Ionic Liquids Today

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COIL-2 Special Issue, Friday, 31th August, 2007.

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>>> Highlights from the 2nd Conference on Ionic Liquids at Yokohoma (August 5-10, 2007)

Content:

I. Editorial

By Tom F. Beyersdorff and Thomas J.S. Schubert.

The increasing number of participants at COIL-2 compared to COIL-1 once more demonstrated the growing world wide interest in ionic liquids. Almost 600 (400 at COIL-1 in 2005) scientists from academia and industry participated in the conference, listened to 9 plenary lectures, 115 invited lectures and talks in 3 paralllel sessions and presented their latest research in 284 posters at COIL-2 held from August 5th-10th in Yokohama. In addition 15 companies, that are either producing, trading or applying ionic liquids, presented their products during the exhibition.

However, one thing that became quite familiar to European scientist at IL conferences was missing: The "BASIL-arena" at the BASF booth (a table-soccer game, where IOLITEC's team has never won a game)!

On this occasion IOLITEC would like to thank the organizing committee for the well organized conference. A special thanks should be directed to all students and other persons who worked in the background for this successful conference.

II What we've learned at COIL-2

Lectures highlighted by Tom F. Beyersdorff, Marco H. Klingele & Thomas J.S. Schubert.

The large number of brilliant lectures and posters does not allow to report on all of them without exceeding the scope of this special issue. Moreover, as the parallel sessions did not allow to visit all lectures, the following pages will give an incomplete and personal selection of interesting lectures & posters.

Ionic Liquids in Biotechnology: Towards Novel Applications and Better Understanding

U. Kragl, S. Klembt, S. Dreyer, P. Izak

We do agree strongly: "Ionic Liquids have made their way into Biotechnology in recent years!". ***U. Kragl*** demonstrated the wide scope of applications of ionic liquids, such as,

- use of alcohol dehydrogenases in IL-water two phase systems,
- the addition of water miscible ILs to increase yield in reaction catalysed by hydrolytic enzymes,
- the use of water miscible ILs in two phase systems for protein purification and stabilisation,
- supported IL membranes for pervaporation in fermentation processes,
- and the use of ILs for extraction of carbohydrates from aqueous solutions.

When will we see the first industrial processes?

"Drug" Ionic Liquids – A New Phase for the Pharmaceutical World

D. R. MacFarlane, P. M. Dean, J. Turanjanin, J. L. Scott, M. Yoshizawa-Fujita, W. L. Hough, M. Smiglak, H. Rodriguez, R. P. Swatloski, S. K. Spear, D. T. Daly, J. Pernak, J. E. Grisel, R. D. Carliss, M. D. Soutullo, J. H. Davis, Jr., R. D. Rogers

It's not a surprise that something really principal is generated if some of the world's leading ionic liquids research groups combine their knowledge. We believe that this talk sets another milestone in ionic liquid research:

The idea behind is that many pharmaceutically active compounds are salts of an active ion in combination with a relatively simple and inert counterion. The replacement of that counterion by an alternative ion that has the characteristics familiar to the ionic liquid world opens up the possibility of creating new pharmaceutical compounds with ionic liquids. Such ionic liquids offer the potential to create tailored properties such as hydrophobicity/hydrophilicity and solubility into the compound by adjustment of the counterion. In the sense that different polymorphs of an active compound are recognised in the pharmaceutical world as different, these ionic liquids are certainly distinct from the other known forms of the active ion. Hopefully "big pharma" has listened carefully…

At the end of this plenary lecture Doug MacFarlane thanked the organisers of COIL-2 for the good organisation and invited the participants to COIL-3 2009 in Australia.

Application of Ionic Liquids to Double-Layer Capcitors

M. Ue

The use of ionic liquids in double layer capacitors was suggested in the mid 1990s. ***M. Ue*** compared the temperature dependence of DLC capacitance for a number of ionic liquids with one of the standard materials, a mixture of Et_3MeN BF_4 with propylene carbonate. While typical ionic liquids such as EMIM BF_4, EMIM TaF_6 or EMIM NTf_2 showed a strong decrease of the capacitance at decreasing temperatures, a new synthesized material, EMIM $BF_3C_2F_5$, showed a performance that was comparable with Et_3MeN BF_4 / PC.

