IoLiTec

Ionic Liquids Today, Issue 1/05

Ionic Liquids Today

Issue 1-05, Monday, 28th February.

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I. Our Intention for Ionic Liquids Today

By Thomas Schubert.

As 2005 begins IOLITEC would like to inform and discuss with scientists from academia and industry the hottest topics, latest developments and opinions in this extremely dynamic field of R&D. Each issue contains a current topic, which will also be discussed at our Forum "ionic liquids" (http://www.iolitec.de/forum).

With our column "Bösmann says: Hot stuff!", we want to put light on an actual paper that focuses on applications and/or new materials. Finally, we'll present interesting new materials with interesting applications and/or properties in each new issue.

II. A brief history of IOLITEC

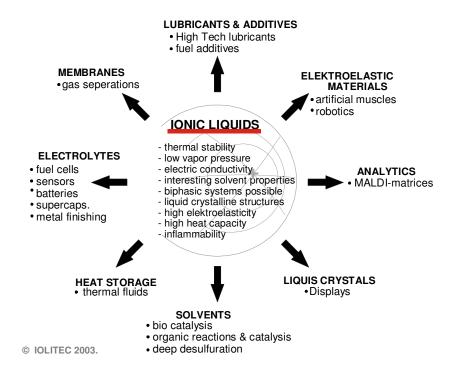
By Thomas Schubert.

First of all, for those who might not know our company, we would like to introduce ourselves by giving you a brief summary of our mission and business:

IOLITEC was founded in 2002 by Andreas Bösmann and Thomas J.S. Schubert, leading specialists in designing tailor made Ionic Liquids and in identifying interesting applications. IOLITEC's business then started rapidly at the BioTechPark Freiburg with contract R&D-services around the versatile field of Ionic Liquids applications.

We have already identified a broad variety of interesting applications with great industrial relevance (see next page). Some others are in preparation and will be presented soon.





In October 2003, we were proud to sign our first employee contract. Meanwhile our team consists of the two founders, two chemists (F. Agel and Dr. T. Beyersdorff), one freelancer (Dr.-Ing. M. Schlatter), one laboratory assistant (S. Geng) and one economist.

In April 2003 the company's idea was awarded with the 4th place at start2grow business-plan-competition and our technology was honoured by the "Freiburger Innovationspreis 2004".

In 2004 we decided to focus on 5 areas:

- 1. Contract R&D-services
- 2. Special Chemistry (Ionic Liquids)
- 3. Sensor-Technology
- 4. Energy
- 5. Nanotechnology

In the near future, we'll develop each focus into an independent division. Our coretechnology "Ionic Liquids", will be the driving force behind each unit.



III. Discussion: How "Green" are Ionic Liquids?

By Thomas Schubert.

If we take a serious look at the papers published over the past 5 years, Ionic Liquids were often associated with the word "green". The sixth sense of most chemist's might have already realised that this statement, with it's importance, could not be the complete story: One prediction assumes that up to 10^{18} substances are theoretically possible. From this broad variety it's almost impossible that all these materials are supposed to be green or satisfy the demand of sustainability. As a consequence, I predict that there are or will be ionic liquids, which you can eat, others, which are (eco)toxic, non-biodegradable or even persistent. Let's get ready to rumble!

IV. Community

By Thomas Schubert.

Latest news from the "Ionic Liquid Community":

- Trendy:

Found at the "Nachrichten aus der Chemie" (in German language), Issue March, 2005, p. 53: At the "Trendbericht technische Chemie 2004" Ionic Liquids opened the article under the topic *New Materials*.

- Congratulations:

Merck KgaA, Darmstadt, has won the "Encouraging Innovation Awards for 2004".

Ion analytics:

Ionic Liquids will be found and the CIA conference 2005 (not the Central Intelligence Agency): "Die Ionenchromatographie . Eine wichtige Methode für die Analytik ionischer Flüssigkeiten"

V. Bösmann says: "Hot stuff!"

By Andreas Bösmann.

Low-melting sugar-urea-salt mixtures as solvents for Diels-Alder reactions.

G. Imperato, E. Eibler, J. Niedermaier, B. König, Chem. Comm. 2005, 1170-1172.



... and now for something completely different !

