that of the first neighbor.



Figure 1. Schematic representation of the γBL , γVL and PC dimer with geometric characteristics used for description of the mutual orientation of the molecules in neat liquids.

Angle, designated here as α , is the angle between the normal vector of the γ BL, γ VL, PC or imidazolium plane and the distance vector connecting the ring centers of the reference and observed molecules. Thus, positions above/below the reference molecule would correspond to α angle around 0° and 180°, while perfect in-plane arrangement of the observed molecules would contribute to the α values close to 90°. Angle β is formed by the normal vectors of the ring planes between the reference and observed molecules. As in the previous case a perfectly parallel arrangement of the planes corresponds to β values of 0° and 180°, whereas the values around 90° are indicative of a T-shaped relative arrangement of the two ring planes. This angle gives information on the stacking between the rings of the molecules. The third angle designated as ψ is that between the vectors along C=O bonds in the reference and observed molecules. Thus, this angle gives information about the relative orientation of molecular dipoles.

N. Z. is grateful to Erasmus + mobility grant enabling his research work at University of Lille. authors acknowledge the contribution of the COST Action CM1206 Exchange on Ionic Liquids.

Solvation dynamics in ionic liquids

Esther Heid¹, Christian Schröder¹

¹Faculty of Chemistry, Department of Computational Biological Chemistry, University of Vienna, Währingerstraße 17, A-1090 Vienna, Austria E-mail: esther.heid@univie.ac.at

The measurement and simulation of time resolved fluorescence sheds light on the solvation dynamics of a chromophore in ionic liquids. Computer simulations are especially helpful to study the sub-picosecond regime of the response, which is usually lost in experiment. Furthermore, the sum signal can be dissected into contributions from cations, anions or different solvation shells.

We show that nonequilibrium molecular dynamics simulations of the time-dependent Stokes shift accurately depict measurements of the solvation dynamics of two imidazolium-based ionic liquids when using polarizable force fields from Ref. [1]. The use of different chromophores, N-methyl-6-oxyquinolinium betaine, as well as Coumarin 153, leads to different solvation responses, both governed by anion movement [2]. This molecularity of solvation dynamics, i.e. the dependence of the timescale of solvent rearrangement on the peculiarities of the chromophore (here the volume and the sign of change in dipole moment upon excitation) was previously also found in polar liquids [3][4].

We furthermore show that the use of linear response theory, although often employed in computational solvation dynamics, is not applicable due to structure changes of the solvation shell after chromophore excitation. Within the linear response framework, the time-dependent Stokes shift is approximated as the correlation function of the energy gap between the ground and excited state from equilibrium molecular dynamics simulations. This approximation fails in the studied systems, especially for the dissection of the shift into cationic and anionic contributions, although the overall response is correctly reproduced (despite its magnitude). The computationally more expensive method of calculating nonequilibrium simulations is therefore inevitable for an accurate reflection of the solvation dynamics in ionic liquids.

We gratefully acknowledge funding by the Austrian Science Fund FWF in the context of Project No. FWF-P28556-N34. E.H. is recipient of a DOC Fellowship of the Austrian Academy of Sciences at the Institute of Computational Biological Chemistry.

- [1] Bernardes, C.E.S.; Shimizu, K.; Canongia Lopes, J.N.; Marquetand, P.; Heid, E.; Steinhauser O.; Schröder. C. *Phys. Chem. Chem. Phys.*, **2016**, *18*, 1665-1670.
- [2] Heid E.; Schröder. C. Phys. Chem. Chem. Phys., 2018, submitted.
- [3] Heid, E.; Moser W.; Schröder. C. Phys. Chem. Chem. Phys., 2017, 19, 10940-10950.
- [4] E. Heid and C. Schröder. J. Phys. Chem. B, 2017, 121, 9639-9646

3D printing devices based on polymerisable ionic liquids: from antimicrobial to photochromic devices

Dominic J. Wales, Qun Cao, Katharina Kastner, Erno Karjalainen, Graham N. Newton, Victor Sans

¹ Faculty of Engineering and School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

²School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

E-mail: victor.sanssangorrin@nottingham.ac.uk

Additive manufacturing techniques, commonly known as 3D printing, offer an unprecedented level of freedom of design, which is having a profound academic and increasingly industrial impact.[1] The ability to rapidly develop and manufacture tailored designs with very complex geometries offers a huge range of possibilities, which have found applications in chemical synthesis, bioengineering and chemical engineering.[2]

Polycationic polymers with analogous structures to ionic liquids, known as poly(ionic liquids) (PILs) are very interesting smart materials due to the array of properties that can be generated by simple variation of anion-cation choice.[3] Ionic liquid properties can be effectively transferred from the bulk liquid to the supported phases.[4] Besides the unique and hugely tuneable properties of these smart materials, they are excellent matrices to stabilise advanced molecular and nanostructured materials.[3] Very recently, the possibility of 3D printing PILs has been demonstrated employing stereolithography [5a] and inkjet [5b].

In this way, the combination of: 1) tuneable PILs, 2) advanced molecular materials, ranging from enzymes and nanoparticles to redox active nanostructured molecules and 3) additive manufacturing offers virtually unlimited number of opportunities to effectively transfer molecular properties across the scales to develop macroscopic active devices, with tailored molecular, nano-, micro- and macrostructured functionalities.[6] A number of case studies will be presented to showcase the potential of these concepts in a broad range of fields, including antimicrobials and photochromic devices.

- [1] Chee Kai, C.; Kah Fai, L.; Chu Sing, L., *Rapid prototyping: Principles and applications,* third edition, **2010**.
- [2] a) Symes, M.D.; Kitson, P.J.; Yan, J.; Richmond, C.J.; Cooper, G.J.T.; Bowman, R.W.; Vilbrandt, T.; Cronin, L., *Nature Chemistry*, **2012**, *4*, 349-354. b) Murphy, S.V.; Atala, A., *Nature Biotechnology*, **2014**, *32*, 773-785. c) Okafor, O.; Weilhard, A.; Fernandes, J.A.; Karjalainen, E.; Goodridge, R.; Sans, V., *React. Chem. Eng.*, **2017**, *2*, 129-36.
- [3] Qian, W.; Texter, J.; Yan, F., Chem. Soc. Rev., 2017, 46, 1124-1159.
- [4] Sans, V.; Karbass, N.; Burguete, M.I.; Compañ, V.; García-Verdugo, E.; Luis, S.V.; Pawlak, M., Chem. Eur. J., 2011, 17, 1894-1906.
- [5] a) Schultz, A.R.; Lambert, P.M.; Chartrain, N.A.; Ruohoniemi, D.M.; Zhang, Z.; Jangu, C.; Zhang, M.; Williams, C.B.; Long, T.E., ACS Macro Letters, 2014, 3, 1205-1209. b) Karjalainen et al., ACS Sus. Chem. Eng., 2018, DOI: 10.1021/acssuschemeng.7b04279.
- [6] Wales et al., 2018, under review.

Choline Chloride and Tartaric Acid NADES: An Efficient Solvent for the Extraction of Phenolic and Carotenoid Compounds

<u>Spyridon Koutsoukos</u>¹, Thalia Tsiaka², Andromachi Tzani¹, Panagiotis Zoumpoulakis^{2,*}, Anastasia Detsi^{1,*}

¹Laboratory of Organic Chemistry, Department of Chemical Sciences, School of Chemical Engineering, National Technical University of Athens, Heroon Polytechniou 9, Zografou Campus, 15780, Athens, Greece.

²Laboratory of Molecular Analysis, Institute of Biology, Medicinal Chemistry & Biotechnology, National Hellenic Research Foundation, 48 Vas. Constantinou Avenue, 11635 Athens, Greece *Email: pzoump@eie.gr
*E-mail: adetsi@chemeng.ntua.gr

Ionic Liquids (ILs) and Natural Deep Eutectic Solvents (NADESs) are considered to be new, safer solvents in green chemistry that can be widely used in different fields of applications.^{1, 2} In this work we present a greener approach for the extraction of biologically active compounds from Greek propolis, shrimp head and body, egg yolk and apricot byproducts using 2:1 Choline Chloride: Tartaric Acid (ChCl:TA) NADES.³ The experiments were conducted using high energy techniques, Microwave Assisted Extraction (MAE) and Ultrasound Assisted Extraction (UAE). The optimum experimental conditions for the extraction of phenolic compounds from propolis⁴ were investigated by performing Design of Experiment (DoE) statistical analysis, whereas the conditions for the extraction of carotenoids from shrimp head and body, egg yolk and apricot byproducts were selected based on previous results of our team's ongoing research.^{5,6}

ChCl:TA was synthesized and characterized using ¹H and NOESY NMR, TGA and DSC spectroscopic techniques. The experiments confirmed that ChCl:TA could be an efficient alternative to traditional solvents for the extraction of compounds with different polarities, depending on the co-solvent used in the process. In case of phenolics, water was used as co-solvent, while for carotenoids extraction ChCl:TA was mixed with small amounts of methanol. The antioxidant activity and total phenolic content of propolis extracts were investigated using DPPH and Folin-Ciocalteu methods respectively. Carotenoids extracts were characterized on their total carotenoid content by measuring the maximum absorbance, determined of the Vis region of the spectrum for each carotenoid standard. Total carotenoid content of apricots, egg yolk and shrimp extracts was determined by the spectrophotometric calibration curve of absorbance versus carotenoid concentration of b-carotene (455 nm), lutein (447 nm) and astaxanthin (478 nm), respectively.

- [1] Tzani, A.; Koutsoukos, S.; Koukouzelis, D.; Detsi, A., J. Mol. Liq., 2017, 243, 212-218.
- [2] Tzani, A.; Douka, A.; Papadopoulos, A.; Pavlatou, E.A.; Voutsas, E.;. Detsi, A., *ACS Sustain Chem Eng*, **2013**, *1*, 1180-1185.
- [3] Paiva, A.; Craveiro, R.; Aroso, I.; Martins, M.; Reis, R.L.; Duarte, A.R.C., *ACS Sustain Chemi Eng*, **2014**, *2*, 1063-1071.
- [4] Huang, S.; Zhang, C.-P.; Wang, K.; Li, G.Q.; Hu, F.-L., Molecules, 2014, 19, 19610-19632.
- [5] Tsiaka, T.; Sinanoglou, V.J.; Zoumpoulakis, P., in *Ingredients Extraction by Physicochemical Methods in Food*, Elsevier, **2017**, 307-365.
- [6] Tsiaka, T.; Zoumpoulakis, P.; Sinanoglou, V.J.; Makris, C.; Heropoulos, G.A.; Calokerinos, A.C., *Anal. Chim. Acta*, **2015**, 877, 100-110.
Enantioselective separation of chiral compounds using aqueous biphasic systems

Mariam Kholany¹, Francisca A. e Silva¹, Tânia E. Sintra¹, Sónia P.M. Ventura¹, João A. P. Coutinho¹

¹ CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal E-mail: mariamkholany@ua.pt

Conventionally, only one of the enantiomers is responsible for the intended effect of a drug, whilst the other may lead to a less potent or even undesired response. Regulatory entities are very strict regarding the commercialization of racemic drugs. Thus, the pharmaceutical industry has been facing challenges related to the creation of methods to produce optically active drugs. Although it is the most powerful approach to obtain enantiopure compounds, asymmetric synthesis generally requires highly enantiopure raw materials and/or highly stereospecific catalysts that make it expensive and limited by the number of reactions needed to obtain highly enantiopure compounds. Racemic resolution is a propitious strategy to follow due to its simplicity, enhanced flexibility, good reliability and lower costs. This approach is commonly achieved by chromatography and crystallization, yet other methods, such as enantioselective liquid-liquid extraction (LLE) can provide a better balance between costs, operational versatility and scale-up opportunities.

Aqueous biphasic systems (ABS) are a specific type of LLE system that rise as a "greener" option with enhanced biocompatibility and tunability, in particular if ionic liquids are used.[1] This work proposes the development of a versatile enantioseparation platform for the chiral resolution of racemic mandelic acid. Under this scenario, ABS using chiral ionic liquids (CILs) as chiral selectors that can simultaneously act as solvents is proposed resorting to the CIL-ABS. The results obtained show that by playing with CILs structure and the process conditions of the purification process it is possible to attain good enantioselective separations.

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. The authors are grateful for the financial support of the Portuguese Foundation for Science and Technology (FCT) for the doctoral grant of SFRH/BD/94901/2013 of F.A. e Silva, IF/00402/2015 of S.P.M. Ventura and for the project PAC – Programa de atividades Conjuntas ref: SAICTPAC/0040/2015.

References:

[1] Freire, M.G.; Cláudio, A.F.M.; Araújo, J.M.M.; Coutinho, J.A.P.; Marrucho, I.M.; Canongia Lopes, J.N.; Rebelo, L.P.N. *Chemical Society Reviews*, **2012**, *41*, 4966-4995.

Gas separation by ionic liquid filters

Rasmus Fehrmann¹, Susanne Mossin¹, Peter W. Jakobsen¹, Anders Riisager¹, Leonard Schill¹

¹Center for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, DK-2800 Kgs.-Lyngby, Denmark E-mail: rf@kemi.dtu.dk

Atmospheric pollution and climate changes are now recognized to be severely influenced by the emission of acidic gasses such as NO_X, SO_X and CO_X from the combustion of fossil fuels in, e.g. power plants, cement factories and ships. Accordingly, these gases have to be effectively removed from flue gasses. Presently this is mainly achieved by relatively energy intensive and resource demanding technologies via selective catalytic reduction (SCR) of NO_X with ammonia, SO₂ wet-scrubbing by lime obtaining gypsum and CO₂ wet-scrubbing with organic amines. The latter leads to particular concern about, e.g. intensive energy requirements for desorption, corrosion of steel pipes and pumps, CO₂ absorption capacity and thermal decomposition of the amine. The structures of ionic liquids (ILs) are well-ordered even in the liquid state with regular cavities which can host selected solute species depending on the IL ion composition or contain reversible binding functionalities. This makes the materials promising for selective, reversible absorption of gaseous pollutants in, e.g. industrial off-gases [1,2]. In this work we demonstrate how more environmental friendly ILs as amino acid based ones can be applied as selective, high-capacity absorbents of CO₂, exemplified by a tetraalkylphosphonium prolinate IL. In the context of CO_2 removal, ILs are considered environmentally friendly because they are not emitted to the environment due to their negligible vapor pressure. In addition, an imidazolium nitrate IL is also investigated regarding absorption of NO. Only few publications deal with possible interferences of other flue gas components with the IL absorbers. Thus we here also investigate the interaction of the selected ionic liquids with SO₂, CO₂, NO and air. Furthermore, different porous, high surface area carriers like mesoporous silica have been applied as supports for the ionic liquids to obtain Supported Ionic Liquid-Phase (SILP) absorber materials. These materials benefit from low mass transport resistance of the often very viscous ILs by the distribution of the liquid as a thin film (or small droplets) on the surface of the highly porous carrier materials enabling fast absorption/desorption rates of the particular gas to be removed by the SILP absorber [3]. These powderous SILP materials may also be extruded with appropriate binders to multichannel rotating filters that might be installed in the flue gas duct of the industrial unit or used as filters for sweetening of bio- and natural gas by reversible selective gas absorption. The gaseous pollutant is then desorbed and obtained in concentrated form for further processing on site to e.g. commercial grade mineral acids or stored in underground reservoirs.

References:

[1] Huang, J.; Riisager, A.; Wasserscheid P.; Fehrmann, R., Chem. Commun., 2006, 38, 4027-4029.

[2]Wu, W.; Han, B.; Gao, H.; Liu, Z.; Jiang, T.; Huang, J., Angew. Chem. Int Ed., 2004, 43, 2415-2417.

[3]Kolding, H.; Thomassen, P.; Mossin, S.; Kegnæs, S.; Riisager, A.; Rogez, J.; Mikaelian, G.; Fehrmann, F., *ECS. Trans.*, **2014**, *4*, 97-108.

How to predict physicochemical properties of ionic liquids from MD simulations

Christian Schröder

¹University of Vienna, Faculty of Chemistry, Institute of Computational Biological Chemistry, Währingerstr. 17, A- 1090 Vienna (Austria) E-mail: christian.schroeder@univie.ac.at

The plethora of cation/anion combinations allows for variation of the physicochemical properties over a very broad range and can be further fine-tuned by side chain modifications of both, cations and anions. However, many physicochemical properties of ionic liquids are correlated to their molecular volume [1].



Figure 1. Physico-chemical properties of ionic liquids and their correlations to the molecular volume.

Using a Designed Regression approach we were able to compute meaningful statistical values for the atomic volumes and polarizabilities of important chemical elements in ionic liquids [2]. Based on these values, molecular volumes can be predicted for new compounds or the effect of a side chain modification on various properties depicted in Fig. 1 can be studied. However, the polarizabilities also enter the polarizable force field to determine density, diffusion coefficients, conductivity or surface tension. From the resulting trajectories of the polarizable MD simulations dielectric, THz and IR spectra can be computed and compared to experimental results. Moreover, as contributions from cations and anions or different types of motion can be evaluated separately, the interpretation of the experimental spectra can be improved this way.

- [1]"General review of ionic liquids and their properties", C. Schröder in "Analytical applications of ionic liquids" ed. by M. Koel, World scientific, 2016.
- [2]Bernardes, C.E.S.; Shimizu, K.; Canongia Lopes, J. S.; Marquetand, P.; Heid, E.; Steinhauser, O.; Schröder, C., *Phys. Chem. Chem. Phys.*, **2016**, *18*, 1665-1670.

Ionic liquids and IoNanofluids as green media in sustainable heat transfer processes

Marzena Dzida, Małgorzata Musiał, Karolina Bałuszyńska, Michał Zorębski, Marcin Libera, Edward Zorębski

¹University of Silesia in Katowice, Institute of Chemistry, Szkolna 9,40-006 Katowice E-mail: marzena.dzida@us.edu.pl

One of the possible research directions for developing modern energy sector is searching for innovative working fluids with exceptional thermophysical properties, which leads to reduce energy consumption and the costs of the system operation. Ionic liquids (ILs) are viewed as green media for many sustainable engineering applications [1]. Pure ILs as well as IoNanofluids (*i.e.* IL + nanoparticles) have thermophysical properties that may significantly improve the heat transfer and heat storage cycles [2,3].

The working fluids should have high heat capacity and thermal conductivity, relatively low viscosity and density, high chemical and thermal stability in a broad range of temperature and low toxicity. We describe the use of imidazolium- and pyrrolidinium-based ILs and the IoNanofluids, consist of alumina oxide nanoparticles dispersed in 1-etyl-3-methylimidazolium ethyl sulfate or 1,3-diethylimidazolium ethyl sulphate as a heat transfer fluids in a new generation of heating or cooling systems. For pure ILs, the temperature and pressure dependence of the density, the isobaric and isochoric heat capacities, the energy storage density, the isentropic and isothermal compressibility coefficients and the isobaric thermal expansion coefficient were determined by the acoustic method [4], as well as the thermal conductivity, viscosity and the Prandtl number as a function of temperature were investigated. For IoNanofluids, the density, viscosity, isobaric heat capacity were measured. The real pictures of IoNanofluids were determined by the unique cryo-TEM imaging. Our research revealed that studied systems exhibit higher heat capacity and energy storage density in comparison with commercial heat transfer fluids. Long-term stability, acceptable density and viscosity cause that investigated IoNanofluids are promising candidates as heat transfer fluids.

- [1] Musiał, M.; Malarz, K.; Mrozek-Wilczkiewicz, A.; Musiol, R.; Zorębski, E.; Dzida, M., ACS Sustainable Chem. Eng., 2017, 5 11024–11033.
- [2] Nieto de Castro, C.A.; Sohel Murshed, S.M.; Lourenço, M.J.V.; Santos, F.J.V.; Matos Lopes, M.L.; França, J.M.P., *Ionanofluids new heat transfer fluids for green process development*, in: A. Mohammad, Inamuddin (Eds.), Chapter 8 in Green Solvents I: *Properties and Applications in Chemistry*, Springer Science+Business Media Dordrecht, 2012.
- [3] Dzida, M.; Bałuszyńska, K.; Zorębski, M.; Kisielewska, A.; Mackiewicz, E.; Piwoński, I.; Domańska- Żelazna, U., *IoNanofluids as working media for new generation solar collectors*, 21st ECTP, 3- 8.09.2017, Graz, Austria.
- [4] Dzida, M.; Zorębski, E.; Zorębski, M.; Żarska, M.; Geppert-Rybczyńska, M.; Chorążewski M., Jacquemin, J.; Cibulka, I., *Chem. Rev.*, **2017**, *117*, 3883–3929.