Unique Role of Ionic Liquids in Solid-state Dye-sensitized Solar Cells

S. Yanagida, N. Masaki, K. Suzuki

Among electrochemical applications of ionic liquids dye sensitized solar-cells (DSCs or DSSCs) become one of the most interesting. ***S. Yanagida*** presented the use of ionic

liquids in a iodine-free solid-state DSSC. In such devices a solid such as highly porous, 10 µm thin TiO_2–layers transport the electrons. If those layers are coated with thin films of an IL cation, the electron transporting function is enhanced, leading to higher, better performances of DSCs.

Hydrophobicity Scale for Designing Ionic Liquids for Ionic Liquid-Water Two-phase Systems

T. Kakiuchi, N. Nishi, Y. Kitazumi, S. Tanaka

Hydrophobicity of ionic liquids is an important property with regard to using them in promising applications such as exctraction, two-phase organic synthesis, and other purposes such as electroanalytical chemistry. Since a number of cations and anions can be combined to prepare ionic liquids, it is helpful to have a guideline to use and to synthesise hydrophobic ILs.

T. Kakiuchi presented such a guideline: He demonstrated that the standard Gibbs energy of ion transfer between a polar organic solvent and water can be a useful measure that can provide a way to prepare selective tailor-made hydrophobic ionic liquids.

Biocatalysis in Supported Ionic Liquids

P. Lozano, E. Garcia-Verdugo, R. Piamtongkam, K. Montague, N. Karbass, T. De Diego, M. I. Burguete, S. V. Luis, J. L. Iborra

That some ionic liquids can be suitable media for biotransformations has been demonstrated in a number of publications. It is also known that immobilized enzymes particles coated with ionic liquids by impregnation show enhanced activities. ***P. Lozano*** reported that the problem of leaching can be avoided if the ionic liquids are attached by covalent bonding to a monolithic macroporous material, used as a support to immobilize enzymes.

How to Predict the Physical Properties of Ionic Liquids.

J. M. Slattery and I. Krossing

J. Slattery presented a powerful approach to predict some fundamental physical properties of ionic liquids such as viscosities, densities and conductivities with sufficient accuracy. They demonstrated that it is possible to predict those properties based on the molecular volume of the ions by using the COSMO-RS-modelling-program. The correlation to "real" materials was verified by comparing the results with properties, determined from IOLITEC's materials, synthesized in the best quality possible.

In summary, the method is very simple and can be applied to concepts of new ionic liquids before synthesizing them.

Durability of Dye-sensitized Solar Cell with Ionic Liquid Electrolyte.

T. Kitamura, H. Matsui, and K. Okada

Since the first report of DSSC by *Grätzel et al.* the development of this new technology was accompanied by the development of ionic liquids as electrolytes.
T. Kitamura from Fujikura Ltd. reported on the use of "nanocomposite-ionic liquid electrolytes" in DSSC and the application of this electrolyte in the production of DSSCpanels which are close to commercialisation. A panel was shown at the exhibition booth as well.

Electromechanical Soft Actuators Based on Carbon Nanotube-Ionic Liquid Gels.

K. Asaka, K. Mukai, I. Takeuchi, T. Sugino, K. Kiyohara, T. Fukushima, and T. Aida

The application of bucky gels made from SWNT and ionic liquids in actuators was presented by ***K. Asaka***. Remarkable amplitudes were realized with this system, which enables applications such as robotics, tactile and optical displays, prosthetic or medical devices by transforming electrical energy directly into mechanical work.