It may seem somewhat unusual to start the first comment on Ionic Liquid literature with a non-Ionic Liquid paper, but the sweetness of the topic justifies some closer reading. First of all the abstract:

My Abstract: Mixtures of sugar-urea-salt give low melting compunds of mp's 65-75°C. They seem to be viscous as expected. The authors performed Diels-Alder reaction of CP and acrylates, reaction rates and endo-exo ratios comparable with IL and scCO₂. No chiral induction despite chiral solvents. (as others have, including myself, observed in other chiral Ionic Liquids).

Extractive workup, yields 72-100%

I feel myself reminded of papers from *Abbott et al.* who studied low melting eutectic mixtures of various ammonium salts with urea.¹ So here other low-melting eutectic mixtures are presented which can be used as solvents for Diels-Alder reactions; probably other reactions are possible as well. Is there any use for this type of solvent?

On first sight, this class of solvent is very unattractive, being a mixture of three components (most of us don't like too many components in their reactions that may interfere). Then the new solvent has to be heated to above 65°C to be liquid, when finally molten it appears to be quite viscous. And what do we get then? A solvent that performs just as well as others do! But if you take a look on some older literature on Ionic Liquids, you will find pretty much the same situation. Only a few years ago, unsuitable Ionic Liquids where used in every type of reaction, the purity ob the IL was questionable, workup procedures where mediocre at best. Nowadays the situation is quite different; researchers have learned quite a lot about Ionic Liquids, new Ionic Liquids are reported every month. So maybe what we see here is the beginning of yet another class of solvents and the difficulties mentioned above are just the teething troubles?

¹ A.P. Abbot, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, *Chem. Commun.* **2003**, 70-71.



A clear advantage of this type of solvent is its very low toxicity and the use of renewable starting materials, so this part of the "eco-debate" can be considered to be done.

So what direction can or should this development take ?

In my opinion, the biggest problem to be adressed is the rather high viscosity. In this context, my suggestion is to use mixtures of sugars and/or salts or try different salts. What about choline chloride?

The authors decided to use an aqueous workup: This might cause problems when drying the recycled solvent. An alternative could be a distillative workup-procedure. In case this doesn't work, one should have some solvents at hand that can be used for a biphasic extraction.

Finally, I'd like to stress that I appreciate the thought of using solvents that are like Ionic Liuqids and potentially can reach "food grade". These materials may open the door to sustainable, or even "green" solvents.

At our Ionic Liquids Forum (http://www.iolitec.de/forum) I'm open to discussion about this article.

IV. Interesting New Materials

By Tom Beyersdorff.

IOLITEC's Portfolio

With our first issue of *Ionic Liquids Today* you'll find our current portfolio at the appendix or take a look at our online-portfolio at www.iolitec.de/ionic.php. By far the most Ionic Liquids are based on the 1-Alkyl-3-methyl-imidazolium-cation in combination with different anions, such as trifluormethanesulfonate, tetrafluoroborate, thiocyanate, dicyanamide or a halide. Our trialkylsulphonium-based Ionic Liquids may also be interesting, especially for electrochemical applications or if a hydrophobic system is needed.



In addition, we offer not only Ionic Liquids, but also useful precursors such as 1-Alkyl-imidazols up to chain length of 10, and anion-sources such as Lithium BTA or Triflic Acid and it's derivatives to complete our portfolio and with respect to customer's needs.

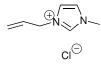
On request, we'll make you our best quote for any patent-free Ionic Liquid which is known by literature or that predictably can be synthesized on a scale from 50 g up to 1 kg.

Finally, together with our partners we are in the position to offer bulk quantities on request.

New Materials

In today's issue we want to introduce three new and interesting materials from our portfolio:

1-Allyl-3-methyl-imidazolium chloride: [Allyl-MIM] Cl



Zhang et al.^[1] reported a remarkable solubility of cellulose in this Ionic Liquid. For example [Allyl-MIM]Cl is able to dissolve up to 10wt% of cellulose at 100°C. As a consequence, it's a promising solvent for cellulose-chemistry. Furthermore, we predict a go and a potential solvent for other polysaccharides.