Ionic liquids as phase forming components of aqueous multiphase systems

<u>Helena Passos</u>¹, Sara H. Costa¹, Ana M. Fernandes², Mara G. Freire¹, Robin D. Rogers^{3,4}, João A. P. Coutinho¹

 ¹CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
 ²QOPNA Unit, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
 ³Department of Chemistry, Otto Maass Chemistry Building, McGill University, 801 Sherbrooke St. West, Montreal, QC, Canada H3A 0B8.
 ⁴525 Solutions, Inc., P.O. Box 2206, Tuscaloosa, AL 35403 E-mail: hpassos@ua.pt

Aqueous multiphasic systems (MuPSs) were introduced by Mace et al.[1] in 2012, by the combination of a large number of polymers and surfactants mixtures in aqueous solutions. MuPSs share all benign characteristics of the well-studied aqueous biphasic systems (ABS); yet, selective and improved separations of high-value compounds are better achieved in presence of more aqueous phases.[2] Furthermore, to the best of our knowledge, MuPSs formed by ionic liquids (ILs) and their possible applications were not explored up to date.

In this work, novel MuPSs formed by quaternary mixtures composed of cholinium-based ILs, polymers, inorganic salts and water were investigated.[3] The influence of several ILs was studied, demonstrating that a triple salting-out is a required phenomenon to prepare MuPS. The respective phase diagrams which define the monophasic, biphasic and triphasic regions, and the "tie-surfaces", were determined, followed by the evaluation of the effect of temperature. Finally, it is shown the remarkable ability of IL-based MuPSs to selectively separate a complex mixture of dyes.

This work was developed in the scope of the project CICECO-Aveiro Institute of Materials (Ref. FCT UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement. The authors also acknowledge FCT for the doctoral grant SRH/BD/85248/2012 of H. Passos. M. G. Freire acknowledges the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° 337753. This research was undertaken, in part, thanks to funding from the Canada Excellence Research Chairs Program.

- [1]Mace, C.R.; Akbulut, O.; Kumar, A.A.; Shapiro, N.D.; Derda, R.; Patton, M.R.; Whitesides, G.M., J. Am. Chem. Soc., 2012, 134, 9094–9097.
- [2] Liang, Y.; Xu, S.; Shang Y.; Peng, C.; Liu, H., Colloid. Surface. A, 2014, 454, 152–158;
- [3]Passos, H.; Costa, S.H.; Fernandes, A.M.; Freire, M.G.; Rogers, R.D.; Coutinho, J.A.P., *Angew. Chem. Int. Ed.*, **2017**, *56*, 15058–15062.

Valorization of industrial tailings using deep-eutectic solvents

<u>Nerea Rodriguez Rodriguez</u>^{1,2}, Lieven Machiels¹, Jeroen Spooren³, Peter Tom Jones⁴, Koen Binnemans¹

¹KU Leuven, Department of Chemistry. Celestijnenlaan 200F – box 2404, 3001 Leuven, Belgium. ²SIM vzw, Technologiepark 935,BE-9052 Zwijnaarde, Belgium.

³KU Leuven, Department of Materials Engineering. Kasteelpark Arenberg 44 – box 2450, 3001 Leuven, Belgium.

⁴VITO – Flemish Institute for Technological Research, Boeretang 200, 2400, Mol, Belgium. E-mail: Nerea.rodriguezrodriguez@kuleuven.be

The primary mining and metal processing industry has been, and still is, landfilling and/or stockpiling vast quantities of metal-containing tailings. This waste stream is considered as one of the largest in Europe. The valorization of fresh and old tailings will solve long-term environmental liabilities, improve the efficiency of actual metal processing processes, and overcome the European dependency on metal imports.

A new solvometallurgical approach for the valorization of industrial residues based on deepeutectic solvents (DESs) is being developed [1]. In this work, the residue from the zinc smelting process was selected. This residue consists mainly in goethite, jarosite, gypsum, franklinite, and magnetite. The zinc is predominantly associated to iron phases in form of spinel [2]. Ideally, the valorization strategy for this residue is to obtain: (1) a zinc-rich stream (preferably with most of the copper and lead), to be recycled again to the process, (2) a stream rich in hazardous component, e.g. arsenic, and (3) a residual fraction containing most of the iron.

Firstly, a variety of DESs were tested as potential leaching agents; the effect of the hydrogen bond donor and hydrogen bond acceptor on the leaching efficiency were considered. The best results were obtained for a DES based on levulinic acid and choline chloride in a 2:1 molar ratio (LevA:ChCl(2:1)). This DES leached high amounts of zinc, while codissolution of iron was limited. The leaching process was optimized by analyzing the effect of different parameters on the leaching efficiency: water content of the DES, temperature, liquid-to-solid ratio, particle size, and leaching time. The water content of the DES was found to be the most crucial parameter affecting the leaching efficiency and selectivity. At optimized conditions, leaching efficiencies were up to 50% for zinc, with less than 5% codissolution of iron. The chemical stability of the DES was also studied.

The Strategic Initiative Materials in Flanders (SIM) is acknowledged for the financial support (Grant nr. HBC.2016.0456); Nyrstar for providing the residue.

References:

[1] Binnemans, K.; Jones, P.T., Journal of Sustainable Metallurgy, 2017, 3, 570–600.

[2]Goodwin, F. E., Zinc and Zinc Alloys, Kirk-Othmer Encyclopedia of Chemical Technology. 1– 47.

Hydrotropic solubilization of ibuprofen in aqueous solutions of ionic liquids

<u>Tânia E. Sintra</u>¹, Karina Shimizu^{2, 3}, Sónia P.M. Ventura¹, Seishi Shimizu⁴, José N. Canongia Lopes^{2, 3}, João A.P. Coutinho¹

 ¹CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
 ²Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal
 ³Instituto de Tecnologia Química e Biológica, UNL, AV. República Ap. 127, 2780-901 Oeiras, Portugal
 ⁴York Structural Biology Laboratory, Department of Chemistry, University of York, Heslington, York Y010 5DD, UK

E-mail: tania.sintra@ua.pt

The therapeutic effectiveness of a drug can be severely limited by its aqueous solubility. Recently, some ionic liquids (ILs) were shown to display a strong ability to enhance the solubility of biomolecules through hydrotropy [1]. In this communication, the capability of aqueous IL solutions to solubilize ibuprofen was demonstrated and a mechanism of solubility enhancement was proposed. How the chemical structures and concentration of ILs affect the solubility of ibuprofen was evaluated and compared with the performance of conventional hydrotropes. The exceptional capacity of ILs to enhance the solubility of this hydrophobic drug has been demonstrated [2]. $[C_4C_1im][SCN]$ and $[C_4C_1im][N(CN)_2]$ seem to be the most promising ILs for ibuprofen solubilisation, for which an increase in the solubility of 60- and 120-fold was observed with IL concentrations of *circa* 1 mol·kg⁻¹, respectively. Furthermore, contrary to previous observations, both anion and cation have been shown to contribute to the hydrotropic mechanism in a synergistic manner. [1]. Dynamic light scattering and molecular dynamic simulations were employed in combination to investigate the mechanism of the IL-mediated drug solubility, whose results indicate that hydrotropic dissolution is driven by the structure of aqueous IL solutions and its role in the formation of IL-drug aggregates [2].

This work was developed within the scope of the project CICECO – Aveiro Institute of Materials POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate, co-financed by FEDER under the PT2020 Partnership Agreement. The authors are grateful for financial support through FCT for the postdoctoral grant SFRH/BPD/94291/2013 of Karina Shimizu, project UID/QUI/00100/2013 and for the IF contract of S.P.M. Ventura reference IF/00402/2015.

- Cláudio, A.F.; Neves, M.; Shimizu, K; Canongia Lopes, J.N.; Freire, M.G.; Coutinho, J.A.P. Green Chemistry, 2015, 17, 3948–3963.
- [2] Sintra, T.E.; Shimizu, K.; Ventura, S.P.M.; Shimizu, S.; Canongia Lopes, J.N.; Coutinho, J.A.P. *Physical Chemistry Chemical Physics*, **2018**, *20*, 2094 2103.

Aqueous biphasic systems on the multistep purification of cytochrome c PEGylated forms

<u>Sónia P.M. Ventura</u>¹, João H. P. M. Santos^{1,2}, Gustavo Carretero³, João A. P. Coutinho¹, Carlota O. Rangel-Yagui²

 ¹CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal
 ² Department of Biochemical and Pharmaceutical Technology, São Paulo University, Av. Prof. Lineu Prestes n 580 Bloco 16, 05508-000 São Paulo, SP Brazil
 ³ Department of Biochemistry, Chemistry Institute, São Paulo University, São Paulo, SP Brazil

E-mail: spventura@ua.pt

The physicochemical properties of proteins have been improved by chemical PEGylation. However, PEGylation reactions lead to a heterogeneous mixture of PEGylated conjugates and unreacted protein, which is a challenge for the design of an efficient downstream process. The purification of PEGylated proteins normally addresses (i) the separation of PEGylated conjugates from the unreacted protein and (ii) the fractionation of the PEGylated conjugates considering their degree of PEGylation.

In this work, a process was proposed to address not only the efficient separation of each of the protein forms but also the recycling of the unreacted protein purified and the ABS phases, subsequently used in a new step of PEGylation with success. Firstly, the partition behavior of cytochrome c and their PEGylated conjugates (Cyt-c-PEG-4 and Cyt-c-PEG-8) on polyethylene-glycol (PEG) + potassium phosphate buffer (pH = 7) aqueous biphasic systems (ABS) was performed. The main results showed that PEGs with intermediate molecular weights allowed the separation of the PEGylated conjugates from the unreacted protein in a single step. It was further shown the efficient separation of different PEGylated forms using ABS, in this case, based on PEGs with high molecular weight. The protein stability after purification was also studied using circular dichroism. A downstream process to separate Cyt-c, Cyt-c-PEG-4 and Cyt-c-PEG-8 with high purities (96.5% Cyt-c, 85.8% Cyt-c-PEG-4, and 99.0% Cyt-cPEG-8) was developed [1].

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. The authors are grateful for the financial support of São Paulo Research Foundation – FAPESP (grant # 2016/22065-5), The National Council for Scientific and Technological Development (CNPq) and the Portuguese Foundation for Science and Technology (FCT) for the doctoral grant of SFRH/BD/102915/2014 of João H. P. M. Santos and IF/00402/2015 of S.P.M. Ventura.

References:

[1] Santos, J.H.P.M.; Carretero, G.; Coutinho, J.A.P.; Rangel-Yagui, C.O.; Ventura, S.P.M. Green Chemistry, 2017, 19, 5800-5808.

Synthesis, physicochemical properties and biological activity of double salt herbicidal ionic liquids derived from synthetic auxins

<u>Tomasz Rzemieniecki</u>¹, Michał Niemczak¹, Agnieszka Biedziak¹, Katarzyna Marcinkowska², Juliusz Pernak¹

¹Department of Chemical Technology, Poznan University of Technology, ul. Berdychowo 4, 60-965 Poznan, Poland ² Institute of Plant Protection—National Research Institute, ul. W. Węgorka 20, 60-318 Poznan, Poland E-mail: tomasz.m.rzemieniecki@doctorate.put.poznan.pl

Among numerous factors, the growth of weeds in the agricultural fields is considered as the most harmful and results in major decrease in yield and quality of crops [1]. The unwanted vegetation is usually neutralized by selective herbicides from the group of growth regulators (*e.g.* 4-chloro-2-methylphenoxyacetic acid – MCPA or 3,6-dichloro-2-methoxybenzoic acid (dicamba)), however they are used in large quantities, which may cause their permeation to rivers and air [2]. These issues have been solved by introducing herbicidal ionic liquids (HILs), a form of herbicides, which due to enhanced surface activity do not require any addition of the adjuvants and are effective in extremely low doses of active ingredient [3]. This concept has been improved by merging two HILs into a double salt in order to cause synergistic interactions between both herbicidally active anions (MCPA and dicamba) and reduce the effective dose even further. Since the prolonged use of a single anti-weed agent usually causes a rapid enhancement of the herbicidal resistance, the obtained double salt herbicidal ionic liquids (DSHILs) preserve herbicidal activity of both anions and may be a perfect solution for reducing this deleterious phenomenon.



Figure 1. Synthetic scheme for DSHILs

This work was supported by PRELUDIUM 6: 2013/11/N/ST5/01626 (NCN, Poland).

- [1] Oerke, E.C. J. Agric. Sci., 2006, 144, 31–43.
- [2] Glozier, N.E.; Struger, J.; Cessna, A.J.; Gledhill, M.; Rondeau, M.; Ernst, W.R.; Sekela, M. A.; Cagampan, S.J.; Sverko, E.; Murphy, C.; Murray, J.L.; Donald, D.B. *Environ. Sci. Pollut. Res.*, 2012, 19, 821–834.
- [3] Pernak, J.; Syguda, A.; Janiszewska, D.; Materna, K.; Praczyk, T. *Tetrahedron*, 2011, 67, 4838– 4844.

Trichloride ionic liquids for oxidative dissolution of SmCo magnets

Xiaohua Li, Koen Binnemans

KU Leuven, Department of Chemistry, Celestijnenlaan 200F, bus 2404, B-3001 Heverlee, Belgium E-mail: xiaohua.li@kuleuven.be

Dissolution of metals and alloys is an essential step for the recycling of metals from end-oflife products. Traditional procedures for metal dissolution are pyrometallurgical and hydrometallurgical processes, which often lead to large consumption of chemicals or energy. An alternative way is dissolving metals and alloys in organic solvents by first oxidising them with halogens to metal halides. However, due to their high reactivity, halogens can attack the organic solvents and form halogenated by-products.

Ionic liquids (ILs) can store halogens by forming polyhalide, such as $[Br_3]^-$, $[I_3]^-$ [ClBr₂]⁻, $[BrCl_2]^-$ and $[BrI_2]^-$ [1]. We have synthesised 10 stable ionic liquids with the trichloride anion ([Cl₃]⁻), combining them with various cations. A total of 8 metals and 2 alloys could be completely dissolved in these trichloride ILs at room temperature, (Fe, Cu, Zn, Ga, Au, In, Ge, Sb, GaAs and InAs), while some metals such as tantalum and platinum did not dissolve. Thus, processes for selectively leaching of metals can be developed using trichloride ILs [2].

We have successfully dissolved samarium–cobalt (SmCo) magnet powders (<30 mesh) in the ionic liquid trihexyltetradecylphosphonium trichloride ($[P_{666,14}][Cl_3]$) with a solid-to-liquid mass ratio of 1:48 at room temperature. The dissolution kinetics are shown in Figure 1. After mixing for 24 h, about 67% of the total mass of Sm, Co and Cu were dissolved and Fe was nearly all dissolved. In our previous study [2] it was found that Sm pieces could not be dissolved. This is most likely due to the presence of a passivating layer on the metal surface, preventing it from being attacked by the trichloride IL. Further study on trichloride ionic liquids is ongoing in our lab.



Figure 1. Dissolution kinetics of SmCo magnet powders (<30 mesh) in [P_{666,14}][Cl₃] at room temperature

The research leading to these results received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Programme: Grant Agreement 694078—Solvometallurgy for critical metals (SOLCRIMET).

- [1] Haller, H.; Riedel, S. Z Anorg Allg Chem., 2014, 640, 1281-1291.
- [2] Li, X.; Van den Bossche, A.; Vander Hoogerstraete, T.; Binnemans, K. Chem Commun. 2018, 54, 475-478.

The Fluorination Effect on Alcohol-IL anion H-Bond Interaction

Inês C. M. Vaz, Margarida Bastos, Luís M. N. B. F. Santos CIQUP, Department of Chemistry and Biochemistry, University of Porto, Porto, Portugal E-mail: inescvaz@gmail.com

The complete understanding of Ionic Liquids' solvation properties enables the sustainable design of optimum solvents for specific application. Within this scope, contributions of our group [1,2] demonstrated that the nanostructuration of Ionic Liquids is reflected in the solvation and mixing properties. Furthermore, in a recent work [3] we explored the effect of the nature of the anion and cation in the solvation of alcohols in ILs. The results showed that the enthalpies of solvation are strongly correlated with the anion hydrogen-bond basicity. The interpretation of this results is in perfect agreement with the existence of a hydrogen-bond interaction between the hydroxyl group and the IL anion.

This work aims at enlighten the effect of the alcohol acidity in the solvation in ILs. For that, the effect of the fluorination in the solvation of tert-butyl alcohols in the $[C_4C_1im][NTf_2]$ ionic liquid was studied. The enthalpy of solution at infinite dilution, of tert-butyl alcohol with different degrees of fluorination was obtained by ITC and the enthalpies of solvation were derived thereafter.



Figure 1. Schematic representation of the fluorination effect in the solvation of tert-butyl-alcohol in ILs.

The results show (as presented schematically in fig. 1) an increase of the alcohol-IL interaction with the increase in alcohol acidity, strongly corroborating the existence of a hydrogen-bonding interaction between the alcohols and the IL anions [3].

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and to FEDER for the financial support to Centro de Investigação em Química, University of Porto (CIQUP) through the project Pest-C/QUI/UI0081/2013 and the SAM project Norte-01-0145-FEDER-000028. Inês C. M. Vaz acknowledges the financial support from Fundação para a Ciência e Tecnologia FCT) for her PhD Research Grant PD/BD/114575/2016.

- [1]Vaz, I.C.M.; Bhattacharjee, A.; Rocha, M.A.A.; Coutinho, J.A.P.; Bastos, M.; Santos, L.M.N.B.F., *Phys. Chem. Chem. Phys.*, **2016**, *18*, 19267-19275.
- [2]Kurnia, K.A.; Neves, C.M.S.S.; Freire, M.G.; Santos, L.M.N.B.F.; Coutinho, J.A.P.; J. Mol. Liq., 2015, 210, 264-271.
- [3]Vaz, I.C.M.; Bastos, M.; Bernardes, C.E.S.; Canongia Lopes, J.N.; Santos, L.M.N.B.F.; *Phys. Chem. Chem. Phys.*, **2018**, *20*, 2536-2548.

Ionic-liquid-based acidic aqueous biphasic systems: a promising alternative in critical metals extraction

<u>Helena Passos</u>¹, Nicolas Schaeffer¹, Matthieu Gras², Vijetha Mogilireddy², João P. Leal³, Germán Pérez-Sánchez¹, José R. B. Gomes¹, Isabelle Billard², Nicolas Papaiconomou², João A. P. Coutinho¹

¹CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal. ²LEPMI - Universite Grenoble-Alpes, F-38000 Grenoble, France.

³C2TN, DECN, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal. E-mail: hpassos@ua.pt

For over a decade, ionic liquids (ILs) have been considered as promising solvent alternatives to volatile organic compounds (VOC). In the field of metal ions extraction, ILs are currently used at a laboratory scale as extracting media for various metals with excellent results. Nevertheless, industrial application of such ILs is limited by (i) the range of available hydrophobic ILs, most being based on fluorinated anions such as bis(trifluoromethanesulfonyl)imide ([NTf₂]⁻), or on ILs incorporating long alkyl chains, (ii) the viscosity of ILs and (iii) production costs significantly higher than those of classical extracting systems currently in operation.

IL-based acidic aqueous biphasic systems (AcABS) represent a promising alternative to solvent extraction process for the recovery of critical metals in which the substitution of the inorganic salt by an acid allows for the 'one pot' approach to the leaching and separation of metals.[1] However, a more fundamental understanding of AcABS formation remains wanting. In this work, the formation mechanisms of AcABS are elucidated through a comparison with traditional ABS. A large screening of AcABS formation with a wide range of ILs identifies the charge shielding of the cation as the primary structural driver for the applicability of an IL in AcABS. Through a systematic study of tributyltetradecylphosphonium chloride ([P44414]Cl) with various chloride salts and acids, we observed the first significant deviations to the cationic Hofmeister series reported for IL-based ABS. Furthermore, the weaker than expected salting-out ability of H_3O^+ compared to Na⁺ is attributed to the greater interaction of H_3O_+ with the [P44414]⁺ micelle surface. Finally, the remarkable thermomorphic properties of [P44414]Cl based systems are investigated with a significant increase in the biphasic region induced by the increase in the temperature from 298 K to 323 K. These finding allows for the extension of AcABS to new acidic systems and highlights their versatility and tuneability.

This work was part of BATRE-ARES project (ERA-MIN/0001/2015) funded by ADEME and FCT. M. Gras would like to acknowledge labex CEMAM and EIT InnoEnergy H2020 for financial support. This work was partly developed in the scope of the project CICECO - Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013)

References:

[1] Papaiconomou, N.; Schaeffer, N.; Chainet, E.; Tedjar, F.; Coutinho, J.A.P.; Billard, I., *Angew. Chem. Int. Ed.*, **2018**, *57*,1563–1566.