Proton Exchange Membranes Based on Aprotic and Protic Ionic Liquids: Different Electrolyte Systems in Comparison

A. Fernicola, M. Navarra, S. Panero, and B. Scrosati

Only limited work has been conducted on the application of ionic liquids in fuel cells. ***A. Fernicola*** presented results on the development of new proton conducting membranes using both aprotic and protic ionic liquids. Membranes made out of 1,2-dimethyl-3-propylimidazolium TFSI, PVdF and HTFSI showed a high thermal stability (250°C), a good conductivity (10^{-2} - 10^{-3} S/cm²) and an excellent methanol crossover control compared to NAFION®.

Charge-Discharge Properties of Li/$LiCoO_2$ Cell Using Ionic Liquids Comprised of Aliphatic Quaternary Ammonium and Perfluoroalky-ltrifluoroborate

H. Matsumoto, Z. Zhou, H. Sakaebe and K. Tatsumi

While the possibility of using ionic liquids, e.g. 1-methy-1-propylpiperidinium bis(trifluorosulfonyl)imide, as electrolytes for Li/$LiCoO_2$ secondary batteries has previously been demonstrated, it has often been argued that the relatively high viscosity of ionic liquids limits lithium ion mobility and thus leads to unpractically low current densities during charging and discharging of the batteries. In this lecture it was reported that the rate properties of the Li/$LiCoO_2$ cell do not simpy depend on the lithium ion mobility but that rather the charge transfer resistance at the interface between lithium metal and an ionic liquid containing a lithium salt plays a key role here.

All that Glistens is not Gold – Bright Metal Deposits from Ionic Liquids

A. Abbott, J. Barron, K. Ettaib, F. Qiu and K. Ryder

This contribution was dealing with the effect of under-potential deposition, speciation, complexation and mass transport on metal nucleation and growth as well as the effect of metal ion concentration on growth rates and mechanism in the electrodepostion of metals from ionic liquids. Strategies were discussed for the

deposition of bright metal deposits and examples for mirror-finish aluminium and nickel were demonstrated.

Influence of Ionic Liquids on the Structure and Grain Size of Electrochemically and Chemically Made Materials

F. Endres

It has previously been shown that the cation of ionic liquids has a strong impact on the structure and grain size of chemically and electrochemically generated materials. In this talk it was demonstrated that the chemical hydrolysis of $TiCl_4$ to TiO_2 can be tuned by the ionic liquid used. Thus, hydrolysis in the presence of bis(trifluorosulfonyl)imide anions at room temperature leads to the preferential formation of nanocrystalline rutile. By varying the hydrolysis parameters nanocrystalline anatase can be obtained.

Synergic Effect of Two-Solvents-in-One-Molecule in Nucleophilic Substitution Fluorination: Two Solvents are *tert*-Alcohol and Ionic liquid

D. Y. Chi, S. S. Shinde and B. S. Lee

This lecture described the design and synthesis of novel functionalised ionic liquids carrying a *tert*-butanol moiety and the application of these materials to nucleophilic substitution especially nucleophilic fluorination. They not only enhance the nucleophilicity of the fluoride ion but also reduce its basicity via weak F···H hydrogen bonds. This minimises side reactions and thus reduces the formation of elimination by-products such as olefins. The use of these ionic liquids could also facilitate an easy access to certain ^{18}F labelled compounds.

Transition-metal Nanoparticles in Imidazolium Ionic Liquids

J. Dupont

This lecture discussed the possibility of using ionic liquids as reaction media for the synthesis of transition metal nanoparticles. The highly ordered structure of ionic liquids both in the solid and the liquid state acts as an "entropic driver" and facilitates

the formation of well-defined nanomaterials. Transition metal nanoparticles in imidazolium ionic liquids posses interesting catalytic properties, e.g. in hydrogenation, C–C coupling and various organometallic reactions.

Toxicological Screening and Assessment of Ionic Liquids

W. R. Pitner, T. Colnot, and U. Welz-Biermann

This presentation argued that while a vast amount of information on the physical, chemical and engineering properties of ionic liquids has been gathered over the last ten years, there is still very little data available on the toxicity and ecotoxicity of these materials. Merck has developed a toxicological screening and assessment program to support the further development on ionic liquids. This program is designed for the screening of a multitude of candidates and to provide an early warning of toxicological and ecotoxicological alerts, for supporting the development of safer ionic liquids at a very early stage and for accumulating valuable expertise to be used in the design of future testing strategies.