Our special offer:*

[Allyl-MIM] Cl: IL-022-50g 115,00 €

IL-022-100g 195,00€



1-Methyl-3-propyl-imidazolium iodide: [Pr-MIM] I 1-Hexyl-3-methyl-imidazolium iodide: [Hex-MIM] I

The use of ionic liquids in dye-sensitised Solar Cells (DSCs) has been discussed earlier $^{2)}$. The major role of Ionic Liquids in these systems is to serve as an electrolyte and/or anion source for the redox couple X^{-}/X_{3}^{--3} . The Ionic Liquids [Pr-MIM] I and [Hex-MIM] are electrolyte and contain a suitable anion they can serve nd their anion is a source for the most commonly used redox-couple I^{-}/I_{3}^{-} . I say: A perfect combination!

Our special offer:*

[Pr-MIM] I:	IL-025-50 g	90,00€

IL-025-100 g 170,00 €

[H-MIM] I: IL-026-50 g 90,00 €

IL-026-100 g 170,00 €

Triethylsulphonium bis(trifluoromethylsulfonyl)imide: [SEt₃] BTA

Why always imidazolium? What about sulphonium? In fact using sulphonium is really not a new idea, but still an interesting alternative: A conductivity of 7.1 mS/cm and an electrochemical window of 4.7 V (GC) are sufficient for some electrochemical applications.^[4] The hydrophobicity of this material might be also interesting...



Our special offer:*

[SEt₃] BTA: IL-030-50 g 90,00 €

IL-030-100 g 170,00 €

Interested? Please contact me by phone +49 (0) 761 6006-552 or by e-mail (order@iolitec.de).

[1] J. Wu, J. Zhang, H. Zhang, J. He, Q. Ren, M. Guo, *Biomacromolecules* **2004**, *5*, 266-268.

[2] P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168.

[3] P. Wang, S.M. Zakeeruddin, J.-E. Moser, M. Grätzel, J. Phys. Chem. B. 2003, 107, 13280.

[4] H. Matsumoto, T. Matsuda, Y. Miyazaki, Chem. Lett. 2000, 1430.

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^{*}All offers are valid until June, 30th, 2005.



<u>Appendix</u>

Our Ionic Liquids Portfolio

Name		ProdNo.
1-Ethyl-2,3-dimethyl-imidazolium trifluoromethanesulfonate purity: 99% (loLi <i>Lyt</i> ®-Quality)	H_3C N CH_3 F CH_3 F CH_3	IL-002-50 g IL-002-100 g
1-Ethyl-3-methyl-imidazolium dicyanamide purity: 98%	H ₃ C N NC NC CH ₃	IL-003-50 g IL-003-100 g
1-Ethyl-3-methyl-imidazolium methanesulfonate purity: 99% (loLi <i>Lyt</i> ®-Quality)	$\begin{array}{c c} H_3C \\ \hline \\ N \\ CH_3 \end{array} \qquad \begin{array}{c c} O \\ \hline \\ H_3C - S \\ \hline \\ O \end{array} \\ O^-$	IL-004-50 g IL-004-100 g IL-004-500 g
1-Ethyl-3-methyl-imidazolium nitrate purity: 99% (IoLi <i>Lyt</i> ®-Quality)	H ₃ C	IL-005-50 g IL-005-100 g
1-Ethyl-3-methyl-imidazolium tetrafluoroborate purity: 99% (loLi <i>Lyt</i> ®-Quality)	H ₃ C	IL-006-50 g IL-006-100 g IL-006-500 g



Name		ProdNo.
1-Ethyl-3-methyl-imidazolium thiocyanate purity: 99% (loLi <i>Lyt</i> ®-Quality)	H_3C N $S = C = N^-$ CH_3	IL-007-50 g IL-007-100 g IL-007-500 g
1-Ethyl-3-methyl-imidazolium tosylate purity: 99% (IoLi <i>Lyt</i> ®-Quality)	H ₃ C O S O S O CH ₃	IL-008-50 g IL-008-100 g IL-008-500 g
1-Ethyl-3-methyl-imidazolium trifluoromethanesulfonate purity: 99% (IoLi <i>Lyt</i> ®-Quality)	$ \begin{array}{c c} & F & O \\ & $	IL-009-50 g IL-009-100 g
1-Butyl-3-methyl-imidazolium dicyanamide purity: 99% (loLi <i>Lyt</i> ®-Quality)	H ₃ C N NC NC NC NC NC NC NC NC N	IL-010-50 g IL-010-100 g
1-Butyl-3-methyl-imidazolium hexafluorophosphate purity: 99% (IoLi <i>Lyt</i> ®-Quality)	H ₃ C F F F CH ₃	IL-011-50 g IL-011-100 g IL-011-500 g