Influence of the anion on ionic liquids mixtures properties: A molecular dynamics study

<u>Iuliia V. Voroshylova</u>^{1,2}, Elisabete S. C. Ferreira^{1,2}, Michal Malček³, Renata Costa², Carlos M. Pereira², M. Natália D. S. Cordeiro¹

 ^{1/2}LAQV@REQUIMTE/CIQUP, Faculdade de Ciências, Universidade do Porto, Departamento de Química e Bioquímica, Rua do Campo Alegre, 4169-007 Porto, Portugal
 ³Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia E-mail: voroshylova.iuliia@fc.up.pt

Ionic liquids (ILs) are promising materials with a number of possible applications. Nevertheless, ILs present some drawbacks, such as relatively high viscosity and low conductivity. Recently, a way of overcoming these drawbacks by mixing different ILs has been proposed [1]. Experimental studies show a pronounced effect of ILs mixing on physical and chemical properties, first of all, on capacitance, in ILs mixtures with small additions of a different anion [2].

In this study we employed molecular dynamics (MD) simulations and quantum mechanical calculations to access on molecular level the ILs mixtures structure and interactions and thus to explain the deviation from expected behavior in properties of these mixtures. For this purpose, we studied three binary mixtures, $[C_4mim][PF_6] + [C_4mim][NTf_2]$, $[C_4mim][PF_6] + [C_4mim][FAP]$, $[C_4mim][FAP] + [C_4mim][NTf_2]$, in wide concentration range at 303 K. The results were analyzed in terms of pair radial distribution functions (RDFs), coordination numbers and self-diffusion coefficients, derived from the simulation trajectories. Hydrogen bonds in the studied systems are examined within the QTAIM framework and compared to the MD simulation results. The influence of the structural properties of ILs mixtures on their dynamic properties is discussed.

It was found that the addition of [FAP]⁻-anion to mixture enhances the non-polar domains segregation and weakens the hydrogen-bond network. In significantly nano-aggregated mixtures the total diffusion slows down notably due to hindering and hydrogen-bond-like interactions formation. Our results show that the difference in anion size, shape and nature is the main reason for nano-segregation and non-ideal behavior of ILs mixtures.



tris(perfluoroethyl)trifluorophosphate [FAP]

Figure 1. Structural formulas of the ions of the studied ionic liquids. This work received financial support from FCT through national funds, and co-financed by the EU (FEDER funds) under PT2020, through projects UID/QUI/50006/2013 and POCI/01/0145/FEDER/007265. IV, ESCF and RC acknowledge FCT for the grants SFRH/BPD/97918/2013, SFRH/BPD/90343/2012 and SFRH/BPD/89752/2012. MM is grateful to the APVV (contract No. APVV-15-0079) and VEGA (contract No. 1/0598/16).

References:

[1] Cha, S.; Kim, D. Phys. Chem. Chem. Phys., 2015, 17, 29786–29792.

[2] Costa, R.; Voroshylova, I.V.; Cordeiro, M.N.D.S.; Pereira, C.M.; Silva, A.F.; *Electrochim. Acta*, **2017**, *261*, 214-220.

Sustainable hydrophobic eutectic formulations for the extraction and deposition of metals

Nicolas Schaeffer¹, Monia Martins¹⁻³, Matthieu Gras⁴, Simão P. Pinho,^{2,3} João A.P. Coutinho¹

¹ CICECO, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

²Associate Laboratory LSRE-LCM, Department of Chemical and Biological Technology, Polytechnic Institute of Bragança, 5300-253 Bragança, Portugal

³Centro de Investigação de Montanha CIMO, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

⁴ LEPMI - Universite Grenoble-Alpes, F-38000 Grenoble, France E-mail: nicolas.schaeffer@ua.pt

Poor metal recovery efficiency from wastes such as waste electrical and electronic equipments leads to a major dissipation of raw materials, which can in turn pose in important health and environmental problem. This project seeks to address this by proposing novel solvent-extraction systems based on environmentally benign hydrophobic eutectic solvents, thereby sustainably maximizing the inherent value of these metals.

The use of hydrophobic eutectic systems avoids their loss to the aqueous phases during extraction and poor metal extraction yields. Moreover, in many cases the eutectic mixture is liquid at room temperature, while both pure components are solid, an important advantage when envisioning possible industrial applications. Terpenes belong to what is probably the largest and most diverse class of natural products with applications in several industries. Terpenes arise as promising constituents of sustainable hydrophobic solvents due to their low water solubility and price. Recently, the mixture of menthol and lauric acid was used in the extraction of indium from aqueous solutions with low acidity [1].

In this work, two eutectic solvents varieties are studied based on terpenes menthol and thymol, in conjunction with long alkyl chain monocarboxylic acids (Figure 1) for the recovery of metals from sulfate media. A screening of transition metal extraction is firstly performed. Using copper as a model element, the extraction mechanisms are assessed by studying the influence of (i) the terpene selection, (ii) the length of the acid alkyl chain (n=10-18), (iii) the terpene to acid ratio for a given mixture, (iv) the pH and (v) the eutectic mixture loading. Finally, selective metal recovery from the eutectic mixture medium will be studied by electrodeposition, a recovery relevant to the recycling of copper from waste printed circuit boards. Density functional theory modelling of the eutectic mixture - metal complex provides further insight into their interaction.



Figure 1. Chemical structure of the terpenes (left) and monocarboxylic acids (right) used in this work

This work was part of BATRE-ARES project funded by ADEME and FCT. This work was partly developed in the scope of the project CICECO - Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013).

References:

[1] Tereshatov, E.E;. Boltoeva, M.Y.; Folden, C.M. Green Chem., 2016, 18, 4616–4622.

Ionic Liquids for CO₂ capture and conversion

Thomas Schubert, Frank Stiemke, Maria Ahrens, Natalia Zabarska, Boyan Iliev

Iolitec Ionic Liquids Technologies GmbH, Heilbronn, Germany E-mail: fair@iolitec.de

Ionic liquids (ILs) – salts that are liquid at temperatures below 100° C – have gained popularity over the past 10 years and have become products of industrial interest, instead of just being lab curiosities. Because of the innumerous possible combinations of cations and anions, one can tailor their properties to fit a specific application. One of the emerging technologies involves the use of ionic liquids for CO₂ capture and conversion.

The current process to capture CO_2 is based on highly corrosive and volatile aqueous amine solutions, but due to their ability to retain CO_2 - both physically and chemically ILs are a good alternative. [1] The use of ILs leads to a reduction of water consumption, release of solvents to atmosphere and corrosion of plant components. At the same time the absorption/stripping rates and CO_2 loading can be elevated.

It turns out that some ILs, i.e. 1-alkyl-3-methylimidazolium tricyanomethanides exhibit a considerable increase of both CO_2 solubility and the diffusivity in binary systems consisting of IL and water in comparison to dry solvents. This is a considerable improvement over most of the CO_2 absorbing ionic liquids where water impairs the efficiency of the CO_2 capture. [2]

The so captured CO_2 can be consecutively used for conversion into other products *e.g.* formate either electrochemically or photochemically in the presence of ILs. Another currently investigated option is to produce oxalic acid and/or glycine.

We will present the view and research results of a company, specialized in the synthesis and technology development in the field of ionic liquids, which has been on the market for more than 15 years.



Figure 1. Low pressure solubility of CO₂ in ILs.

- [1]Ortloff, F., Roshitz, M., Graf, F., Kolb, T., Ahrens, M., Schubert, T.J.S., *Sep. and Purif. Techn.*, **2014**,*195*, 413–430.
- [2]Romanos, G. E. Lawien, F. Z. Likodimos, V. Falaras, P. Kroon, M. C. Iliev, B. Adamova, G. Schubert, T. J. S., J. Phys. Chem. B., 2013, 117, 12234-12251.

Butyric acid extraction by phosphonium ionic liquid with decanoate anion

Ján Marták and Štefan Schlosser

Institute of Chemical and Environmental Engineering, Slovak University of Technology Radlinského 9, 812 37 Bratislava, Slovakia; e-mail: stefan.schlosser@stuba.sk

Hydrophobic ionic liquids (ILs), especially tetraalkylphosphonium and tetraalkylammonium ones, show great potential as extractants of carboxylic acids. Structure of cation and especially anion greatly influences extraction properties of ILs [1]. Extraction of butyric acid (BA) by trihexyltetradecylphosphonium decanoate (Cyphos IL-103) was studied in this work in wider concentration interval at 25°C. Loading of IL by BA (number of BA molecules per one IL ion pair) achieved value more than 10 (Fig. 1). Dependence of IL loading by water on BA loading goes through sharp minimum at about acid loading of 3 documenting competitive extraction of acid and release of water from solvent as extraction proceeds (Fig. 2). This is similar as it was observed in BA extraction by IL with phosphinate anion [2]. New mechanism and model of BA extraction, proposed in paper [2], fits well presented equilibrium data and formation of stoichiometrically defined (p, 1) complexes, $(BAH)_pIL$, with p up to 16 is suggested (Fig. 1). Stability constant of two H-bonds acid/IL of 546 and 61.1 m³.kmol⁻¹ are by two and one order of magnitude higher than stability constants of acid/acid H-bonds in complexes, respectively. Moreover, the first acid/IL Hbond stability constants of 546 m³.kmol⁻¹ is much lower comparing with this in BA extraction by phosphonium IL with phosphinate anion which is of about 1610 m³.kmol⁻¹ [2]. This may have positive influence on easier stripping of acid from the solvent by short path vacuum distillation which can be of technological importance [1, 3].



Support of the Slovak grant agency under project APVV-15494 is acknowledged.

- [1] Schlosser, Š.; Marták, J.; Blahušiak, M.; Chem. Pap., 2018, 72, 567-584.
- [2] Marták, J.; Schlosser, Š., J. Chem. Eng. Data, 2016, 61, 2979-2996.
- [3] Blahušiak, M.; Schlosser, Š.; Cvengroš, J., Sep. Purif. Technol., 2012, 97, 186-194.

Centrifugal partition chromatography applied on the fractionation of phenolic compounds from lignin depolymerization

<u>Sónia P.M. Ventura</u>¹, João H. P. M. Santos¹, Mafalda R. Almeida¹, Cláudia I. R. Martins¹, Ana C. R. V. Dias², Mara G. Freire¹, João A. P. Coutinho¹

¹CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal ²CESAM - Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, 3810-193 Aveiro, Portugal. E-mail: spventura@ua.pt

Phenolic compounds are abundant biomolecules exhibiting a wide range of physiological properties, with significant industrial application in pharmacy and as nutraceuticals. In this work, aqueous biphasic systems (ABS) formed by polyethylene glycol and sodium polyacrylate, and inorganic salts or ionic liquids as electrolytes, were used on the purification of caffeic, ferulic and protocatechuic acids, vanillin and syringaldehyde, followed by the use of fast centrifugal partition chromatography (FCPC). The separation of the five phenolic compounds was firstly optimized, proving the crucial role of the electrolyte nature. The ABS composed of PEG 8000/NaPA 8000 with NaCl as electrolyte was selected as the most efficient and further used in FCPC to support its scale-up. After the optimization of the operational conditions, the complete separation of each phenolic acid, as well as the separation of the aldehyde-rich fraction was obtained with FCPC. High recoveries were obtained, between 65% and 87%. Based on these results, an integrated process using CPC in a continuous regime was developed allowing the complete separation of monomeric phenolic lignin-based compounds.

Envisaging its industrial application, the environmental impact of the integrated process was evaluated. The reuse or not of the ABS coexisting phases were studied as two different scenarios possible to associate to this process. The carbon footprint of both scenarios (with and without reuse of solvents after ultrafiltration) was estimated. This green metric showed the importance of the reuse of these polymeric phases regarding the process sustainability, being the carbon footprint decreased in 36%. Novel approaches for the recovery of the phenolic compounds have been also developed [1].

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), and CESAM (UID/AMB/50017), financed by national funds through the FCT/MEC and when appropriate cofinanced by FEDER under the PT2020 Partnership Agreement. The authors are grateful to FCT for the PhD grant of SFRH/BD/102915/2014 of J.H.P.M. Santos, IF contracts IF/00402/2015, IF/00587/2013 of S Ventura and A Dias, the project SAICTPAC/0040/2015. M.G.F. acknowledges ERC for the grant ERC-2013-StG-337753.

References:

[1]Santos, J.H.P.M.; Almeida, M.R.; Martins, C.I.R.; Dias, A.C.R.V.; Freire, M.G.; Coutinho, J.A.P.; Ventura, S.P.M., *Separation of phenolic compounds by centrifugal partition chromatography*, *Green Chem.*, **2018**, submitted.

Herbicidal ionic liquids comprising phenoxy acids as effective crop protection agents

<u>Michał Niemczak</u>¹, Katarzyna Materna¹, Anna Syguda, Filip Walkiewicz, Katarzyna Marcinkowska², Tadeusz Praczyk², Juliusz Pernak¹

 ¹Poznan University of Technology, Department of Chemical Technology, ul. Berdychowo 4, 60-965 Poznań
 ²Institute of Plant Protection – National Research Institute, ul. W. Węgorka 20, 60-318 Poznań E-mail: michal.niemczak@put.poznan.pl

One of the main problems in the cultivation of plants is their destruction by harmful organisms such as weeds. Their negative effect is manifested by the fact that they are in competition with crop plants for light, water and nutrients. Currently, the most common method of controlling weeds is the use of herbicides. The herbicide market offers many different products including derivatives of phenoxy acids. These unique compounds have been commercialized as synthetic herbicides since the 1940s and they are still commonly used in worldwide weed control.

Ionic liquids (ILs) may be defined as substances composed exclusively of ions, which form phases that are liquids below the temperature of 100°C. Their high application potential of inspired us to obtain organic salts containing the phenoxy family of herbicides in the anion. Thus, herbicidal ionic liquids (HILs) were introduced to the world literature [1]. So far, HILs have been successfully synthesized from phenoxyacids such as 2,4-dichlorophenoxyacetic acid (2,4-D) [2], 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP) [3], 4-chlorophenoxyacetic acid (4-CPA) [4], 4-chloro-2-methylphenoxyacetic acid (MCPA) [1], 2-(4-chloro-2-methylphenoxy)propionic acid (MCPP) [5] and 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB). The second generation of HILs derived from phenoxy acids are bifunctional compounds which are formed by combining an appropriate herbicidal anion with a cation that also exhibits biological activity, *e.g.* as a plant growth regulator.. HILs as non-volatile compounds turned out to be are much safer in use in comparison to the compounds offered commercially. Due to their enhanced herbicidal efficiency, the required dose of active ingredient per hectare could be significantly reduced. Moreover, the chemical structure of the cation may be modified to regulate the toxicity and biodegradability of HILs. Therefore, reports describing eco-friendly and biodegradable HILs derived from renewable sources appeared recently.

This presentation summarizes the recent achievements in synthesis and characterization of herbicidal ionic liquids containing different phenoxy carboxylates including their physicochemical properties as well as biological activity against dicotyledonous weeds.

- [1]Pernak, J.; Syguda, A.; Janiszewska, D.; Materna, K.; Praczyk, T., *Tetrahedron*, **2011**, 67, 4838– 4844.
- [2]Pernak, J.; Syguda, A.; Materna, K.; Janus, E.; Kardasz, P.; Praczyk, T., *Tetrahedron*, **2012**, *68*, 4267–4273.
- [3]Niemczak, M.; Biedziak, A.; Czerniak, K.; Marcinkowska, K., Tetrahedron, 2017, 73, 7315-7325.
- [4] Syguda, A.; Marcinkowska, K.; Materna, K., RSC Adv., 2016, 6, 63136-63142.
- [5]Pernak, J.; Czerniak, K.; Niemczak, M.; Chrzanowski, Ł.; Ławniczak, Ł.; Fochtman, P.; Marcinkowska, K.; Praczyk, T., *New J. Chem.*, **2015**, *39*, 5715–5724.

Violacein recovery from *Yarrowia lipolytica* cells with Aqueous Solutions of Surface-Active ionic liquids

<u>Mariam Kholany</u>¹, Margarida Martins¹, Sónia P.M. Ventura¹, Pauline Trébulle², Jean-Marc Nicaud², João A. P. Coutinho¹

¹ CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

² Micalis Institute, INRA, AgroParisTech, Université Paris-Saclay, 78350 Jouy-en-Josas, France *E-mail: mariamkholany@ua.pt*

Recently, academia and industries have been paying close attention to products extracted from natural sources. Violacein is an indole derivative pigment, which has attracted much attention recently owing to its promising biological activities. Many pharmacological properties have been attributed to violacein, due to its antibacterial, antiviral, antioxidant and antitumor activities. Since this pigment is expressed intracellularly, efficient downstream processes, including the cell disruption are required. The most commonly applied methods of cell disruption are either mechanical or organic solvent dependent.

Violacein was biosynthesized by genetically engineered strains of *Yarrowia lipolytica*. In this work, the cells were used to assess an alternative approach employing alternative solvents and aiming the most efficient release of the violacein. In this sense, aqueous solutions of different surface-active compounds, including surface-active ionic liquids and common surfactants, were tested regarding their capacity to release the molecule.[1] The best alternative solvents were selected and showed to be 53% more efficient releasing the violacein from the cells when compared with the conventional solvent, ethanol. The process conditions were also optimized, such as the solid-liquid ratio, extraction time and amount of alternative solvent.

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. The authors are grateful for the financial support of the Portuguese Foundation for Science and Technology (FCT) for the doctoral grant of SFRH/BD/122220/2016 of M. Martins and the IF/00402/2015 of S.P.M. Ventura. Pauline Trébulle was supported through the "IDI 2016" project funded by the IDEX-Saclay, ANR-11-IDEX-0003-02.

References:

[1] Passos, H.; Freire, M.G.; Coutinho, J.A.P. Green Chem., 2014, 16, 4786-4815.

Polymerizable ionic liquids as green materials for patterning of microscale elements

<u>Krzysztof Rola</u>¹, Adrian Zając², Maciej Czajkowski¹, Joanna Cybińska^{1,3}, Marcin Śmiglak², Katarzyna Komorowska^{1,4}

¹Wroclaw Research Centre EIT+, ul. Stablowicka 147, 54-066 Wroclaw, Poland ²Poznan Science and Technology Park of Adam Mickiewicz University Foundation, ul. Rubiez 46, 61-612 Poznan, Poland

³University of Wroclaw, Faculty of Chemistry, 14 F. Joliot-Curie Street 50-383 Wroclaw, Poland ⁴Wroclaw University of Science and Technology, Faculty of Fundamental Problems of Technology, Department of Optics and Photonics, 27 Wybrzeze Wyspianskiego Street 50-370 Wroclaw, Poland E-mail: krzysztof.rola@eitplus.pl

Ionic liquids, often regarded as green solvents, are herein considered as new materials for fabrication of micro-scale components. The nano and micro elements are formed through polymerization of room temperature ionic liquids (RTILs) by means of electron beam [1]. The fabrication of microstructures requires the deep understanding of mechanisms of polymerization as well as the dynamics of the process for different experimental conditions. The proper results depend also on the composition of RTIL mixture.

In this study we present the properties of selected ionic liquids and discuss the possibility of application of different imidazolium-based ionic liquids with allyl substituent for electron beam induced polymerization. The microstructures of the best quality, i.e. uniform shape, low roughness and good adhesion to silicon surface were obtained with used compounds. The basic properties of the material are presented. The viscosity, electrical conductivity and optical properties of the material indicate that it can be successfully used in preparation of micro-scale elements. Moreover, micro-scale structures can be also manufactured on other surfaces. The components made by electron beam-activated polymerization of the RTIL are presented in Fig. 1.



Figure 1. SEM images of prepared microstructures on Si: a) microrings matrix, b) cross-section trough lines pattern, both fabricated by electron beam activated polymerization of RTIL

The work financed by the National Science Center within the Grant Opus UMO-2015/19/B/ST8/02761

References:

[1]Minamimoto, H.; Irie, H.; Uematsu, T.; Tsuda, T.; Imanishi, A.; Seki, S.; Kuwabata, S., *Langmuir*, **2015**, *31*, 4281–4289.

Selection and evaluation of ionic liquids for the recovery of platinum group metals from spent autocatalysts

<u>Olga Lanaridi</u>¹, Sonia Platzer¹, Winfried Nischkauer^{1,2}, Andreas Limbeck², Amal Siriwardana³, Laura Sánchez Cupido³, Jokin Betanzos Hidalgo³, Iakovos Yakoumis⁴ and Katharina Schröder (born K.Bica)¹

¹Institute of Applied Synthetic Chemistry, Vienna University of Technology, Vienna, Austria ²Institute of Chemical Technologies and Analytics, Vienna University of Technology, Vienna, Austria ³Materials for Energy and Environment Area, Energy and Environment Division, TECNALIA,

⁵Materials for Energy and Environment Area, Energy and Environment Division, IECNALIA, Parque Cientifico y Tecnológico de Guipuzcoa, San Sebastián, Spain ⁴Monolithos Catalysts & Recycling Ltd., Athens, Greece E-mail: olga.lanaridi@tuwien.ac.at

The recycling of platinum group metals (PGMs) is currently a topic of vast significance, mainly due to their considerable cost and the constantly increasing gap between their natural supply and their rising demand in industry and technology [1,2]. While Europe is the leading PGM consumer (41% of worldwide PGM resources in 2014), with the highest percentage used in the automotive industry, it is at the same time the poorest in PGMs from a geological perspective. Nowadays, spent catalysts are being recycled by use of hydro- and pyrometallurgical processes, which employ harsh conditions.