III New Materials at COIL-2

By Tom F. Beyersdorff, Marco H. Klingele & Thomas J.S. Schubert.

As demonstrated just by a few highlighted lectures, still many new interesting applications were identified by researchers from different disciplines. But are those developments still made just with BMIM PF_6 or EMIM NTf_2? Of course not: Not only users, but also developers of ionic liquids presented a number of new materials at COIL-2.

Of course, IOLITEC will be state-of-the-art and intends to synthesize and test them. Please take our portfolio on your watch list if you are interested in latest developments!

N. Matsumi described ionic liquids with organoboron side chains for the selective Li-ion transport which is of great importance for Li-batteries.

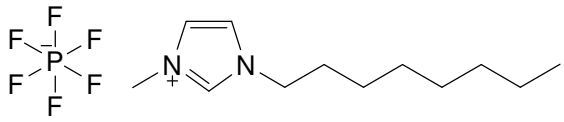
K.Tsunashima synthesized novel tetraalkylphosphonium based ionic liquids with short alkyl chains (C2-C8) which show low viscosities and wide electrochemical windows. This might make these materials potential electrolytes for Li-batteries.

Very early Announcement:

Finally we believe that COIL-3 in 2009 will continue the successful advancement of this conference series. We wish Prof. MacFarlane best of luck with the organisation of the conference!
Information on COIL-3 can be found at: www.coil-3.org!

IV COIL-2 Special Offers

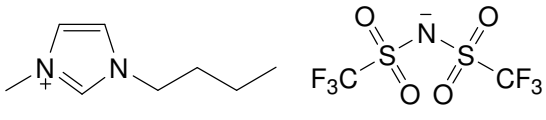
1-Octyl-3-methylimidazolium hexafluorophosphate: OMIM PF_6



OMIM PF_6 (99%)*:

IL-0020-HP-50 g	**77,50 €**
IL-0020-HP-100 g	**125,00 €**
IL-0020-HP-250 g	**225,00 €**
IL-0020-HP-500 g	**402,50 €**
IL-0020-HP-1 kg	**705,00 €**

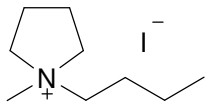
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide: BMIM NTf_2



BMIM NTf_2 (99%)*:

IL-0029-HP-50 g	**115,00 €**
IL-0029-HP-100 g	**200,00 €**
IL-0029-HP-250 g	**425,00 €**
IL-0029-HP-500 g	**720,00 €**
IL-0029-HP-1 kg	**1.225,00 €**
IL-0029-HP-5 kg	**5.100,00 €**

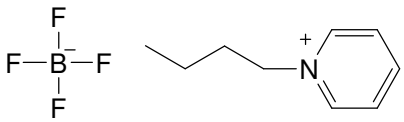
1-Butyl-1-methylpyrrolidinium iodide: BMPyrr I



BMPyrr I (99%)*:

IL-0050-HP-50 g	**92,50 €**
IL-0050-HP-100 g	**142,50 €**
IL-0050-HP-250 g	**315,00 €**
IL-0050-HP-500 g	**572,50 €**
IL-0050-HP-1 kg	**1.020,00 €**

1-Butylpyridinium tetrafluoroborate: BuPy BF_4



BuPy BF_4 (99%)*:

IL-0089-HP-50 g	**85,00 €**
IL-0089-HP-100 g	**112,50 €**
IL-0089-HP-250 g	**232,50 €**
IL-0089-HP-500 g	**382,50 €**
IL-0089-HP-1 kg	**625,00 €**

*** All special offers are valid until September 30th, 2007.**

All prices are FOB Denzlingen, costs for shipping and handling and custom charges are not included in the prices and are payable by customer.

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