



Ionic Liquids Today, Issue 1/06

Ionic Liquids Today

Issue 1-06, Wednesday, 15th February, 2005.

Content of the first issue:

- I. Editorial
- II. Bösmann says: Hot stuff!
- III. Clean-Tech Applications
- IV. Community
- V. Tom Beyersdorff: My new materials.

I. Editorial

By Thomas Schubert.

The first time I came into contact with ionic liquids was in 1999 during a conference about catalysis at the University of Utrecht: A young man approximately of the same age as me told something about a new kind of solvents with no vapour pressure, the so-called "ionic liquids". Through the eyes of an inexperienced young chemist the advantages were striking, but I also mentioned that it could be – as so often before - just be another interesting footnote!

About 2 years later it was a great pleasure for me to work with (at this time) Dr. Peter Wasserscheid in Aachen. In 2003 he received the chair for Chemical Reaction Engineering at the University of Erlangen.

Today many companies from very different industrial sectors have identified ionic liquids not just as a new kind solvents or process chemicals, but also as performance chemicals in broad variety of other applications. Prof. Wasserscheid's work played a major role in this context.

We at Ionic Liquids Technologies are by-and-by with ionic liquids research together with both: academic research groups and R&D-groups from many industrial companies. That's why we believe that there will be a breakthrough not only as solvents, but also in performance chemicals within the next years in many fields of technology!

Congratulations, I: Prof. Dr. Peter Wasserscheid, University of Erlangen, received the famous **Gottfried-Wilhelm-Leibniz-Award 2006**. Prof. Wasserscheid is one of the pioneers and today one the moulded scientists in ionic liquid research. His article from the Angewandte Chemie 2001 is probably one of the most cited in ionic liquids research.

Ionic Liquids Today, Issue 1/06

My colleague and co-founder, Andreas Bösmann worked in the group of Prof. Wasserscheid on his PhD-thesis. And I'm proud as well having worked with him during my time in Aachen in 2001/2002. I'm sure that this can't be his last award (not only because he's just 35 and a famous Swedish award is missing!).

Congratulations, II: Prof. Dr. Ingo Krossing, ETH Lausanne, has accepted the **call from the University of Freiburg.** In April 2006 he assumes the chair for Inorganic Chemistry (formerly Prof. Vahrenkamp). "To us it's such a luck to have another state-of-the-art scientific working group just around the corner", Thomas Schubert, IOLITEC's Managing Director says. "It will help us to widen the already excellent co-operation with the University of Freiburg. Together with all the groups from the University of Freiburg, the Fraunhofer Institutes and the Freiburger Materials Research Center, our goal is to establish a cluster of excellence concerning ionic liquids.", Schubert added.

Dissolving Cellulose in ionic liquids: BASF announces co-operation with Prof. R. Rogers, University of Alabama. In addition, they acquired the corresponding exclusive intellectual property rights.

Cytec-Phosponium Ionic Liquids now available from IOLITEC: In a variety of applications, phosphonium ionic liquids are the materials of choice. "The phosphonium-based ionic liquids show a good performance as solvents or in biotech-applications, like protein-stabilization and crystallization.", Dr. Tom Beyersdorff, IOLITEC's Head of Special Chemistry says. "I'm sure that our R&D-division identifies soon a couple of other in screening tests!", he adds, "we'll keep you informed!".

IOLITEC's team extended: Since September 2005 we extended our team with Dr. Marcin Gonsior and Dipl.-Ing. Berthold Seßler.

Dr. Marcin Gonsior, 28, finished his PhD-thesis in the Group from Prof. Dr. Krossing, ETH Lausanne. During his PhD-Thesis at the University of Karlsruhe, he worked on the synthesis of weakly coordinating anions. In particular he worked on the stabilization of reactive phosphorous and arsenic cations. With the beginning of March 2006, he heads our Division Nanomaterials / Coatings.



Dipl.-Ing. Berthold Seßler, 56, was formerly Managing Director of Sessler Galvanotechnik, Würzburg. He's a well known specialist in electroplating technology with a over 30 years experience. He'll strengthen IOLITEC's activities on the field nanocoating and electroplating.





Ionic Liquids Today, Issue 1/06

II. Bösmann says: "Hot stuff!"

By Andreas Bösmann.

Acute toxicity of ionic liquids to the zebrafish (*Danio rerio*)

Carlo Pretti, Cinzia Chiappe, Daniela Pieraccini, Michela Gregori, Francesca Abramo, Gianfranca Monni and Luigi Intorre, *Green chemistry* 2006, (Advance Article).

Abstract: Acute toxicity and histological damage derived from exposure of zebrafish to some common and less common ionic liquids have been evaluated.

In this issue I'm not writing about exciting new developments of Ionic Liquids and their applications, but about the above article by Chiappe and co-workers about the toxicity of (selected) Ionic Liquids and its impact and implications.

This article has caused pretty much commotion, not by itself but by being cited as "warning shot for green chemistry" by the journal *Nature*. The negative impact after spreading through the journals and publications could be disastrous, so here we go with yet another opinion.