The PLATIRUS (PLATInum group metals Recovery Using Secondary raw materials) project is an international collaboration for the development of a cost-efficient and miniaturized recovery process of PGMs, funded by the EU in the frame of H2020 [3]. The aim of the PLATIRUS project is the reduction of the European deficit of the Platinum Group Metals, by employing a novel cost efficient and benign PGM recovery and raw material production process relying on iono- and solvometallurgical leaching, which can be upscaled to industrial relevant levels. The focus of the PLATIRUS approach is higher recycling yield and lower energy consumption, with simultaneous use of green and environmentally friendly technologies that target the negative environmental impact of currently employed strategies.

The main advantage of ionometallurgical leaching techniques is the lack/restraint of usage of toxic and/or dangerous reagents, such as aqua regia or cyanides. To this end, a set of different ionic liquids was synthesized, characterized and applied for the leaching of PGMs from spent autocatalyst at ambient temperature. Once the leaching process was optimized, the separation of PGMs was investigated with task-specific ionic liquids, selected according to key performance indicators, such as higher extraction yields, low environmental impact and reduced costs [3].

The PLATIRUS project is funded by the European Union's Horizon 2020 Research and Innovation Programmme under grant agreement No730224.

References:

[1] Platinum 2013 Interim Review, Johnson Matthey

- [2] World Platinum Investment Council, Platinum Quarterly Q3, 2015
- [3] http://www.platirus.eu/, last accessed 08-01-2017

When toxicity is a good thing - case of antibiotic resistant bacteria

Anna Rybińska-Fryca¹, Ewelina Wyrzykowska¹, Anita Sosnowska¹, Tomasz Puzyn¹

¹Laboratory of Environmental Chemometrics, Faculty of Chemistry, University of Gdańsk E-mail: rybinska@qsar.eu.org

The bacterial resistance to antibiotics is a serious public health problem. There are several ways to eliminate this problem and one of these is exploitation of antimicrobial activity of ionic liquids (ILs) and utilizes them as active pharmaceutical ingredients (APIs) [1]. Previous reports showed that choline- and ampicillin-based ILs could be effective antimicrobial agents [2-3]. Nevertheless, synthesis and experimental testing of each possible IL is time-consuming and ineffective. For that reason, we developed qualitative structure-activity relationship (QSAR) model for toxicity prediction against pathogenic bacteria, *Staphylococcus aureus* that could be used as a first step in designing new APIs.

Structure of ionic liquids was described by so-called molecular descriptors, which are numeric representation of the structure. We decided to use simple 2D descriptors that provide information about size, branching of the molecule as well as type and number of atoms etc. Then, the decision tree algorithm was used to select the most important descriptors for further analysis. Finally, the classification model (based on selected descriptors and SVM method) was developed. By using presented model, we are able to predict toxicity (expressed by Minimal Inhibitory Concentration) against *Staphylococcus aureus* for new ILs. We believe that combining theoretical models with plan of the research will decrease time and cost of process of designing new ILs-based APIs.

This material is based on research funded by the National Science Center (Poland) (Grant No. UMO-2012/05/E/NZ7/01148)

References:

[1] Egorova, K.S.; Gordeev, E.G.; Ananikov, V.P. Chem Rev., 2017, 117, 7132-7189.

- [2] Siopa, F.; Figueiredo, T.; Frade, R.F.M.; Neto, I.; Meirinhos, A.; Reis, C.P.; Sobral, R.G.; Afonso, C.A.M.; Rijo, P. *Chemistryselect*, **2016**, *1*, 5909-5916.
- [3] Ferraz, R.; Teixeira, V.; Rodrigues, E.; Fernandes, R.; Prudencio, C.; Noronha, J.P.; Petrovski, Z.; Branco, L.C. *RSC Adv.*, **2014**, *4*, 4301-4307.

Hydroboration in poly(ethylene glycols) – green approach to alkenyl boronates

Jakub Szyling^{1,2}, Mateusz Klarek^{1,2}, Kinga Stefanowska^{1,2}, Adrian Franczyk¹, Jędrzej Walkowiak^{1,*}

¹Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, 61-614 Poznan, Poland ²Faculty of Chemistry Adam Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznan, Poland E-mail: j.szyling@amu.edu.pl

Poly(ethylene glycols) (PEGs) due to their unique physicochemical properties (low melting points, good solvent properties, negligible vapour pressure, high stability in both acidic and basic media, miscibility with several polar and non-polar solvents, practically free of toxicity and a low price) are commonly used in many branches of science and industry (e.g. medicine, biotechnology, cosmetic, pharmaceutical, food and chemical industry) [1]. In the last decade, several examples of the application of PEGs as solvents for TM-catalyzed reactions *e.g.*: hydrogenation or C-C bond formations, were reported [2-3]. The moderate polarity of PEGs permitted for immobilization of polar, organometallic, molecular catalysts and their effective recycling and reuse. Therefore, in contrast to e.g. perfluorinated solvents, scCO₂ or water, modification in catalyst structure is not needed to increase its affinity to solvent. PEGs have the abilities to dissolve a wide range of organic, organometallic or even inorganic compounds, making them an excellent alternative to toxic volatile organic solvents [4-5].

Despite many advantages of synthetic methods based on PEGs, the formation of alkenyl boronates via hydroboration of alkynes in these solvents has never been explored.

In this communication, the new, highly efficient method based on the immobilization of the molecular catalyst $Ru(CO)Cl(H)(PPh_3)_3$ in PEGs for regio- and stereoselective alkyne hydroboration under repetitive batch mode will be presented. Detailed studies concerning reaction conditions and PEGs structure on process efficiency will be provided.

Financial support from The National Centre for Research and Development in Poland, Lider Programme No. LIDER/26/527/L-5/13/NCBR/2014

- [1] Bailey, F.J. Poly(ethylene oxide), Academic Press, 1976.
- [2] Liu, R.; Cheng, H.; Wang, Q.; Wu, C.; Ming, J.; Xi, C.; Yu, Y.; Cai, S.; Zhao, F.; Arai, M. *Green Chem.*, 2008, 10, 1082-1086
- [3] Vafaeezadeh M.; Hashemi, M.M. J. Mol. Liq., 2015, 207, 73-79.
- [4] Chen, J.; Spear, S.K.; Huddleston J.G.; Rogers, R.D. Green Chem., 2005, 7, 64-82.
- [5] Jessop, P.G. Green Chem., 2011, 13, 1391-1398

Supercritical CO₂ as an alternative medium for the synthesis of alkenyl silanes

<u>Kinga Stefanowska</u>^{1,2}, Jakub Szyling^{1,2}, Katarzyna Salamon^{1,2}, Adrian Franczyk¹, Jędrzej Walkowiak^{1,*}

¹Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, 61-614 Poznan, Poland
² Faculty of Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznan, Poland E-mail: kinga.stefanowska@amu.edu.pl

Alkenyl-derivatives of silanes are important classes of organosilicon compounds, which find many applications in academia and industry [1]. For example, tri- and disubstituted silylethenes are widely used in the synthesis of unsaturated systems *via* chemical transformations based on desilylation reactions. They are also useful precursors for the industrial production of polysiloxanes [1].

Transition-metal catalyzed hydrosilylation of alkynes has been shown to be one of the most powerful methods for the synthesis of alkenyl silanes [1]. The main advantages of this process are: the possibility for selective formation of specific isomer of Si-H addition, 100% atom efficiency, the mild reaction conditions and uses of commercially available catalysts which are tolerable for many functionalities. In addition, the replacement of toxic and volatile organic solvents, which are commonly used in this process with green, environmentally friendly supercritical or compressed CO₂ allows to recycle of expensive catalysts, makes separation of the product easy and significantly reduces the cost of the process [2-5].

In the communication, we report the detailed studies on the hydrosilylation of the terminal and internal alkynes with different types of silanes. The influence of the reaction conditions as well as the type of solvent (traditional and green one) on the efficiency and selectivity of the processes will be discussed.

Financial support from The National Centre for Research and Development in Poland, Lider Programme No. LIDER/26/527/L-5/13/NCBR/2014 is gratefully acknowledged.

- [1] Marciniec B., Maciejewski H., Pietraszuk C., Pawluć P., *Hydrosilylation. A Comprehensive Review on Recent Advances* (ed. B. Marciniec), **2008**, Springer, Hoboken.
- [2] Walkowiak, J.; Franció, G.; Leitner, W.; Supercritical Fluids as Advanced Media for Reaction and Separation in Homogeneous Catalysis, in Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Four Volumes, 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- [3] Leitner, W., Acc. Chem. Res., 2002, 35, 746-756.
- [4] Skouta, R., Green Chemistry Letters and Reviews, 2009, 2, 121-156.
- [5] Rayner C.M., Organic Process Research & Development, 2007, 11, 121-132.

Application new chiral ionic liquids based on (-)-menthol as a solvent in Diels-Alder reaction

Marcin Gano, Ewa Janus

West Pomeranian University of Technology Szczecin, Faculty of Chemical Technology and Engineering, Institute of Chemical Organic Technology, Pułaskiego 10, 70-322 Szczecin, Poland E-mail: mgano@zut.edu.pl

A new chiral pyrrolidinium ionic liquids with bis(trifluoromethylsulfonyl)imide (NTf₂) and bis(pentafluoroethylsulfonyl)imide anions based on natural terpene alcohol, (1R,2S,5R)-menthol and tertiary amine 1-(2-hydroxyethyl)pyrrolidine has been used as solvent in model Diels-Alder reaction between croton aldehyde and cyclopentadiene in the present of Lewis acid as a catalyst (Figure 1).



Figure 1. Model Diels-Alder reaction between croton aldehyde and cyclopentadiene in chiral ionic liquids

A series of Lewis acids general from triflates group: $Zn(OTf)_2$, $Cu(OTf)_2$, $Sn(OTf)_2$, $Yb(OTf)_3$, $Y(OTf)_3$, $Bi(OTf)_3$, $In(OTf)_3$, $Sc(OTf)_3$, $Mg(OTf)_2$, $Nd(OTf)_3$ and $ZnCl_2$, $SnCl_4$ were used as catalysts in Diels-Alder reaction. Influence of type of catalyst, amount of catalyst and also temperature were determined. As a solvent a new chiral ionic liquids N-(2-hydroxyethyl)-N-[(1R,2S,5R)-(-)-2-isopropyl-5-methylcyclohexyl-1-oxymethyl]pyrrolidinium bis(trifluoromethyl-sulfonyl)imide and N-(2-hydroxyethyl)-N-[(1R,2S,5R)-(-)-2-isopropyl-5-methylcyclohexyl-1-oxymethyl]pyrrolidinium bis(pentafluoroethylsulfonyl)imide were used. Conversion of croton aldehyde, diastereoselectivity *endo/exo* end enantioselectivity was determined. Under the best reaction conditions, different dienophiles as a *trans*-hex-2-en-1-al, *trans*-pent-2-en-1-al and 2-methylpent-2-en-1-al were tested in the reaction with cyclopentadiene.

New ionic liquids based on systemic acquired resistance inducers combined with benzethonium cation

Patrycja Czerwoniec^{1,2}, Ryszard Koczura³, Henryk Pospieszny⁴, Marcin Śmiglak^{1,2*}

 ¹ Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 b, 61-614 Poznan, Poland
 ² Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubież 46, 61-612 Poznan, Poland

³ Faculty of Biology, Adam Mickiewicz University, ul. Umultowska 89, 61-614 Poznan, Poland ⁴ Institute of Plant Protection - National Research Institute, ul. Władysława Węgorka 20, 60-318 Poznan, Poland

E-mail: patrycja.czerwoniec@gmail.com

Continuous growth of the human population is a main factor contributing to increase in the demand for food, which forces farmers to use more effective methods of growing crops. Serious threats to crop yields are pathogens, insects or other pests and atmospheric conditions. These factors pose a challenge to modern agronomists in searching for new and effective methods to protect plants. The biggest unsolved problem in agriculture are viral diseases. At present, there are no chemical methods with the ability to inhibit the spread of viral diseases, and because of that, viruses cause every year huge losses in plant production worldwide. However, the plants during the evolutionary process developed many mechanisms allowing them to defend against pathogens. One of those is systemic acquired resistance (SAR) phenomenon, induced by pathogen attack or artificially, by using an elicitor (immune inducer).[1] Elicitors are a modern group of compounds that imitates the pathogen-plant interactions, what leads to stimulation of natural signaling pathways which induce the natural immunity of the plant.

We have successfully synthesized new salts based on systemic acquired resistance inducers combined with benzethonium cation. Following the synthesis we determined antibacterial and SAR inducing properties.

This work was supported by the National Science Centre (Poland), project OPUS (No. UMO-2015/17/B/NZ9/01676).

References:

[1] Tiryaki, I.; Tunaz, J., J. Cell Mol. Biol., 2003, 3, 9-14.

Evaluation of the antimicrobial and antibiofilm activities of a series cholinium amino acids

Paula Ossowicz¹, Ewa Janus¹, Tsvetelina Paunova-Krasteva², Stoyanka Stoitsova², Maya Guncheva³

¹West Pomeranian University of Technology Szczecin, Faculty of Chemical Technology and Engineering, Institute of Organic Chemical Technology, Pułaskiego str. 10, 70-322 Szczecin, Poland

 ²Bulgarian Academy of Science, The Stephan Angeloff Institute of Microbiology, Department of General Microbiology, Sofia, 26 Georgi Bonchev str., 1113 Sofia, Bulgaria
 ³Bulgarian Academy of Sciences, Institute of Organic Chemistry with Centre of Phytochemistry, Acad. G. Bontchev str. Bl. 9, 1113 Sofia, Bulgaria E-mail: possowicz@zut.edu.pl

A series of ionic liquids containing a cholinium cation and charged amino acid anions were synthesized by neutralization of choline hydroxide solution with different amino acids. They are thoroughly characterized by ¹H NMR and FT-IR. Physicochemical properties such as specific rotations and thermal stability were measured.

The antibacterial and the antibiofilm activity of the compounds have been evaluated against six bacterial strains – the Gram negative bacteria: *Escherichia coli* (NBIMCC 420, National Bank for Industrial Microorganisms and Cell Cultures, Bulgaria), *Escherichia coli* (ATCC 25922), *Pseudomonas aeruginosa* (ATCC 15692); and the Gram positive bacteria: *Staphylococcus aureus* (ATCC 29213), *Staphylococcus saprofiticus* (ATCC 15305), *Bacillus subtilis* 168. Within the tested series, [Chol][Lys] was the most toxic IL and the concentration inhibiting 50% (IC50) was in the range between 1.67 and 5.23 mmol/L, which is in agreement with the data found in the literature for other choline amino acids [1]. *Pseudomonas aeruginosa, Bacillus subtilis* and *Staphylococcus aureus aureus* were resistant to almost all other compounds. The six ILs strongly suppressed the biofilm formation caused by *Escherichia coli* 25922 and *Staphylococcus saprofiticus*, and exhibited a moderate antibiofilm activity against *Escherichia coli* 420 and *Pseudomonas aeruginosa*. It is noteworthy to be mentioned that the cell viability of murine fibroblast cells (3t3cells) exposed to high concentrations (up to 4.7 mmol/L) of [Chol][Asp] and [Chol][Glu] for 48h was not affected. At the same time, for the other four compounds we observed up to 15% reduction of the 3t3 cell viability even while used at concentrations as high as 0.67 mmol/L for 48h.

The assayed ILs have low antibacterial activity, but most of them have potential as antibiofilm forming agents. This is important for future applications, bearing in mind the increasing notion about the role of biofilm infections as well as the intrinsic resistance of biofilms to traditional antimicrobials. In addition, having in mind their low cytotoxicity toward fibroblast cells probably after successful tailored modification of the structure aiming to increase their antibacterial activity but keeping their low fibroblast cytotoxicity they could have potential in preparation of wound dressing materials.

References:

[1] Hou, X.D.; Liu, Q.P.; Smith, T.J.; Li, N.; Zong, M.H. PlosOne, 2013, 8, e59145.

Ion chromatography as an excellent tool for ion exchange control in ionic liquids synthesis

Andrea Szpecht^{1,2}, Adrian Zajac², Dawid Zielinski², Marcin Smiglak^{1,2*}, Hieronim Maciejewski^{1,2}

¹Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 B, 61-614 Poznan, Poland ²Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubiez 46, 61-612 Poznan, Poland E-mail: andrea.szpecht@amu.edu.pl

Over the last couple of years science keeps focusing more and more on green chemistry, that is why ionic liquids have seen an upward trend in the research. Their unique and easily tunable properties make them very desirable in handful of studies, such as catalysis [1], lubricants [2], green solvents [3] and many more.

New, unsaturated ammonium-based ionic liquids with various anions have been synthesized. Method applied was simple, convenient and yet not of popular use amongst IL's researchers [4]. The first step was to obtain halide-based salts containing unsaturated group in the cation structure. The next step was to exchange halide anion for either triflate, tosylate, methyl sulfonate and methanesulfonate anion. Exchange reaction advances quickly at room temperature, with minimal amount of acetonitrile as solvent. In the course of the reaction, gaseous chloromethane is the only byproduct.

Use of ion chromatography, as analysis of ionic liquids anion and anion impurities, *e.g.* halides, is rarely used and presented. Ion chromatography is used for separation and quantitative analysis of cations and anions in an ionic solution using the ion exchange method of liquid chromatography. The amount of an anion is measured by the change in conductivity as the species passes through the detector. The retention time of anions depends on their size, charge and polarizability [5]. This method can be easily accommodated to help chemist to monitor the ionic liquid anion exchange reactions. Here we present convenient method of synthesis new ionic liquids and determination of anions using standard ion chromatography system.

This work was supported by the National Science Centre (Poland), project OPUS (No. 2014/15/B/ST5/04257).

- [1] Kukawka, R.; Pawlowska-Zygarowicz, A.; Dutkiewicz, M.; Maciejewski, H.; Smiglak, M. *RSC Advances*, **2016**, *6*, 61860-61868.
- [2] Guo, Y.; Qiao, D.; Han, Y.; Zhang, L.; Feng, D.; Shi, L. Ind. Eng. Chem. Res., 2015, 54, 12813-12825.
- [3] Bui, T.T.L.; Nguyen, D.D.; Ho, S.V.; Nguye, B.T.; Uong, H.T.N. Fuel, 2017, 191, 54-61.
- [4] Ignat'ev, N.V.; Barthen, P.; Kucheryna, A.; Willner, H.; Sartori, P. *Molecules*, **2012**, *17*, 5319-5338.
- [5] Rutz, C.; Schmolke, L.; Gvilava, V.; Janiak, C. J. Inorg. Gen. Chem., 2017, 643, 130-135.

Poly(ethylene glycols) and ionic liquids as an alternative media for borylative coupling of vinylboronates with olefins

<u>Tomasz Sokolnicki</u>^{1,2}, Mateusz Klarek^{1,2}, Jakub Szyling^{1,2}, Kinga Stefanowska^{1,2}, Adrian Franczyk¹, Jędrzej Walkowiak^{1,*}

¹Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, 61-614 Poznan, Poland ²Faculty of Chemistry Adam Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznan, Poland E-mail: tomasz.sokolnicki@amu.edu.pl

Unsaturated organoboron reagents, due to their high reactivity, low toxicity and ease of storage, are one of the most useful and valuable intermediates in the C-C, C-N, C-O or C-X (X = halogen) bond-forming reactions and other demetallation protocols. Among the many possibilities to obtain alkenyl boronates *e.g.* metathesis of vinylboronates with alkenes or alkynes hydroboration, borylative coupling of vinylboronates with olefins results in exclusive formation of (E)-alkenyl boronates. This reaction is carried out under homogeneous conditions in organic, volatile solvents (DCM, benzene, THF, toluene), which ensure the process selectivity and efficiency, but on the other hand, the homogeneity of the reaction mixture generates problems with products separation from transition metals as well as recovery and reuse of often expensive molecular catalysts [1-4].

Therefore, the search for new methods leading to such compounds and improvement of existing protocols taking into account process sustainability and environment protection through application of green solvents such as poly(ethylene glycols) (PEGs) or ionic liquids (ILs) as well as recycling of catalytic system is of great importance [5-6].

In this communication, the new and highly effective protocols for borylative coupling of vinylboronates with olefins in a wide scope of modified and unmodified PEG as well as ILs will be presented. Influence of PEGs and ILs structures on ruthenium hydride catalyst (Ru(CO)Cl(H)(PPCy₃)₂) immobilization as well as on process efficiency will be discussed.