Name		ProdNo.
1-Butyl-3-methyl-imidazolium tetrafluoroborate purity: 99% (loLi <i>Lyt</i> ®-Quality)	H ₃ C	IL-012-50 g IL-012-100 g IL-012-500 g
1-Butyl-3-methyl-imidazolium trifluoromethanesulfonate purity: 99% (loLi <i>Lyt</i> ®-Quality)	F—C—S—O— CH ₃	IL-013-50 g IL-013-100 g
1-Butyl-3-methyl-imidazolium chloride purity: 99% (IoLi <i>Lyt</i> ®-Quality)	H ₃ C N CI CH ₃	IL-014-50 g IL-014-100 g IL-014-500 g
1-Ethyl-3-methyl-imidazolium bromide purity: 99% (loLi <i>Lyt</i> ®-Quality)	H ₃ C N N Br -	IL-015-50 g IL-015-100 g IL-015-500 g
Triethylsulfonium bis(trifluoromethylsulfonyl)imide, purity: 99% (loLi <i>Lyte</i> ®-Quality)	Et + Et 0 CF3 CF3 O S O CF3	IL-030-50 g IL-030-100 g IL-030-500 g
N-Methyl-N-trioctylammonium bis(trifluoromethylsulfonyl)imide, purity: 99% (loLiLyt®-Quality)	Oct	IL-017-50 g IL-017-100 g IL-017-500 g



Name		ProdNo.
1-Hexyl-3-methyl-imidazolium hexafluorophosphate purity: 99% (loLi <i>Lyt</i> ®-Quality)	Hex N N F F F F F	IL-018-50 g IL-018-100 g IL-018-500 g
1-Hexyl-3-methyl-imidazolium tetrafluoroborate purity: 99% (IoLi <i>Lyt</i> ®-Quality)	Hex F F F Me	IL-019-50 g IL-019-100 g IL-019-500 g
1-Methyl-3-octyl-imidazolium hexafluorophosphate purity: 99% (loLi <i>Lyt</i> ®-Quality)	Oct F F	IL-020-50 g IL-020-100 g IL-020-500 g
1-Methyl-3-octyl-imidazolium tetrafluoroborate purity: 99% (loLi <i>Lyt</i> ®-Quality)	Oct F - F F F F F F F F	IL-021-50 g IL-021-100 g IL-021-500 g
1-Allyl-3-methyl-imidazolium chloride purity: 98% (loLi <i>Lyt</i> ®-Quality)	N N CI -	IL-022-50 g IL-022-100 g IL-022-500 g
1-Methyl-3-propyl-imidazolium iodide	Pr N 1 -	IL-025-50 g IL-025-100 g
1-Hexyl-3-methyl-imidazolium iodide	Hex N 1 - Me	IL-026-50 g IL-026-100 g
1-Ethyl-3-methyl-imidazolium trifluoroacetate	F ₃ C—CO ₂	IL-027-50 g IL-027-100 g



Portfolio Key Intermediates

Name		ProdNo.
Lithium bis(trifluoromethylsulfonyl)imide >97%	+ 0	KI-001-100 g KI-001-500 g KI-001-1 kg
Trifluoromethansulfone methylester	F ₃ C—S—OMe	KI-002-50 g KI-002-100 g
1-Ethyl-imidazole, 98%	Et N	KI-003-100 g
1-Butyl-imidazole, 98%	Bu N	KI-004-100 g
1-Hexyl-imidazole, 98%	Hex	KI-005-100 g
1-Octyl-imidazole, 98%	Oct N	KI-006-100 g
1-Decyl-imidazole, 98%	Dec N	KI-007-100 g