Financial support from The National Centre for Research and Development in Poland, Lider Programme No. LIDER/26/527/L-5/13/NCBR/2014

- [1] Occhiato, E.G.; Lo Galbo, F.; Guarna, A., J. Org. Chem., 2005, 70, 7324-7330.
- [2] Marciniec, B.; Jankowska, M.; Pietraszuk, C., Chem. Commun., 2005, 663-665.
- [3] Szyling, J.; Franczyk, A.; Pawluć, P.; Marciniec, B.; Walkowiak, J., Org. Biol. Chem., 2017, 15, 3207-3215.
- [4] Shade, R.E.; Hyde, A.M.; Olsen, J.-C.; Merlic, C.A., J. Am. Chem. Soc., 2010, 132, 1202-1203.
- [5] Chen, J.; Spear, S.K.; Huddleston, J.G.; Rogers, R.D., Green Chem., 2005, 7, 64-82.
- [6] Jessop, P.G.; Green Chem., 2011, 13, 1391-1398.

Extraction of Platinum Group Metals from Chloride Leachate of Endof-Life Car Exhaust Catalysts using Undiluted Ionic Liquids

Viet Tu Nguyen¹, Sofia Riaño¹ and Koen Binnemans¹

¹KU Leuven, Department of Chemistry, Celestijnenlaan 200F, 3001 Heverlee, Belgium E-mail: viettu.nguyen@kuleuven.be

Platinum group metals (PGMs) (i.e. Pt, Pd, Rh) are key materials for catalysts for automotive exhaust gas treatment. The significant increase in the deficit of PGMs forecasted for the coming years (i.e. 93.6 tonnes or 3.3 million oz Pt in 2020) is calling for more attention to recover these critical elements [1].

The Horizon2020 PLATIRUS project (PLATInum group metals Recovery Using Secondary raw materials) aims at reducing the European deficit of PGMs, by upscaling to industrial relevant levels a novel cost-efficient and miniaturized PGMs recovery and raw material production process. The targeted feedstocks are end-of-life car exhaust catalysts, electronic waste, tailings and slags from nickel and copper smelters [2].

In fact, the separation and purification processes of PGMs face a continual challenge due to their refractory chemical properties and the formation of many chemical species in chloride media, which is typically chosen for their hydrometallurgical recycling. In addition, the conventional liquid–liquid extraction of PGMs using molecular extractants (i.e. TBP, Cyanex 923, TOPO, Alamine 336, Chelex 100) suffers from drawbacks of slow kinetics and poor selectivity [3].

More recently, ionic liquids have been widely considered in hydrometallurgy towards green extraction of metals [4, 5]. In practice, ionic liquids with hydrophobic cations in combination with simple anions (i.e. Cl^- , NO_3^- , etc.) such as Cyphos IL 101 and Aliquat 336, are preferred in solvent extraction. Nevertheless, previous studies reveal that these ionic liquids are mostly used as new extractants and/or ion-exchangers in the classical approach, i.e., diluted in molecular solvents [6, 7].

In the framework of the PLATIRUS project, we developed the split-anion extraction approach [8] as an innovative and sustainable recovery of individual PGMs from acidic chloride media using undiluted ionic liquids. Different types of ionic liquids were synthesized, characterized and tested for the selective extraction and separation of PGMs.

References:

- [1] Johnson Matthey, PGM Market Report May 2017, http://www.platinum.matthey.com/, last accessed 10/02/2018.
- [2] PLATIRUS (H2020, GA No. 730224): PLATInum group metals Recovery Using Secondary raw materials, http://www.platirus.eu, last accessed 10/02/2018
- [3] Nguyen, V.T.; Lee, J.-C.; Chagnes, A.; Kim, M.-S.; Jeong, J.; Cote, G., *RSC Adv.*, **2016**, *6*, 62717–62728
- [4] Hoogerstraete, T.V.; Binnemans, K., Green Chem., 2014, 16, 1594–1606.
- [5] Wellens, S.; Thijs, B.; Binnemans, K., Green Chem., 2012, 14, 1657–1665.
- [6] Cieszynska, A.; Wiśniewski, M., Hydrometallurgy, 2012, 113–114, 79–85.
- [7] Nguyen, V.T.; Lee, J.-C.; Jeong, J.; Kim, B.-S.; Cote, G.;. Chagnes, A., Ind. Eng. Chem. Res., 2015, 54, 1350–1358.
- [8] Larsson, K.; Binnemans, K., Hydrometallurgy, 2015, 156, 206–214.

F_009

Volatility Study of [C_NPy][NTf₂] Ionic Liquids

<u>Ana I.M.C. Lobo Ferreira</u>¹, Carlos F. Miranda¹, José N. Canongia Lopes², Luís P.N. Rebelo³, Luís M.N.B.F. Santos ¹

¹CIQUP, Department of Chemistry and Biochemistry, University of Porto, Porto, Portugal ²CEQ, Instituto Superior Técnico Universidade Lisboa, Portugal. ³DQ, LAQV/REQUIMTE, FCT-UNL, Portugal E-mail: ana.ferreira@fc.up.pt

The vapor pressure at several temperatures for the 1-alkylpyridinium bis(trifluoromethylsulfonyl)imide series, $[C_nPy][NTf_2]$ (n=3, 5-9), was measured by a Knudsen effusion method combined with a quartz crystal microbalance. The experimental vapor pressure data were fitted to the integrated form of the Clausius-Clayperon equation and the enthalpies and entropies of vaporization were derived.



The derived thermodynamic properties of vaporization of the 1-alkylpyridinium bis(trifluoromethylsulfonyl)imide series, $[C_nPy][NTf_2]$ (*n*=5-9), are analyzed together with the results obtained previously for the shorter alkyl chain length $[C_nPy][NTf_2]$ [1], and the volatility of the Imidazolium series $[C_nC_1im][NTf_2]$ [2], in order to evaluate the effect of the alkyl side chains of the cation and to get additional insights concerning the nanostructuration of ionic liquids. It was found that the lower volatility of the alkylpyridinium derivatives (is five times lower than that of the imidazolium series) is driven by their higher enthalpy of vaporization.

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and to FEDER for the financial support to Centro de Investigação em Quiímica, University of Porto (CIQUP) through the project Pest-C/QUI/UI0081/2013 and the SAM project Norte-01-0145-FEDER-000028. AIMC Lobo Ferreira acknowledges the financial support from Fundação para a Ciência e Tecnologia (FCT) for her PhD Research Grant SFRH/BPD/84891/2012.

- [1] Rocha, M.A.A.; Santos, L.M.N.B.F., J. Chem. Therm., 2013, 585, 59-62.
- [2] M.A.A. Rocha et al., J. Phys. Chem. B, 2011, 115, 10919-10926.

Design of chiral ionic liquids for highly selective asymmetric transfer hydrogenation in aqueous medium

Ádám Márk Pálvölgyi¹, Veronica Zeindlhofer², Jacqueline Bitai¹, Katharina Bica¹, and Christian Schröder²

 ¹ Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, 1060 Vienna, Austria.
 ²Department of Computational Biological Chemistry, University of Vienna, Währinger Str. 17, 1090 Vienna, Austria. E-mail: adam.palvoelgyi@tuwien.ac.at

Chirality plays an overwhelming role in chemistry. Due to its environmental and economical benefits over other methods, asymmetric catalysis provides a good strategy to obtain enantiomerically enriched compounds. Catalytic transfer hydrogenation is a particularly attractive route for the reduction of multiple bonds using small organic molecules as hydrogen donor with a wide application range towards the production of enantiopure fine chemicals. [1]

For this purpose four carbamate-based hydrophilic chiral ionic ligands were synthesized starting from the commercially available diamine **1**. The modular design with an *N*,*N* structural motive allowed the formation of coordinating chiral ionic liquids, while the adaptation of solubility to the given reaction conditions could be obtained via the choice of anion.[2] The efficiency of chiral ionic ligands **2-5** was tested in asymmetric transfer hydrogenations with different substrate to establish a structure-activity relationship. Taking in account environmental aspects, the catalytic reactions were carried out in aqueous media. All chiral ionic liquids were found to be suitable catalysts for the asymmetric transfer hydrogenation reactions of ketones and imines, and excellent yields with high enantioselectivity were observed by using chiral ionic ligand **2**.



Figure 1. Brief synthesis of carbamate-based chiral ionic ligands (left side) and their most successful applications for asymmetric transfer hydrogenation reactions of ketones and imines (right side)

Financial support by the Austrian Science Fund (project P29146-N34) is gratefully acknowledged.

References:

[1]Noyori, R.; Hashiguchi, S., Acc. Chem. Res., **1997**, *30*, 97-102.

[2]Vasiloiu, M.; Gärtner, P.; Zirbs R.;. Bica, K., Eur. J. Org. Chem. 2015, 11, 2374-2381.

The influence of selected choline based DES on growth and survival abilities of *Bacillus licheniformis* and *Kluyveromyces lactis*

Karolina Adamczyk², Judyta Strakowska¹, <u>Leszek Broniarek</u>¹, Mateusz Hoppe¹, Jakub Hoppe^{1,3}, Marcin Śmiglak^{1,3*}

¹Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubiez, 46 61-612 Poznan, Poland

²BBH Biotech Polska sp. z o.o., ul. Rubiez, 46 61-612 Poznan, Poland ³Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89b, 61-614 Poznan, Poland E-mail: lbroniarek@gmail.com

The entirety of biology on Earth as we know is based on the fact that water is an indispensable factor for all living creatures to exist. Figuring out if there is a possibility to exist and thrive without water could give us answers to the question if it is possible that we are alone in the universe, as well as, open the possibilities to study a concept of life forms that are not carbon based.

Microorganisms chosen for the study were a mesophilic bacteria *Bacillus licheniformis* and yeast *Kluyveromyces lactis*. Both of them are used in industry for enzymes production. *B. licheniformis* is an efficient producer of alkaline serine protease (subtilisin), which is used in biological laundry detergents [1]. In turn, *K. lactis* is referred to one of the most important (biotechnologically and scientifically) non-Saccharomyces yeast, which effectively synthesizes the enzyme beta-galactosidase (lactase). Nowadays lactase is widely used in the food industry, especially for the production of lactose-free dairy products [2].

Microorganisms mentioned above were cultivated in increasing concentrations (from 0 to 100%) of nontoxic choline chloride-based DES. Precisely, six types of choline-based DES was chosen: choline chloride/urea, choline chloride/urea/ethylene glycol, choline chloride/urea/glycerol, choline chloride/glycerol, choline chloride/ethylene glycol/glycerol and choline chloride/ethylene glycol. In our work we have analyzed the ability maintain growth or survive in such harsh environment for the microorganisms. Cultivation of *B. licheniformis* and *K. lactis* were conducted in conditions appropriate for them.

This work was supported by the National Science Center (Poland), project OPUS (No. UMO-2015/19/B/NZ9/03711).

References:

[1] Schallmey, M.; Singh, A.; Ward, O. P., Canadian Journal of Microbiology, 2004, 50, 1-17.

[2] Athès, V.; Lange, R.; Combes, D. The FEBS Journal, 1998, 255, 206-212.

Continuous conversion of carbon dioxide to propylene carbonate using supported ionic liquids

<u>Aitor Sainz Martinez¹</u>, Christian Hauzenberger¹, Katharina Bica¹

¹ Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, 1060 Vienna, Austria e-mail: aitor.martinez@tuwien.ac.at

The implementation of CO_2 capture from flue gases provides an enormous stream of potential raw material for chemical production. In this regard, ionic liquids have attracted considerable interest as they can be used as tailored catalysts for the conversion of CO_2 to chemical feedstocks, such as cyclic carbonates [1]. However, while a large pool of catalytically active ionic liquids is available for this reaction, examples for the continuous conversion of CO_2 to cyclic carbonates are rare. This lack of ionic liquid-based continuous flow processes is surprising, as the liaison of ionic liquids with (supercritical) CO_2 and the convenient immobilization on solid support provides an ideal pre-requisite for this purpose [2].

In here, we present our investigations towards the use of supported ionic liquids as catalysts for the conversion of $scCO_2$ as solvent and reagent, aiming for the continuous production of propylene carbonate from propylene oxide and CO_2 . A set of eight ionic liquids based on imidazolium, ammonium or phosphonium core structures with halide anions and optional side chain functionalization was evaluated first under homogeneous conditions in batch mode. As to be expected, all ionic liquids with a hydroxyl group as substituent revealed to have high reactivity. In a similar way, ionic liquids with bromide as anion showed higher reaction rates following the order of nucleophilicity and size.

Eventually, the conversion of propylene oxide with CO_2 was further studied in continuous flow using supported ionic liquids on mesoporous silica. Considerable differences in the catalytic activity of ionic liquid in batch and continuous-flow processes were found, and the impact of ionic liquid structure, support material and immobilization strategy on long-term process stability will be discussed [3].

Financial support by the Hochschuljubiläumsstiftung der Stadt Wien (H-286949/2016) is gratefully acknowledged.

- [1]Cokoja, M.; Wilhelm, M.E.; Anthofer, M.H.; Herrmann, W.A.; Kuhn, F.E., *ChemSusChem* **2015**, *8*, 2436–2454.
- [2]Fehrmann, R.; Riisager, A.; Haumann, M., Supported Ionic Liquids: Fundamentals and Applications, Wiley-VCH Verlag, 1st ed., 2014.
- [3] Hauzenberger, C.; Sainz Martinez A.; Bica, K., ACS Sus. Chem. Eng. 2018, submitted.

Ionic liquids with bis-ammonium cation as new feeding deterrents

Damian Krystian Kaczmarek¹, Tomasz Klejdysz²

¹Department of Chemical Technology, Poznan University of Technology, ul. Berdychowo 4, 60-965 Poznan, Poland ² Institute of Plant Protection – National Research Institute, ul. W. Węgorka 20, 60-318 Poznan, Poland

E-mail: damian.rom.kaczmarek@doctorate.put.poznan.pl

During past decades, the growing demand for food production resulted in increase in the variety of crop protection methods focused no obtaining the highest possible yield. Protection of cereals does not end at the time of harvest, but also grains in warehouses should be protected. The occurrence of storage insects in granaries, *i.e.* grain weevil or confused flour beetle, is a significant problem, which often lead to decrease in the quantity as well as the quality of stored grain. The most cost-effective way of neutralizing the pest involves the use of antifeedants or insecticides. Insecticides may be a reliable choice in extreme cases of infestation, however they usually exclude the room from use for a prolonged period of time. Therefore, feeding deterrents should be used for preventive purposes, since they cause no major harm to the stored crops. Antifeedants proved to affect the insects' taste receptors, rendering the treated grain unattractive to the pest. [1]

Since the known natural antifeedants are rare compounds of complex chemical structure, a variety of synthetic substitutes have been studied concerning their deterrent activity. In particular, the ionic structure of quaternary ammonium salts allows the selection of the appropriate cation and anion to obtain the desired physicochemical and biological properties of the final product. Previous studies have shown that salts with a substituent possessing at least ten carbon atoms in the cation are usually characterized by high deterrent activity and may be utilized as efficient antifeedants. [2]

As the result of extensive research, ionic liquids containing a bis-ammonium cation and anions derived from popular and non-toxic sweeteners have been found to possess desirable properties. Such compounds possess enhanced thermal stability and high affinity to popular protic solvents, such as water, methanol or ethanol. These features, together with their high biological activity, confirmed in tests on several species of stored product pests, ensure their appropriate application potential.



Figure 1. Synthetic feeding deterrents.

- [1] Yan, Y.X.; Liu, J.Q.; Wang, H.W.; Chen, J.X.; Chen, J.C.; Chen, L.; Zhou, L.; Qiu M.H. Chem Biodivers, 2015, 12, 1040–1046.
- [2] Łęgosz, B.; Biedziak, A.; Klejdysz, T.; Pernak J. Eur. J. Chem., 2016, 7, 217–224.

Ionic liquids with tryptophanate anion

Daria Czuryszkiewicz¹

¹Department of Chemical Technology, Poznan University of Technology, ul. Berdychowo 4, 60-965 Poznan, Poland E-mail: daria.m.czuryszkiewicz@doctorate.put.poznan.pl

The synthetic plant growth hormones available currently on the market differ notably in mode of action, efficacy, toxicity to warm-blooded organisms and environmental impact. Therefore, many research centres are intensively working on designing new compounds that may be more effective, environmentally friendly as well as relatively cheap in production.

This work presents the efficient method of synthesis of new ionic liquids (ILs) with tryptophanate anion. The synthesis of ionic liquids with the tryptophanate anion proceeds as a result of the neutralization reaction. The optimization of the reaction time was carried out in a stoichiometric ratio (1 mole of tryptophan to 1 mole of hydroxide). The process was visualized using FTIR spectroscopy which allowed to determine the optimal synthesis time (30 minutes). The developed methodology allowed to obtain tetraalkylammonium tryptophanates with high yield exceeding 95%. The melting temperature measurement showed that all obtained tryptophanates have melting point lower than 100 °C, which allows them to be classified in the group of ILs. The analysis of NMR spectra allowed the confirmation of structures. Analysis of the ¹³C NMR spectrum showed a chemical shift from the carboxyl group of 10 ppm relative to the pure tryptophan, which indicates the change of the structure for the analysed products. Synthesized tryptophan compounds are vulnerable to atmospheric air which results in decomposition, therefore all obtained tryptophanates were stored in a vacuum desiccator under phosphorus pentoxide.

The performed studies showed that basic physicochemical properties – melting temperature and solubility of ILs were highly dependent on the structure of the utilized cation. All compounds are soluble in methanol, acetone, 2-propanol and DMSO and are not dissolved in ethyl acetate and hexane.



Figure 1. Synthesis of tetraalkylammonium tryptophanate.

Project financed by Ministry of Science and Higher Education Republic of Poland as a part of the "Diamond Grant", no DI2016018446.
Solvation of alcohols in Ionic Liquids: A pathway for the design of IL-based solvents

Inês C. M. Vaz, Margarida Bastos, Luís M. N. B. F. Santos CIQUP, Department of Chemistry and Biochemistry, University of Porto, Porto, Portugal E-mail: inescvaz@gmail.com

The properties and functionality of Ionic Liquids (ILs)-based materials can be fine-tuned by the correct choice of cation/anion and by the possibility of mixing other ionic or molecular solutes. For a rational design of ILs for specific applications a better understand of the interplay between the molecular interactions, nanostructuration and different properties is mandatory. With this aim, our group has been using alcohols as molecular solutes to study ILs solvation. The choice of alcohols is related with the presence of the hydroxyl group which can interact with the IL by dispersive or H-bonds interactions whereas the non-polar tail which can interact with the non-polar domain of the IL. In this work, we will present results regarding the solution/solvation of different alcohols in different ionic liquids, putting together the highlights of our recent work using isothermal titration calorimetry (ITC).



Figure 1. Schematic representation of the main interactions present in alcohol-IL system.

The solvation of propanol, butanol and pentanol in ILs of the series $[C_NC_1im][NTf_2]$, recently published [1], will be presented together with more recent results concerning the solvation of linear alcohols of higher molecular weight in the same IL series. The obtained results reflect the nanostructuration of Ionic Liquids, evidenced the critical alkyl size CAS, and suggest the preferential location of the alcohols at the interface between polar and non-polar domains of the ILs. The solvation of propanol in ILs with different cations and anions [2] will also be discussed, allowing a comprehensive analysis of the anion and cation effect.

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, and to FEDER for the financial support to Centro de Investigação em Química, University of Porto (CIQUP) through the project Pest-C/QUI/UI0081/2013 and the SAM project Norte-01-0145-FEDER-000028. Inês C. M. Vaz acknowledges the financial support from Fundação para a Ciência e Tecnologia (FCT) for her PhD Research Grant PD/BD/114575/2016.

- Vaz, I.C.M.; Bhattacharjee, A.; Rocha, M.A.A.; Coutinho, J.A.P.; Bastos M.; Santos, L.M.N.B.F. Phys. Chem. Chem. Phys., 2016, 18, 19267-19275.
- [2] Vaz, I.C.M.; Bastos, M.; Bernardes, C.E.S.; Canongia Lopes, J.N.; Santos, L.M.N.B.F. *Phys. Chem. Chem. Phys.*, **2018**, *20*, 2536-2548.

Alkynes hydroboration in ionic liquids – green approach to alkenyl boronates

<u>Jakub Szyling</u>^{1,2}, Kinga Stefanowska^{1,2}, Mateusz Klarek^{1,2}, Adrian Franczyk¹, Hieronim Maciejewski^{2,3}, Jędrzej Walkowiak^{1,*}

¹Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, 61-614 Poznan, Poland ²Faculty of Chemistry Adam, Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznan, Poland ³Poznan Science and Technology Park, Adam Mickiewicz University Foundation Rubiez 46, 61-612 Poznan, Poland. E-mail: j.szyling@amu.edu.pl

Transition-metal (TM) catalyzed hydroboration of alkynes provides a straightforward, 100% atom economical, and simple method for the synthesis of unsaturated organoboron compounds. They are one of the most versatile intermediates currently available in organic chemistry transformations [1]. The homogeneous character of this reaction provides high process selectivity but on the other hand, such traditional catalytic pathways suffer from the necessity of the use of a large amount of volatile organic solvents to ensure appropriate solubility of reaction components and catalyst. The contamination of the products by TM species and especially problems with the recovery and reuse of the molecular, expensive catalyst, are the biggest drawbacks of homogeneous catalysis. For these reasons, the effective methods for the catalyst immobilization, which will build long lasting and efficient processes, are still the challenge for modern synthesis of organoboron compounds [2].

The investigation into alkynes hydroboration in environmentally benign media for catalyst immobilization has been poor explored [3]. Recently, we described for the first time an effective hydroboration of terminal and internal alkynes in supercritical CO_2 (sc CO_2) under repetitive batch mode. Self-dosing catalyst system allowed to its multiple reuse and to avoid contamination of the products by TM [4].

In this communication, a highly efficient synthetic protocol leading to alkenyl boronates *via* catalytic hydroboration of various alkynes by the immobilization of the commercially available catalyst Ru(CO)Cl(H)(PPh₃)₃ in ionic liquids (RuH@IL) or in the biphasic IL/supercritical CO₂ system (RuH@IL/scCO₂) will be presented. This approach permitted the reuse of the molecular complex anchored to IL, making these catalytic systems the most productive for the recyclable hydroboration of alkynes according to the methods previously described in the literature.

Financial support from The National Centre for Research and Development in Poland, Lider Programme No. LIDER/26/527/L-5/13/NCBR/2014.

- [1] Burgess, K.; Ohlmeyer, M. J., Chem. Rev., 1991, 91, 1179-1191.
- [2] Cole-Hamilton, D. J.; Science, 2003, 299, 1702-1706.
- [3] Yao, Z.-J.; Hong, S.; Zhang, W.; Liu, M.; Deng, W., *Tetrahedron Lett.*, **2016**, *57*, 10913-10917.
- [4] Szyling, J.; Franczyk, A.; Stefanowska, K.; Klarek, M.; Maciejewski, H.; Walkowiak, J., *ChemCatChem*, **2018**, *10*, 531-539.

Micellar route of the synthesis of alkyl xylosides - an unexpected effect of amphiphilic imidazolium ionic liquids

Janusz Nowicki, Julia Woch, Małgorzata Mościpan

Institute of Heavy Organic Synthesis "Blachownia", Kedzierzyn-Koźle, Poland E-mail: nowicki.j@icso.com.pl

Pentosane surfactants, in particular alkyl xylosides, are characterized by excellent surface and application properties compared to alkyl glucosides. The basic method of the synthesis of alkyl xylosides is Fisher glycosidation carried out in elevated temperature in the presence of acidic catalysts.

Recently, we have described an innovative method of the synthesis of alkyl glucosides according to Fisher glucosidation method from glucose and aliphatic alcohols. We demonstrated that dodecylbenzenesulfonic acid effectively catalyze the formation of corresponding alkyl glucosides [1]. It's well known, that alkylimidazolium hydrogen sulfate ILs are characterized by both acidic and surfactant properties [2,3]. Their dual functionality, also in relation to ILs homologous series effect, has been confirmed e.g. in epoxide ring opening reaction [2]. In this presentation we would like to present an interesting and innovative method of the synthesis of alkyl xylosides in micellar route with the use of acidic surfactant ILs.

In model reaction of xylose with 1-octanol into alkyl xylosides (90 °C, 24 hr) in the presence of homologous series of 1-alkyl-3-metylimidazolium hydrogensulfate ILs as surfactant catalysts we achieved very high conversion of xylose (Figure 1). The selectivity to alkyl xylosides were > 95%, which confirm high efficiency of developed method [4].



Figure 1. Effect of amphiphilic ILs on xylose conversion

Figure 1 showed also the effect of homologous series of imidazolium ILs. This effect is related to surfactant properties of imidazolium ILs, in particular with the length of alkyl chain in IL molecule.

Authors acknowledges support for this research by the Polish Ministry of Science and Higher Education for statutory research. This work was also done within the frameworks of COST Actions MP1106 "Smart and green interfaces - from single bubbles and drops to industrial, environmental and biomedical applications (SGI)" and CM 1206 "EXIL - Exchange on Ionic Liquids".

- [1] Nowicki, J.; Woch, J.; Mościpan, M.; Nowakowska-Bogdan, E., *Appl. Catal. A General*, **2017**, *539*, 13-18.
- [2] Nowicki, J.; Łuczak, J.; Stańczyk, D., RSC Adv., 2016, 6, 11591-11601.
- [3] Jungnickel, Ch.; Łuczak, J.; Ranke, J.; Fernández, J.F.; Müller, A.; Thöming, J., *Colloid Surface* A, **2008**, *316*, 278-284

Paraffin based emulsions as impregnates for food packaging

Julia Woch¹, Jolanta Iłowska¹, Jan Gniady, ¹ Janusz Nowicki¹, Rafał Grabowski¹, Jolanta Drabik²

¹ Institute of Heavy Organic Synthesis "Blachownia", Kedzierzyn-Kozle, Poland ² Institute for Sustainable Technologies – National Research Institute, Radom, Poland e-mail: woch.j@icso.com.pl

Among different types of packaging materials, paper and paperboard are still irreplaceable in food industry. As those fibrous materials show little or no barrier properties, for the purpose of food storage these materials have to be impregnated. Biodegradable paraffin emulsions, prepared with consideration of green chemistry principles, are suitable impregnating agents. All ingredients of paraffin emulsion must be non-toxic for human.

The poster presents overall information about the interdisciplinary project EKOPOLPAK linking the scientific approach and industrial activities, aiming to develop secure and cost-effective food packaging comprising safe and renewable raw materials. The work is thematically divided and carried out in eight entities as the Consortium named ECOBOX.

New impregnates for paper and cardboard packaging are developed by ICSO based on reasonably priced, safe, paraffin-based raw materials and novel emulsifiers, being the natural resources derivatives. Compositions are analyzed for content of heavy metals, PAHs or other xenobiotics. Their stability over time is evaluated by light scattering. Biodegradability of the impregnates is determined by OECD methods. Rheological studies are applied for simulation of coating of emulsions on paper and cardboard.

Final packaging undergo analyses to evaluate their quality and examination in terms of global and specific migration and organoleptic assessment, according to procedures required by UE legislation. Trial batches undergo technical evaluation. The methodology of coating with emulsions and the paper recycling procedure are developed by industrial partners.

This work was supported by The National Centre for Research and Development in the program BIOSTRATEG II (BIOSTRATEG/298537/7/NCBR/2016).

Biobased chiral ionic liquids with monoterpene moiety

J. Feder-Kubis¹

¹ Wrocław University of Science and Technology, Faculty of Chemistry, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland E-mail: joanna.feder-kubis@pwr.edu.pl

Various series of chiral ionic liquids containing (1R,2S,5R)-(–)-menthol substituent were designed, synthesized and characterized. Their structural views of presented salts differ significantly and contain following elements: ammonium, asymmetric imidazolium, symmetric imidazolium and pyridinium cation with the alkyl or alkoxymethyl chain (with chain length from CH₃ to C₁₄H₂₉), and numerous types of the organic and inorganic anions (see Scheme 1).

The synthesized chiral salts indicate a number of interesting biological properties, including: (i) antimicrobial [1], (ii) stabilizing and activating of various enzymes [2], (iii) as an effective agent of wood preservatives [3], (iv) and stimulating the plant's immune system [4].



Scheme 1. Novel synthesis of mesoporus silica nanospheres using task-specific ionic liquids with (+)-fenchol moiety

The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wroclaw University of Technology.

- [1] Feder-Kubis, J.; Tomczuk, K. Tetrahedron, 2013, 69, 4190-4198.
- [2] Feder-Kubis, J.; Bryjak, J. Acta Biochim. Pol., 2013, 60, 741-745.
- [3] Zabielska-Matejuk, J.; Feder-Kubis, J.; Stangierska, A.; Przybylski, P. *Holzforschung*, **2017**, *71*, 9, 751-757.
- [4] Feder-Kubis, J.; Śmiglak, M.; Pospieszny, H.; Lewandowski, P.; Kukawka, R. App. of patent no. P-415275; date of filing the innovation: 14.12.2015.

Task-specific ionic liquids containing natural occurring bicyclic terpene derivative as effective template for mesoporous silica nanoparticles

J. Feder-Kubis¹, K. Wiercigroch-Walkosz², M. Karbowiak², Katarzyna Materna³

¹ Wrocław University of Science and Technology, Faculty of Chemistry, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

² University of Wrocław, Faculty of Chemistry, 14 Joliot-Curie Str. 50-383 Wrocław, Poland
 ³ Poznan University of Technology, Department of Chemical Technology, 60-965 Poznan, Poland E-mail: joanna.feder-kubis@pwr.edu.pl

Ionic liquids (ILs) could behave like surfactants and be a good template to synthesize new type of morphology of mesoporous nanomaterials. For that reason, new task-specific ionic liquids containing bicyclic terpene moiety were designed and prepared. As a starting materials chiral pool of monoterpene from the renewable natural plant resources were used, namely: (1R)-endo-(+)-fenchol. Obtained 3-alkyl-1-[(1R)-endo-(+)-fenchoxymethyl]imidazolium chlorides belong to Chiral Ionic Liquids (CILs), where the chirality resides in the cation and is associated with the presence of optical active monoterpene. Discussed salts are hydrophobic, air- and moisture-stable under ambient conditions. Moreover, they are non-volatile and non-flammable. Their surface active properties were determined by the drop shape method. The critical micelle concentration (CMC) decreased with increasing hydrophobic group chain length, and thus the lowest value, equal to 0.3 mM, was obtained for R = C₁₄H₂₉.

Respectively, a novel synthesis of mesoporous silica nanospheres (MSNs) via a facile twophase system, using new task-specific ionic liquids as a template, were provided. The synthesis of MSNs is carried out in a biphasic system in which silica precursor is delivered heterogeneously from a top organic layer to the bottom aqueous layer containing a base catalyst and CILs. The active substance could be incorporate into the silica shell of MSNs during its growth or after synthesis of MSNs using the microemulsion method. The porosity of the silica shell and type of incorpolation affects the quantity of the incorporated substance.



Scheme 1. Novel synthesis of mesoporus silica nanospheres using task-specific ionic liquids with (+)-fenchol moiety

This research was financed by the National Science Centre (Poland) grant no. 2013/09/D/ST5/03904.

Ionic Liquids for photonics

Krzysztof Rola¹, Adrian Zając², Joanna Cybińska^{1,3}, Marcin Śmiglak², Katarzyna Komorowska^{1,4}

¹ Wroclaw Research Centre EIT+, ul. Stablowicka 147, 54-066 Wroclaw, Poland ²Poznan Science and Technology Park of Adam Mickiewicz University Foundation, ul. Rubiez 46, 61-612 Poznan, Poland

³ Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland
 ⁴Department of Optics and Photonics, Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology, Wybrzeże Wyspianskiego 27, 50-370 Wroclaw, Poland E-mail: katarzyna.komorowska@eitplus.pl

In recent years there has been a growing interest in new methods of nano- and microstructuring of polymers due to the increasing popularity of application of polymer or polymerbased materials in photonics. Polymer-based sensors and biosensors are of particular interest, especially in low-cost disposable POCT (point-of-care testing) devices. Broadly defined polymer materials are a material platform which may contain passive as well as active components because of a wide range of additional functionalities that can be added to a material. Modifying, mixing and doping of polymers does not result in a loss of their polymeric properties, while giving them new functions.

We discuss a possibility of application of ionic liquid in photonics - a new method of structures fabrication and synthesis of nanocrystals. The nano- and micro- structure fabrication is based on polymerization of ionic liquids by electron and ion beam irradiation [1]. Nature of ionic liquids makes it possible to use vacuum techniques and consequently put a substrate with an ionic liquid layer into a chamber of SEM (scanning electron microscope) equipped with FIB (focused ion beam) source. The high resolution of SEM and the small spot size of the electron beam allows one to fabricate structures of nanometric size. The ionic liquid or the polymerizable mixture can gain the new functionality, such as the change of refractive index or the light emission through doping with nanocrystals or luminophores. In our research the nanophosphates obtained in reaction in task specific phosphate ionic liquids were used. For the first study the Eu³⁺ and Tb³⁺ doped orthophosptaes were chosen, as they are stable and exhibit very efficient luminescence and relatively long life times of emission.

The work financed by the National Science Center within the Grant Opus UMO-2015/19/B/ST8/02761

References:

[1] Minamimoto, H.; Irie, H.; Uematsu, T.; Tsuda, T.; Imanishi, A.; Seki, S.; Kuwabata, S. *Langmuir*, **2015**, *31*, 4281–4289.

Synthesis of alkenyl-substituted silsesquioxanes and spherosilicates by hydrosilylation reaction in conventional and non-conventional solvents

<u>Kinga Stefanowska</u>^{1,2}, Jakub Szyling^{1,2}, Katarzyna Salamon^{1,2}, Adrian Franczyk¹, Jędrzej Walkowiak¹

¹Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, 61-614 Poznan, Poland
² Faculty of Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznan, Poland E-mail: kinga.stefanowska@amu.edu.pl

Alkenyl-substituted silsesquioxanes and spherosilicates are among the most interesting examples of polyhedral oligomeric silsesquioxanes (POSS). These compounds have a unique, threedimensional structure which is based on the nanometer-sized inorganic core surrounded by organic functional groups [1]. Additionally, the presence of unsaturated double bonds in the molecules of alkenyl-substituted derivatives makes them extremely high reactive in a number of commonly used in organic synthesis reactions [2]. These transformations can lead to obtain derivatives with conjugated π -bonds, useful components for the preparation of organic or polymer light-emitting diodes (OLED, PLED) [3].

Numerous examples of alkenyl silsesquioxanes and spherosilicates were previously synthesized by hydrosilylation [4], silylative coupling [5], cross-metathesis [5] and Heck [6] reactions. However, only hydrosilylation of the terminal and internal carbon-carbon triple bonds provides the opportunity for the synthesis of 2-substituted- and 1,2-disubstituted-1-ethenyl-derivatives.

In the communication we report our studies on the hydrosilylation of a wide spectrum of terminal and internal alkynes with alkyl-, aryl- as well as heteroatom-containing (SiR₃, GeR₃) substituents with monofunctional silsesquioxane (HSiMe₂O)(*i*-Bu)₇Si₈O₁₂) and octafunctional spherosilicate (HSiMe₂O)₈Si₈O₁₂. By developed method, a series of new alkenyl-substituted silsesquioxanes and spherosilicates were obtained in high yields and characterized by ¹H, ¹³C, ²⁹Si NMR, FT-IR spectroscopy and ESI HR-MS spectrometry. The influence of the alkynes structure on the hydrosilylation rate (monitored by IR-*in situ*) and selectivity of the process will be presented. Moreover, detailed research on the optimization of reaction conditions concerning uses of homogeneous catalysts as well as conventional organic solvents and compressed or supercritical CO₂ will be also discussed.

Financial support from The National Centre for Research and Development in Poland, Lider Programme No. LIDER/26/527/L-5/13/NCBR/2014 is gratefully acknowledged.

- [1] Li, G.; Wang, L.; Ni, H.; Pittman, Jr. C. U., J. Inorg. Organomet. Polym., 2001, 11, 123-154.
- [2] Cheng, G.; Vautravers, N.R; Morris, R.E; Cole- Hamilton, D.J., Org. Biomol. Chem., 2008, 6, 4662-4667.
- [3] Chan, K.L.; Sonar, P.; Sellinger, A., J. Mater. Chem., 2009, 19, 9103-9120.
- [4] Cordes, D.B.; Lickiss, P.D.; Rataboul, F., Chem. Rev., 2010, 110, 2081-2173.
- [5] Żak, P.; Marciniec, B.; Majchrzak, M.; Pietraszuk, C., J. Organomet. Chem., 2011, 696, 887-891.

Synthesis a new chiral pyrrolidinium organic salt based on terpene alcohol *endo*-(1S)-borneol

Marcin Gano, Ewa Janus

West Pomeranian University of Technology, Szczecin, Faculty of Chemical Technology and Engineering, Institute of Chemical Organic Technology, Pulaskiego 10, 70-322 Szczecin, Poland E-mail: mgano@zut.edu.pl

A series a new chiral pyrrolidinium organic salts based on natural terpene alcohol (-)-borneol (endo-(1S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ol) and tertiary amine 1-(2-hydroxyethyl)pyrrolidine have been synthesized in multistep reaction (Figure 1).



Figure 1. Three steps of synthesis of chiral pyrrolidinium organic salts

The structures of all 7 synthesized organic salts were determined by NMR and HRMS analysis. Physicochemical properties, such as melting point, thermal stability, density, dynamic viscosity optical rotation, refractive index and phase transition temperatures were determined. Salts containing $N(SO_2CF_3)_2$ and $N(SO_2C_2F_5)_2$ anion are liquids at room temperature. Salts with $C_4F_9SO_3$, PF_6 and BF_4 anions have melting point below 100°C. All salts are stable to 200°C, except of salt with Cl anion. Salts with $N(SO_2CF_3)_2$, $N(SO_2C_2F_5)_2$, $C_4F_9SO_3$, PF_6 and BF_4 anions decomposed in two stages. All compounds are optical active. Chiral ionic liquid with $N(SO_2C_2F_5)_2$ anion have higher value of density and dynamic viscosity in comparison to $N(SO_2CF_3)_2$.

Chiral ionic liquids can be used as solvents in many asymmetric organic reaction.

Green approaches towards the synthesis of quinazolinone derivatives

Maria Bairaktari¹, Ioanna Kostopoulou¹, Andromachi Tzani¹ and Anastasia Detsi^{1*}

¹Laboratory of Organic Chemistry, Department of Chemical Sciences, School of Chemical Engineering, National Technical University of Athens, Iroon Polytechniou 9, Zografou Campus, GR 15780, Athens, Greece *Email: marw.mp@windowslive.com

Quinazolinones belong to an interesting class of heterocycles that possess a wide range of biological and pharmaceutical activities like anticancer, antimicrobial, anti-inflammatory. As part of our ongoing research aimed at the development of greener methodologies for the efficient synthesis of bioactive heterocycles [1-2], we hereby present the synthesis of novel quinazolinone analogues using green chemistry tools.

In the first part of the study, the synthesis of 2-methyl-3-amino-quinazolin-4(3H)-one analogues [Fig. 1, (I)] was accomplished through a two-step methodology starting from anthranilic acids, using Microwave Assisted Organic Synthesis, MAOS). The developed synthetic approach provides the desired compounds in decreased reaction times, higher yields and simpler work-up as compared to the conventional synthetic methods.



Fig.1: General structure of quinazolinone derivatives

In the second part, we attempted to synthesize guinazolinone and dihydroquinazolinone analogues using green solvents, such as Natural Deep Eutectic Solvents (NaDES). NaDES are eutectic mixtures derived from natural products such as tartaric acid, choline chloride, carbohydrates etc., they are recyclable and biodegradable and their properties can be tailored to meet the demands of the reactions. In this context, we have synthesized the NaDES choline chloride / tartaric acid in 2:1 ratio and have used it as a solvent and catalyst for the synthesis of 2,3-disubstituted dihyroquinazolin-4(1H)-ones by a multicomponent reaction (MCR) among isatoic anhydride, benzaldehydes and aromatic amines. The reactions proceed smoothly and provide the products in good yields in short reaction times. The same NaDES was successfully used for the synthesis of quinazolinones of type (I), via the MCR among anthranilic acid, benzoyl chloride and aniline.

The next goal is to study the developed synthetic approach using NaDES for MCRs in combination with the microwave or ultrasonic irradiation techniques, in order to achieve higher yields and shorter reaction times.

- [1] Tzani, A.; Douka, A.; Papadopoulos, A.; Pavlatou, E.A.; Voutsas, E.; Detsi, A. ACS Sustainable Chemistry and Engineering, 2013, 1, 1180-1185.
- [2] Tzani, A.; Elmaloglou, M.; Kyriazis, C.; Aravopoulou, D.; Kleidas, I.; Papadopoulos, A.; Ioannou, E.; Kyritsis, A.; Voutsas, E.; Detsi, A. Journal of Molecular Liquids, 2016, 224 (Part A), 366-376.

Separation of ethylbenzene/styrene systems using ionic liquids in ternary LLE

Monika Karpińska,¹ Michał Wlazło,¹ and Urszula Domańska² ¹Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland ² Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland E-mail: mkarpinska@ch.pw.edu.pl

The aim of this work was to study the applicability of three dicyanamide-based ionic liquids (ILs) in the separation of ethylbenzene/styrene compounds. The experimental values for liquidliquid phase equilibrium (LLE) were obtained for various ternary mixtures of {IL (1) + styrene (2) + ethylbenzene (3)} at T = 298.15 K and ambient pressure. Three ILs have been studied: 3-(2methoxyethyl)-1-methylimidazolium dicyanamide, $[(C_2OCH_3)MIM][DCA],$ 1-(4-methoxy-4oxobutyl)-3-methylimidazolium dicyanamide, [(C₃COOMe)MIM][DCA], choline dicyanamide, [Chol][DCA] [1]. The chromatography analysis shown that the studied ILs have not been found in the raffinate phase, which is very convenient for new technology. The effect of IL cation was examined with respect to the calculated selectivities and the solute distribution ratios of styrene extraction. The measurements shown interesting results and were compared with our previous data [2,3]. These chosen ILs have shown good results in terms of selectivity and solute distribution ratio. It was observed that the best separation effectiveness has [(C₃COOMe)MIM][DCA] in comparison with other studied ILs in this work, but lower than [N-C₃OHMIM][DCA] presented by us earlier. The non-random two liquid NRTL model was used to correlate experimental tie-lines.

This work has been supported by the Ministry of Science and Higher Education in Poland in the years 2017–2020 (UMO-2016/23/B/ST5/00145).

- [1] Karpińska, M.; Domańska, U. J. Chem. Thermodyn., 2018, submitted.
- [2] Karpińska, M.; Domańska, U.; Wlazło, M. J. Chem. Thermodyn., 2016, 103, 423-431.
- [3] Karpińska, M.; Wlazło, M.; Domańska, U. J. Sol. Chem., 2018, accepted.

Theoretical study of the addition of solvents to ionic liquids

<u>Nádia M. Figueiredo¹</u>, Iullia V. Voroshylova^{1,2}, Volodymyr A. Koverga¹, M. Natália D. S. Cordeiro¹

¹Departamento de Química e Bioquímica, LAQV@REQUIMTE, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal ²Departamento de Química e Bioquímica, CIQ (UP), Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal E-mail: nadiamartins91@gmail.com

The imidazolium based ionic liquid family has been extensively studied in recent years, combining these cations with different anions. The intrinsic properties of ionic liquids are affected by dilution with molecular solvents, such as water or alcohols, altering their aggregation, self-diffusion, viscosity and electrical conductivity, for example.[1]

The aim of this work is to employ classical molecular dynamics (MD) simulations to study the structural and dynamic properties of pure 1-ethyl-3-methylimidazolium dicyanamide ([EMIM⁺][DCA⁻]) ionic liquid and its binary mixtures with water and alcohols, at room temperature (298.15K), in wide concentration range. MD simulations were carried out using the GROMACS 5.1.4 package. The OPLS-AA force field, refined as described in [2] was used, as it showed good agreement between experimental and theoretical values. The results are discussed in terms of radial distribution functions, coordination numbers and H-bonds analyses. Density, conductivity, selfdiffusion and aggregation behavior are also assessed.

This study represents the first step in an ongoing comprehensive MD study of these systems, and providing molecular-level insight into their structural and dynamic properties with relevance for future applications in the design of nanostructures, applications in catalysis, electrochemistry or synthesis.[3]

This work received financial support from Fundação para a Ciência e a Tecnologia (FCT/MEC) through national funds and cofinanced by the European Union (FEDER funds) under the Partnership Agreement PT2020, through Projects UID/QUI/50006, POCI/01/0145/FEDER/007265, and NORTE-01-0145-FEDER-000011 (LAQV@REQUIMTE), as well as through Projects UID/QUI/00081/2013 and POCI-01-0145-FEDER-006980 (CIQUP). I.V.V. acknowledges also FCT postdoc grant with reference SFRH/BPD/97918/2013.

- Carrete, J.; Méndez-Morales, T.; Cabeza, O.; Lynden-Bell, R.M.; Gallego, J.L.; Varela, L.M., J. Phys. Chem. B, 2012, 116, 5941-5950.
- [2] Doherty, B.; Zhong, X.; Gathiaka, S.; Li, B.; Acevedo, O., J. Chem. Theory Comput., **2017**, *13*, 6131-6145.
- [3] Pádua, A.A.H.; Costa Gomes, M.F.; Canongia Lopes, J.N.A.; Acc. Chem. Res., 2007, 40, 1087-1096.

Surface-Active Amino Acid Ionic Liquids

Paula Ossowicz¹, Ewa Janus¹

¹West Pomeranian University of Technology Szczecin, Faculty of Chemical Technology and Engineering, Institute of Organic Chemical Technology, Pułaskiego Str. 10, 70-322 Szczecin, Poland E-mail: possowicz@zut.edu.pl

A series of surface-active ionic liquids based on the amino acid anions and alkyltrimethylammonium cation, where alkyl was dodecyl, hexadecyl or octadecyl was synthesized. These ionic liquids were characterized by surface tension (γ_{CMC}) and the critical micelle concentration (CMC) in aqueous solutions. The surface excess (Γ_{max}) and minimum area per molecule (A_{min}) were also calculated. The aqueous solutions containing alkyltrimethylammonium salts of amino acids exhibit similar surface activity to the commonly used surfactants.

New salts combining a alkyltrimethylammonium cation and amino acid anion were synthesized via a two-step procedure showed in scheme 1. Their synthesis was characterized by high overall yield and simple purification. In the first step the halide anion in alkyltrimethylammonium halide was changed with a hydroxide anion, using ion exchange resin. In the second step, a neutralization reaction between amino acid and alkyltrimethylammonium hydroxide was conducted. Various amino acids, such as glycine, L-valine, L-leucine, L-isoleucine, L-methionine, L-histidine, L-arginine were used to the synthesis new salts.



Scheme 1. General synthesis of alkyltrimethylammonium amino acid salts

Structures of synthesized compounds were confirmed by ¹H NMR, ¹³C NMR and FTIR. The properties such as specific rotation, thermal stability, solubility in typical solvents were also determined and compared. All prepared salts, except glycine salts, are optically active. Alkyltrimethylammonium salts rotate the plane of polarized light in the same direction as starting amino acid. Exceptions were hexadecyltrimethylammonium and octadecyltrimethylammonium L-histidinate, which rotated in opposite direction. The initial decomposition temperatures for alkyltrimethylammonium salts are between 160.2 and 212.2°. The highest thermal stability demonstrated octadecyltrimethylammonium L-histidinate and the lowest – dodecyltrimethylammonium glycinate.

Synthesized salts were soluble in water and generally in ethanol and acetone, but they did not dissolve in ethyl acetate, diethyl ether or n-hexane.

These ionic liquids can be potential used as ingredients of hair cosmetics, skin-care cosmetics, disinfectant cleaners and other products. Amino acid part can enhance conditioning effect on hair and skin.

Catalytic hydroboration of 1,3-diynes in traditional and green solvents

<u>Tomasz Sokolnicki^{1,2}</u>, Mateusz Klarek^{1,2}, Jakub Szyling^{1,2}, Kinga Stefanowska^{1,2}, Adrian Franczyk¹, Jędrzej Walkowiak^{1,*}

¹Centre for Advanced Technologies, Adam Mickiewicz University, Umultowska 89c, 61-614 Poznan, Poland ²Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89B, 61-614 Poznan, Poland E-mail: tomasz.sokolnicki@amu.edu.pl

The hydroboration reaction belongs to the most convenient methods used for the synthesis of unsaturated organoboron compounds. Alkenyl boronates due to its high reactivity, low toxicity and ease of storage are versatile intermediates in synthetic organic chemistry, in bond forming reactions and other demetallation protocols e.g. Suzuki coupling, protodeborylation, halodeborylation [1,2]. The importance of organoboron chemistry was recognized with two Nobel Prizes awarded to H. Brown in 1979 and A. Suzuki in 2010 for development of new powerful methods to the introduction of boryl functionalities into organic molecules.

Addition of boranes to unsaturated bonds proceeds in elevated temperatures without the catalyst; however, most of these reactions are performed in the presence of TM-complexes, which provide appropriate regio- and stereoselectivity. Hydroboration is usually carried out under homogeneous conditions in organic, volatile solvents, which ensure process efficiency. On the other side, homogeneity of the reaction mixture generates problems with product separation from transition metal complex and reuse of expensive molecular catalysts [3].

For this reasons, many researchers are constantly looking for new procedures that can overcome these drawbacks. One of the solutions is an application of neoteric solvents e.g. scCO₂, polyethylene glycols (PEGs), ionic liquids (ILs) or fluorous media. Such procedure, on the one hand, provides elimination of toxic solvents and on the other one allows for immobilization of catalyst in a reaction medium and its reuse, what makes a process more sustainable and green [4, 5].

In the communication, a new protocol for the hydroboration of 1,3-diynes in the presence of commercially available ruthenium catalysts in traditional and green solvents will be presented. The optimization of the hydroboration parameters to obtain high products yield and selectivity, as well as, the influence of the solvent type on process efficiency will be also discussed.

Financial support from The National Centre for Research and Development in Poland, Lider Programme No. LIDER/26/527/L-5/13/NCBR/2014

- (a) Pereira, S.; Srebnik, M. Organometallics, **1995**, *14*, 3127–3128; (b) Szyling, J.; Franczyk, A.; Pawluć, P.; Marciniec, B.; Walkowiak, J. Org. Biol. Chem., **2017**, *15*, 3207-3215; (c) Pyziak, J.; Walkowiak, J.; Marciniec, B. Chem. Eur. J., **2017**, *23*, 3502-3541.
- [2] Suzuki, A. Angew. Chem. Int. Edit, 2011, 50, 6722-6737.
- [3] Barbeyron, R.; Benedetti, E.; Cossy, J.; Vasseur, J.J.; Arseniyadis, S.; Smietana, M. *Tetrahedron*, **2014**, *70*, 8431-8452.
- [4] Jessop, P.G. Green Chem., 2003, 5, 123-128.
- [5] (a) Subramanian, B. Ind. Eng. Chem. Res., 2010, 49, 10218–10229; (b) Szyling, J.; Franczyk, A.; Stefanowska, K.; Klarek, M.; Maciejewski H.; Walkowiak, J. ChemCatChem, 2018, 10, 485-485.

Development a new and efficient methods for the synthesis of ionic liquids through the ion exchange reactions carried out in a continuous flow conditions

Anna Pawlowska-Zygarowicz^{1,2}, Dawid Zielinski², Marcin Smiglak^{1,2*}

 ¹ Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 b, 61-614 Poznan, Poland
 ² Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubież 46, 61-612 Poznan, Poland *E-mail: anna.pawlowska@amu.edu.pl

The first described synthesis of ionic liquids through metathesis concerned ILs that are not sensitive to water, moisture from the air and are chemically stable.[1] However, the dynamic development of this field, forces to search for more sophisticated methods of synthesis of ionic liquids (depending on the choice of cations and ions). In the literature, one cannot find many information about research on new methods of synthesis of ionic liquids using ion exchange reaction carried in a continuous flow conditions using a packed column. This is an interesting alternative to the commonly used ion exchange reactions, which are performed in separatory funnels, using for example methylene chloride(acetone)/water solvent biphasic systems.[2] The use of the continuous flow conditions allows for the recycle and reuse of methylene chloride and regeneration of the column. As a result of the performed research we optimize proposed reactions with the respect to the flow rate of reactants and solvent to obtain ionic liquids with high purity and high yield.

The first step in the synthesis of selected ionic liquids was the quaternization reaction between methylpyrrolidine or methylpiperidine and chlorohexane to obtain the ionic liquids. Then, obtained compounds were submitted to ion exchange reaction in flow through the column with filling. The column was made of glass, and the ion exchange was carried out either by (i) pumping liquid phase containing the IL precursor through the solid phase containing exchanged anion or (ii) exchange reaction where in one liquid phase IL precursors is dissolved and in the second phase the exchanged anion is dissolved (using parallel and countercurrent flow).

At the end, it is important to determine the purity of the obtained ionic liquids. It is equally important to determine if all contaminants, that have an effect on the properties of the resulting liquid, have been removed after the purification procedure. In our studies we have used ion chromatography (IC) as it is widely used analytical method to determine the purity of the obtained ionic liquids.

This work was supported by the National Science Centre (Poland), project PRELUDIUM (No. UMO-2017/25/N/ST4/02573).

- [1] Wilkes, J.S.; Zaworotko, M.J., Chem. Commun., 1992, 0, 965-967.
- [2] Dinares, I.; Garcia de Miguel, C.; Ibanez, A.; Mesquida, N.; Alcalde, E., *Green Chem.*, **2009**, *11*, 1507-1510.

New methods of carrying out chemical reactions with the use of flow reactors

<u>Anna Pawlowska-Zygarowicz</u>^{1,2}, Rafal Kukawka^{1,2}, Dawid Zielinski², Marcin Smiglak^{1,2*}

 ¹ Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 b, 61-614 Poznan, Poland
 ² Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubież 46, 61-612 Poznan, Poland *E-mail: anna.pawlowska@amu.edu.pl

The main goal of scientific research is to conduct chemical reactions using flow reactors (microreactor made of glass or silicon and a glass column with filling) in order to optimize and intensify them. The advantages of microreactors, such as the ability to conduct synthesis at high temperature, intensified heat exchange or controlled reactants retention time in the reactor, cause wide interest in this technique among scientists. In presented work microreactors were used to develop new method for the synthesis of organofunctional siloxanes via hydrosilylation reaction, with higher than before, or equal, efficiency and selectivity, with simultaneous lowering of the process temperature and catalyst concentration.[1] In addition, by using ionic liquids as solvents for the Karstedt catalyst, it was possible to recover the ionic liquid/catalyst phase and use it in subsequent catalytic cycles, thereby further reducing catalyst and solvent consumption and allowing a catalyst-free product to be obtained.[2]

Another aim of the research was to develop a new, efficient method for the synthesis of ionic liquids (ILs) carried out in a continuous flow through ion exchange reaction. Ion exchange reactions are being optimized for the phase flow speed and the choice of both solid and liquid phases. With the use of an ion chromatograph, the purity of the obtained ionic liquids can be determined and compared with the purity of ionic liquids obtained via traditional methods.

Furthermore, the use of dual functional ionic liquids, having magnetic and acidic properties, as catalysts in the Friedel - Crafts acylation reaction will be checked to allow avoiding the problems resulting from the use of metal halides as catalysts. Ionic liquids will have a dual role - the solvent and catalyst of the Lewis acid reaction, which should simplify the synthesis of aromatic ketones, which are widely used in chemistry (for example intermediates in synthesis of drugs or cosmetics). In addition, the use of microreactors made of various materials will determine whether the material used has an effect on the reaction and results obtained.

This work was supported by the National Science Centre (Poland), project PRELUDIUM (No. UMO-2017/25/N/ST4/02573).

- [1]Kukawka, R.; Pawlowska-Zygarowicz, A.; Dutkiewicz, M.; Maciejewski, H.; Smiglak, M., *RSC Adv.*, **2016**, *6*, 61860-61868.
- [2]Pawlowska-Zygarowicz, A.; Kukawka, R.; Maciejewski, H.; Smiglak, M. Optimization and intensification of hydrosilylation reaction using microreactor system, New J. Chem., in review.

Solid–liquid equilibria for a pyrrolidinium-based common-cation ternary ionic liquid system, and for a pyridinium-based ternary reciprocal ionic liquid system

<u>Olga Stolarska^{1,3}</u>, Meysam Mirarabrazi², Christian Robelin², Marcin Smiglak^{1,3*}

¹ Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland ²Centre for Research in Computational Thermochemistry, Department of Chemical Engineering, École Polytechnique, Montréal, Canada ³Poznan Science and Technology Park, Adam Mickiewicz University Foundation, Poznan, Poland E-mail: olga.stolarska@amu.edu.pl

Although the research on ionic liquids has focused on the design of single compounds with "tailor-made" properties, ionic liquid ternary mixtures may be considered [1], where the 1st component could for example control and define the chemistry of the system, the 2nd component could allow for fine tuning of the physical properties (such as density and viscosity) of the system, and the 3rd component could be cheap and inert, thus lowering the global cost of the system. The thermodynamic properties of the following prototype systems [(1), (2), and (3)] were modelled, using all available experimental data from the literature along with data obtained from DSC: (1) $[C_2 mim]$ Cl-AlCl₃ (phase diagram, emf measurements, partial enthalpies of mixing) where $C_2 mim =$ 1-ethyl-3-methyl-imidazolium; (2) the common-cation system $[C_4mpyrr]{Cl, Br, BF_4}$ (phase diagram) where C_4 mpyrr = 1-butyl-1-methyl-pyrrolidinium; (3) the ternary reciprocal system $[C_2py]$, $[C_4py] // Cl$, Br (phase diagram) where $C_npy = 1$ -alkyl-pyridinium. The liquid solution was modelled successfully with the Modified Quasichemical Model [2], which does not consider yet specific short-range interactions such as hydrogen bonding and van der Waals. For system (3), the missing thermodynamic properties of the pure compounds were assessed using the Volume-based Thermodynamics (VBT) from Glasser and Jenkins, making it possible to estimate the exchange Gibbs energy for the reaction $[C_2py]Cl_{(liquid)} + [C_4py]Br_{(liquid)} = [C_2py]Br_{(liquid)} + [C_4py]Cl_{(liquid)}$. The experimental diagonal sections [C₂py]Cl-[C₄py]Br and [C₂py]Br-[C₄py]Cl were satisfactorily reproduced using solely the optimized model parameters for the four common-ion subsystems.

This work was supported by the National Science Centre (Poland), project SONATA (No. 2011/03/D/ST5/06200).

- [1] Plechkova, N.V.; Seddon, K.R. Chem. Soc. Rev., 2008, 37, 123-150.
- [2] Pelton, A.D.; Chartrend, P. Metall. Mater. Trans., 2001, 32A, 1409-1416.
- [3] Mirarabrazi, M.; Stolarska, O.; Smiglak, M.; Robelin, C. Phys. Chem. Chem. Phys., 2018, 20, 637-657.

Eutectic mixtures of ionic liquids - determination of the eutectic point and analysis of the relationship between the structure of ions and the properties of obtained eutectic mixtures

<u>Olga Stolarska^{1,3}</u>, Ana Soto², Héctor Rodríguez², Marcin Smiglak^{1,3*}

¹ Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland
²Department of Chemical Engineering, University of Santiago de Compostela, Santiago de Compostela, Spain
³Poznan Science and Technology Park, Adam Mickiewicz University Foundation, Poznan, Poland E-mail: olga.stolarska@amu.edu.pl

In view of numerous advantages stemming from the use of organic salts (including ionic liquids), a growing interest in the investigation of mixtures of such salts for their use in a variety of potential applications could also be observed in recent years.[1] Such approach via the formation of salt mixtures, allows to maintain the ionic character of the system while simultaneously influencing chosen features of the resulting mixture. To obtain stable system of two salts one of two approaches could be used. First option is a straightforward mixing two or more salts that are already liquid at the operation temperature. As an alternative, the system consisting of three or more different ions can be obtained via the combination of salts with higher melting points that produce a eutectic system.[2] Through the investigation of the solid-liquid equilibria, of more than twenty systems of ionic liquids or organic salts with a melting point not exceeding 250°C, the determination of the eutectic composition of the mixtures have been carried out. At the same time the increments in the liquid range of operation as compared to the parent compounds were defined.[3,4] We have also conducted the preliminary analysis of the dependence between the type of ions present in the mixture (particularly with regard to their size, structure and charge distribution) and the melting point depression of the mixtures,.

This work was supported by the National Science Centre (Poland), project SONATA (No. 2011/03/D/ST5/06200).

- [1] Niedermeyer, H.; Hallett, J.P.; Villar-Garcia, I.J.; Hunt, P.A.; Welton, T. Chem. Soc. Rev., **2012**, *41*, 7780-7802.
- [2] Smiglak, M.; Bridges, N.J.; Dilip, M.; Rogers, R.D. Chem. Eur. J., 2008, 14, 11314-11319.
- [3] Stolarska, O.; Soto, A.; Rodríguez, H.; Smiglak, M. RSC Adv., 2015, 5, 22178-22187.
- [4] Stolarska, O.; Rodríguez, H.; Smiglak, M. Fluid Phase Equilibria, 2016, 408, 1–9.

New generation of ionic liquids based on fungicidal ion

Rafal Kukawka^{1,2}, Ewa Stróżyk¹, Judyta Strakowska², Marcin Smiglak^{1,2*}

¹Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 b, 61-614 Poznan, Poland ²Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubież 46, 61-612 Poznan, Poland E-mail: kukawka.rafal@gmail.com

Crop protection in modern agricultural industry is still a field that requires new and more efficient methods, which can improve quantity and quality of crops due to exposure of plants to factors such as fungi, bacteria and insects. Excessive consumption of Plant Protection Products, especially fungicides and, related to it, negative impact on human health and environment (through for example phenomenon called Colony Collapse Disorder (CCD) of bees) is becoming an increasing problem that requires a comprehensive and effective solutions.

Since 1990 popularity of room temperature quaternary ammonium salts (major class of ionic liquids) is still raising, due to the fact that both ions in ionic liquid can be independently modified and thus properties of ions may separately be incorporated into the final IL salt. In recent years, dual functional ionic liquids with biological functions started to be investigated in fields of plant protection products as herbicidal [1] and antifungal [2] agents or inducers of plant resistance.[3] In addition, ionic liquids containing long alkyl chains have a significant effect on the change of hydrophilic properties, which makes it possible to limit their mobility in soil and groundwater. Furthermore, long alkyl chain ILs guarantee significant surface activity, which in turn intensifies wettability of the plant surface and enables direct contact between used plant protection product and pathogens on the plant. This could eliminate the need to use additional compounds such as surfactants or adjuvants. [4]

Herein, we present new, active dual functional ionic liquids based on currently used fungicidal agents with modified properties of solubility in water, dissolution rate, volatility, reduced or increased phytotoxicity and antifungal activity towards *Alternaria alternata* (fungus that infects cereal crop and many types of fruits and vegetables) and the influence on beneficial microbe *Trichoderma viride* (a non-pathogenic saprophytic fungus coexisting in the plant root zone that does not cause infection). These new ionic liquids can revolutionize agrochemical industry through reducing negative impact of pesticides on bees colonies.

This work was supported by the National Science Centre (Poland), project Preludium no UMO-2015/19/N/NZ9/02922. Moreover, Rafal Kukawka is Adam Mickiewicz University Foundation scholarship holder in the academic year 2017/2018.

- [1]Pernak, J.; Giszter, R.; Biedziak, A.; Niemczak, M.; Olszewski, R.; Marcinkowska, K.; Praczyk, T. J. Agric. Food Chem., 2017, 65, 260-269.
- [2] Bica, K.; Cooke, L. R.; Nugent, P.; Rijksen, C.; Rogers, R. D. Green Chem., 2011, 13, 2344-2346.
- [3] Smiglak, M.; Lewandowski, P.; Kukawka, R.; Budziszewska, M.; Obrepalska-Steplowska, A.; Krawczyk, K.; Zwolinska, A.; Pospieszny, H. *ACS Sustainable Chem. Eng.*, **2017**, *5*, 4197-4204.
- [4]Niemczak, M. Synteza i właściwości dwufunkcyjnych herbicydowych cieczy jonowych, *Rozprawa Doktorska*, Politechnika Poznańska, **2015**, 26-27.

Supported Ionic Liquid Catalysts as efficient tool for hydrosilylation reaction

<u>Rafal Kukawka</u>^{1,2}, Anna Pawlowska-Zygarowicz^{1,2}, Joanna Działkowska¹, Hieronim Maciejewski^{1,2}, Katharina Schröder³, Marcin Smiglak^{1,2*}

 ¹ Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 b, 61-614 Poznan, Poland
 ²Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubież 46, 61-612 Poznan, Poland
 3 Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163 A-1060 Vienna, Austria

E-mail: kukawka.rafal@gmail.com

Synthesis of many of organosilicone compounds is based on hydrosilylation reaction. However, the major problem is the difficulty in the separation of catalyst from a reaction mixture.[1] The presence of metal in the reaction products, even at the trace quantities, is unacceptable for many applications (especially in food and cosmetic industry). Therefore efforts are made to utilize heterogeneous catalysts. One of the possible solutions to this problem is carrying the reactions in biphasic system with catalyst dissolved in ionic liquid[2, 3] or using catalyst immobilized on supported ionic liquid phase (SILP) which allows to immobilize a transition metal catalyst in thin ionic liquid film present on porous silica particles.[4] The combination of ionic liquids, inorganic supports and metalorganic complexes can allow the synthesis of organosilicon compounds with possibility to reuse IL/catalyst system and may be solution for a variety of problems of currently used processes.

Herein, we present new method for the synthesis of organofunctional silanes via hydrosilylation reaction in batch with using ionic liquids and SILP materials. The main advantages of using SILP materials is (i) easy separation of catalyst after reaction, (ii) decrease in amount of catalyst needed to obtain product with high yield, and (iii) catalytic activity of the recycled system up to 20 cycles.

This work was supported by the National Science Centre (Poland), project OPUS no. UMO-2014/15/B/ST5/04257 and COST Action CM1206. Moreover, Rafal Kukawka is Adam Mickiewicz University Foundation scholarship holder in the academic year 2017/2018.

- [1]Marciniec, B.; Maciejewski, H.; Pietraszuk, H.; Pawluć, P. in Applied Homogenous Catalysis with Organometallic Compounds, Cornils, I.B.; Herman, W.A.; Beller, M.; Paniello, R. (Eds) Willey, 2017, 569-620.
- [2]Kukawka, R.; Pawlowska-Zygarowicz, A.; Dutkiewicz, M.; Maciejewski, H.; Smiglak, M. RSC Adv. 2016, 6, 61860- 61868.
- [3]Kukawka, R.; Januszewski, R.; Kownacki, I.; Smiglak, M.; Maciejewski, H. Cat. Commun. 2018, 108, 59-63.
- [4] Fehrmann, R.; Riisager, A.; Haumann, M. (Eds.) Supported Ionic Liquids: Fundamentals and Applications, Wiley, Weinheim **2014**.

Synthesis of new platinum and rhodium complexes on-containing ionic liquids and determination of their structures

<u>Magdalena Jankowska – Wajda</u>¹, Artur Stefankiewicz^{1,2}, Hieronim Maciejewski^{1,3}

 ¹ Faculty of Chemistry, A. Mickiewicz University, Umultowska 89b, 61-614 Poznan, Poland
 ² Center for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, 61-614 Poznan, Poland
 ³Poznan Science and Technology Park, A. Mickiewicz University Foundation, Rubiez 46, 61-612 Poznan, Poland
 E-mail: magdajw@amu.edu.pl

In recent years, we observe growing interest in catalytic processes conducted with the participation of different organosilicon compounds. In addition to the well-known hydrosilylation reaction [1], such processes as silylative coupling and silylcarbonylation [2, 3] should also be mentioned here.

Currently, new types of active catalysts are being searched for. Obviously, a catalytic systems, which makes it possible to secure the advantages of both homogeneous and heterogeneous catalysis would greatly enhance the interest of industry in catalysis. Therefore efforts have been made to apply new metal complexes in order to obtain high catalytic activity in many recycled runs and easy product isolation at the same time. This problem can be solved effectively by using own newly synthesed and characterized of new ionic platinum and rhodium complexes.

Ionic liquids have received much attention because of their versatile applications [4–6] such as electrolytes in electrochemistry, environmentally friendly solvents in organic synthesis, and immobilizing phases for biphasic catalysis. They are also regarded as precursor materials for catalysts.

In this communication, we present the results of synthesis of new platinum and rhodium complexes containing ionic liquids and determination of their structures.

The project UMO-2014/15/B/ST5/04257 was funded by the National Science Centre, Poland.

- [1] Marciniec B., Maciejewski H., Pietraszuk C., Pawluć P., *Hydrosilylation. A Comprehensive Review on Recent Advances* (Ed: B. Marciniec), Springer, London, **2009**.
- [2] Marciniec B., *Applied Homogeneous Catalysis with Organometallic Compounds* (Ed: Cornils B. and. Herrmann W.A), VCH, Weinheim, **1996**, vol. 1.
- [3] Eilbracht, P.; Bärfacker, L.; Buss, C.; Hollmann, C.; Kitsos-Rzychon, B.E.; Kranemann, C.L.; Rische, T.; Roggenbuck, R.; Schmidt A., *Chem. Rev.*, **1999**, *99*, 3329-3366.
- [4] Wasserscheid, P.; Keim, W., Angew. Chem. 2000, 39, 3772-3789.
- [5] Dupont, J.; de Souza, R.F.; Suarez, P.A.Z., *Chem. Rev.*, **2002**, *102*, 3667-3692.
- [6] Gordon, C.M., Appl. Catal. A, 2001, 222, 101-117.

New ionic liquids based on systemic acquired resistance inducers combined with phytotoxicity reducing cholinium cation

Patrycja Czerwoniec^{1,3}, Rafał Kukawka^{1,3}, Piotr Lewandowski^{1,3}, Henryk Pospieszny², Marcin Smiglak^{1,3*}

 ¹ Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 b, 61-614 Poznan, Poland,
 ²Institute of Plant Protection - National Research Institute, ul. Władysława Węgorka 20, 60-318 Poznan, Poland,
 ³ Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubież 46,

n Science and Technology Fark, Adam Micklewicz, University Foundation, ut. Kubic 61-612 Poznan, Poland, E-mail: patrycja.czerwoniec@gmail.com

Modern agriculture at present times is facing many challenges. On the one hand, society requires crops and plant-related products free from contaminations of plant protection products (PPP) residues. On the other, crop quantity and quality should be sufficient due to continuously increasing demand for food. Unfortunately most often crop yields are reduced by pathogens, insects, other pests or weather conditions, so that tasks posed to modern agriculture focuses on finding new and more sophisticated methods of plant protection, even not chemical-based.

One of the promising method of plant protection is the activation of the systemic acquired resistance (SAR). Systemic acquired resistance has a broad spectrum action against pathogens, most often simultaneously against bacteria, viruses and fungi. This phenomenon is one of the defense mechanism against pathogens which were developed in the evolutionary process. Systemic acquired resistance is activated by pathogen attack or artificially, by compounds imitating the plant-pathogen interaction. Activation of this phenomenon is followed by transportation of the signaling substances such salicylic acid or salicylic acid methyl ester to every part of the plant. This signaling compounds activate metabolic pathways in which defense compounds and pathogenesis-related (PR) proteins are synthesized. Those proteins have antifungal, antiviral and antimicrobial activity.[1]

We have successfully synthesized new ionic liquids composed of the anion of plant resistance inducers and essential nutrient for plant cells cholinium cation. Following the synthesis we determined thermal stabilities, melting points, phytotoxicity and SAR inducing properties.

This work was supported by the National Science Centre (Poland), project OPUS (No. UMO-2015/17/B/NZ9/01676).

References:

[1] Shah J., Current Opinion in Plant Biology, 2009, 12, 459-464.

Synthesis and Characterization of Polymerizable Ionic Liquids as Precursors of Nanoscale Polymeric Materials

<u>Adrian Zajac</u>¹, Andrea Szpecht^{1,2}, Olga Stolarska^{1,2}, Katarzyna Komorowska^{3,4}, Krzysztof Rola³, Marcin Smiglak^{1,2*}

¹Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubiez 46, 61-612 Poznan, Poland

²Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 B, 61-614 Poznan, Poland
 ³ Wrocław Research Centre EIT+, ul. Stablowicka 147, 54-066 Wroclaw, Poland

⁴ Department of Optics and Photonics, Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology, Wroclaw, Poland

E-mail: adrian.zajac@ppnt.poznan.pl

Ionic liquid (ILs) are relatively well known group of organic compounds, nevertheless they still attract unabated interest of the scientific community and industry. It is due to their very valuable, often unique, properties, together with wide range of modulability, and, therefore, various functionalities.[1] Polymeric ILs can combine this variety with features of a polymeric material.

Herein, we would like to present effective and facile synthesis, physicochemical studies and nanoscale polymerization potential of nitrogen based ILs bearing unsaturated groups. Experiments revealed that, at certain conditions, polymerization process affords nanostructures of very well-defined topography, potentially useful as micro-scale components (*Figure 1*).



Figure 1. Synthesis of polymerizable ILs and their polymeric nanostructures.

This work was supported by the National Science Centre (Poland), project OPUS (No. 2015/19/B/ST8/02761).

References:

[1]Smiglak, M.; Pringle, J. M.; Lu, X.; Han, L.; Zhang, S.; Gao, H.; MacFarlane, D. R.; Rogers, R.D., *Chem. Commun.* **2014**, *50*, 9228-9250.

Ionic Liquids in the Synthesis of Ligands for Transition Metal-Based Catalysts

<u>Adrian Zajac</u>¹, Andrea Szpecht^{1,2}, Olga Stolarska^{1,2}, Sandra Rutecka², Magdalena Jankowska-Wajda², Marcin Smiglak^{1,2}, Hieronim Maciejewski^{1,2*}

¹Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubiez 46, 61-612 Poznan, Poland ²Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 B, 61-614 Poznan, Poland

²Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89 B, 61-614 Poznan, Poland E-mail: adrian.zajac@ppnt.poznan.pl

Extensive research on ionic liquids has proven their valuable, often unique, properties, together with wide range of modulability, and, therefore, various functionalities.[1,2] Despite of that, this group of organic compounds still reveals new possibilities of applications and, therefore, attracts significant attention of science and industry.

Herein, we would like to present their usability in the synthesis of phosphorus(III)-based ligands for transition metal catalysts. The research included the synthesis of selected nitrogen-based ionic liquids bearing modifiable substituents, such as unsaturated, halogen- or hydroxy-substituted groups, their characterization and transformation into phosphinyly ligands with the maintenance of ionic nature (*Figure 1*).



Figure 1. Synthesis of ionic liquid-phosphinyl ligands.

This work was supported by the National Science Centre (Poland), project OPUS (No. 2014/15/B/ST5/04257).

References:

[1] Smiglak, M.; Metlen, A.; Rogers, R. D., Acc. Chem. Res. 2007, 40, 1182-1192.

[2] Smiglak, M.; Pringle, J. M.; Lu, X.; Han, L.; Zhang, S.; Gao, H.; MacFarlane, D. R.; Rogers, R. D., *Chem. Commun.* 2014, 50, 9228-9250.

Deep eutectic solvents as a suitable medium for enzymatic reactions

Jakub Hoppe^{1,2}, Marcin Śmiglak^{1,2*}

¹Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89b, 61-614 Poznań, Poland ² Poznan Science and Technology Park, UAM Foundation, ul. Rubież 46, 61-612 Poznań, Poland E-mail: kuba.hoppe@gmail.com

Within the framework of green chemistry, solvents occupy a strategic place. To be qualified as a green medium, these solvents have to meet different criteria such as availability, non-toxicity, biodegradability, recyclability, non-flammability, and low price. Until now, the number of available green solvents was rather limited. However, a new family of ionic fluids, so-called Deep Eutectic Solvents (DES), are now rapidly emerging as a cheap biodegradable solvents with many possible applications. A DES is a fluid generally composed of two or three cheap and safe components (glycerol, ethylene glycol) that are capable of self-association, often through hydrogen bond interactions, to form a eutectic mixture with a melting point lower than that of each individual component. DESs are generally liquid at temperatures much below room temperature. These DESs exhibit similar physico-chemical properties to the traditionally used ionic liquids, while being much cheaper, less biotoxic and environmentally friendlier. Owing to these remarkable advantages, DESs are now of growing interest in many fields of research, also as a promising medium for enzymatic reactions [1,2].



Figure 1. Selected deep eutectic solvents as a medium for enzymatic reactions.

In order to carry out the research, 18 different eutectic mixtures were prepared. The obtained mixtures were tested for physicochemical properties and enzymatic reaction efficiency.

This work was supported by the National Science Centre (Poland), project OPUS (UMO-2015/19/B/NZ9/03711).

- [1] Zhao, H.; G. A. Baker, G.A.; and Holmes, S.; J. Mol. Cat. B: Enzymatic, 2011, 72, 163–167.
- [2] Gutierrez, M.C.; Ferrer, M.L.; Yuste, L.; Rojo, F.; del Monte, F.; *Angew. Chem., Int. Ed.*, **2010**, *49*, 2158–2162.

Effect of choline-based deep eutectic solvents on catalytic properties of β-galactosidase from *Kluyveromyces lactis*

<u>Judyta Strakowska</u>¹, Radosław Drozd³, Jakub Hoppe^{1,2}, Karolina Adamczyk⁴, Leszek Broniarek¹, Mateusz Hoppe¹, Marcin Śmiglak^{1,2*}

¹Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubiez, 46 61-612 Poznan, Poland

²Faculty of Chemistry, Adam Mickiewicz University, ul. Umultowska 89b, 61-614 Poznan, Poland

³West Pomeranian University of Technology, Faculty of Biotechnology and Animal Husbandry,

Department of Immunology, Microbiology and Physiological Chemistry, al. Piastów 45, 70-311 Szczecin, Poland

> ⁴BBH Biotech Polska sp. z o.o., ul. Rubiez, 46 61-612 Poznan, Poland E-mail: judyta.strakowska@gmail.com

Choline chloride-based deep eutectic solvents (DES) have unique properties like nontoxicity, biodegradability or cheap production. Those are just few reasons that caused their increasing popularity from year to year. The application of choline-based deep eutectic solvents is especially desirable in field of Green Chemistry. Also it concerns research about the interactions between DES and enzymes [1].

 β -galactosidase, EC 3.2.1.23 (other names: beta-galactosidase, lactase, lactozym) is an enzyme that belongs to the class of hydrolases, that is responsible for cleavage of O-glycosyl bonds. One of many producers of β -galactosidase is microorganism *Kluyveromyces lactis*, which is considered biotechnologically and scientifically as one of the most important non-Saccharomyces yeast. Nowadays lactase is widely used in food industry, especially for the production of lactose-free dairy products [2].

We would like to present our research regarding the influence of six types of deep eutectic solvents based on choline chloride on activity, kinetics, stability and optimal temperature of reaction catalyzed by β -galactosidase from *K. lactis*. For performing enzymatic reaction used 6 deep eutectic solvents based on choline chloride. For all DESs we have prepared mixtures with water (containing phosphate buffer) from 10% to 90% of water.

In case of all six analyzed deep eutectic solvents and all varieties of water content, activities of β -galactosidase was decreased in comparison to control. Kinetic constants (K_m, V_{max}) of the β -galactosidase indicated that most likely inhibitory effect of choline-based DES is observed. There was no indication of influence of choline-based DES on the enzyme stability. It suggests that analyzed mixtures do not have significant impact on the enzyme structure. However, analyzed DES's shifted the optimal temperature of the enzymatic reaction of β - galactosidase from 45°C to 35°C.

Obtained results indicate that choline-based DES could be useful in controlling the activity of the β - galactosidase in bioprocessing.

This work was supported by the National Science Center (Poland), project OPUS (No. UMO-2015/19/B/NZ9/03711).

- [1] Radošević, K.; Cvjetko Bubalo, M.; Gaurina Srček, V.; Grgas, D.; Landeka Dragičević, T.; Radojčić Redovniković, I. *Ecotoxicology and environmental safety*, **2015**, *112*, 46-53.
- [2] Athès, V.; Lange, R.; Combes, D. *The FEBS Journal*, **1998**, 255, 206-212.

AUTHOR INDEX

Bairaktari, Maria	80
Broniarek, Leszek	67
Chrzanowski, Łukasz	
Cybinska, Joanna	
Czerwoniec, Patrycja	60, 92
Czuryszkiewicz, Daria	70
Drozd, Radosław	25
Dzida, Marzena	
Feder-Kubis, Joanna	75,76
Fehrmann, Rasmus	
Figueiredo, Nádia	82
Gano, Marcin	59, 79
Heid, Esther	
Hoppe, Jakub	95
lliev, Boyan	49
Jankowska-Wajda, Magdalena	91
Kaczmarek, Damian	69
Karpińska, Monika	
Kholany, Mariam	35, 53
Komorowska, Katarzyna	77
Koutsoukos, Spyridon	34
Kukawka, Rafal	89, 90
Lanaridi, Olga	55
Li, Xiaohua	
Lobo Ferreira, Ana I.M.C.	65
Niemczak, Michał	52
Nowicki, Janusz	73
Ossowicz, Paula	61, 83
Pálvölgyi, Ádám Márk	66

Passos, Helena	6
Pawlowska-Zygarowicz, Anna	6
Riaño, Sofia	6
Riisager, Anders	4
Rodriguez Rodriguez, Nerea4	0
Rogers, Robin D	0
Rola, Krzysztof	4
Rybińska-Fryca, Anna	6
Rzemieniecki, Tomasz	3
Sainz Martinez Aitor	8
Sans, Victor	3
Santos, Luís M. N. B. F	1
Schaeffer, Nicolas	8
Schlosser, Štefan	0
Schröder, Christian	7
Schröder, Katharina	2
Sintra, Tânia4	1
Sokolnicki, Tomasz	4
Stefanowska, Kinga	8
Stolarska, Olga	8
Strakowska, Judyta9	6
Swadźba-Kwaśny, Gosia	3
Szpecht, Andrea	2
Szyling, Jakub	2
Tu Nguyen, Viet	4
Vaz,Inês	1
Ventura, Sónia P.M	1
Voroshylova, Iuliia V	7
Woch, Julia	4
Zając, Adrian	4
Zec, Nebojša3	1

Zeindlhofer,	Veronika				
--------------	----------	--	--	--	--