The use of quaternary ammonium salts as antibacterial and antifungal agents has quite a tradition now, indicating that this class of substances is, for some organisms, quite toxic. There have been reports that also a subclass of ammonium salts called "Ionic Liquids" can be toxic to small aquatic organisms, e.g. by *Jastorff et al.*¹

So what's new? Now we know that some Ionic Liquids are very toxic to zebra fish, and some others are not. This was very much to be expected, regarding the structural variety of Ionic Liquids (maybe the lower toxicities are a bit surprising, regarding the close relationship to the biocides mentioned above).

Concerning the structures of Ionic Liquids in this paper, it is obvious that the rule of thumb "longer alkyl chains make more toxic ammonium salts" holds as well for Ionic Liquids. The two substances exhibiting high toxicity are the ones with long chains, the others possess butyl or shorter chains. That fits very nicely with the theory that long-chain Ionic Liquids are incorporated into lipid-bilayer membrane of organisms, changing their ion-permeability and finally killing the organism. This is further supported by histological examination of the fish, showing damages at the structures of the gills and of the skin.

In this context, it's worth to be noted that 13 out of 15 Ionic Liquids have LC₅₀-values above 100 mg/L. This does not mean they are non-toxic, but they are just not very toxic.

¹ Jastorff et al., *Ecotoxicology and Environmental Safety* **58**(3) 396-404.



Ionic Liquids Today, Issue 1/06

In other words, no further differentiation was made between those Ionic Liquids, so one cannot deduce any information on which Ionic Liquid is the least toxic or on how to design low-toxicity Ionic Liquids.

It would be good to know if for example the seven BMIM-based Ionic Liquids (BMIM = 1-butyl-3-methyl-imidazolium) in this test exhibit different toxicities, enabling the reader to decide (if the choice exists) which Ionic liquid to choose.

Another missing information is the correlation of data to other experimental results, e.g. to studies conducted by *Maginn et al.*² and *Bernot et al.*³ on *Daphnia magna* (a freshwater crustacean).

Finally, it must be mentioned that this paper gives information on the toxicity of some Ionic Liquids on fish. This does not say that those Ionic Liquids rated as "lower toxic" are not toxic to daphnia, humans or other animals. BMIM-Cl for instance is rated as "not acutely toxic" to fish, but as "acutely toxic" to humans. Just the other way round, Ammoeng 100 is very toxic to fish, but has a $LD_{50} > 2000 \text{ mg/kg}$ in mice. So this paper gives information just on what it says, not more!

After all this criticism, it has to be remarked that this article is nevertheless a valuable contribution to the toxicological assessment of Ionic Liquids. New Ionic Liquids are developed on a daily basis and it is good to see some of the materials developed more recently in a toxicity-test.

Another important feature is that it brought the fact that Ionic Liquids are not always green (well-known in the closer community, but not always spoken out) to a broader audience by being cited by *Nature*. It is a bit sad that it happened in the rather undifferentiated way *Nature* did it, since not all Ionic Liquids have to be discredited like that.

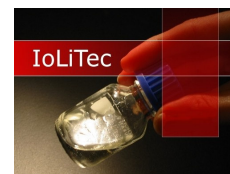
To come to an end, some things are to be learned:

- Ionic Liquids are not always "green"
- keep the side-chains short
- we need more data on Toxicity
- don't feed your fish with Ionic Liquids
- not all Ionic Liquids are the same: some will kill you, others kill you softly and there will be also one you're allowed to eat!

There are Ionic Liquids around that are not too toxic, and once we have learned what structural features cause toxicity, we can make our new Ionic Liquids even less toxic !

² http://www.nd.edu/~ed/Research/IL_toxicology.html

³ Bernot et al, *Environmental Toxicology and Chemistry*, 24(1), 87-92.



Ionic Liquids Today, Issue 1/06

III. Cleantech applications, Part I

By Thomas Schubert.

Over the past years, a number of interesting articles about the use of ionic liquids as media for synthesis and catalysis as well for separation technology and chemical engineering were published. In this context, ionic liquids were often labelled as "green solvents", which is, gently spoken (please see also "hot stuff!"), definitely not the whole true for the whole class of ionic liquids. Nevertheless, beside the overwhelming number of applications, where the use of ionic liquids as innovative solvents is described, we identified applications, which correspond also with "green-" or "clean-technology", but focusing on other physical and electrochemical properties.

After a dramatic increase of oil prices in 2005 the responsible care with all kind of resources and in particular of fossil energy sources became more important than ever. In this context, ionic liquids are interesting in a variety of cleantech applications.

In this issue I'd like to concentrate on applications based on **thermodynamic properties** of ionic liquids in cleantech application. In part II, which is planned for the upcoming issue, we focus on **electrochemical properties**.

Part I: Cleantech applications based thermodynamic properties

Some Ionic Liquids show a unique combination of physical and in particular interesting thermodynamic properties. They

- **are liquid over wide temperature range,**
- **have a negligible vapour pressure,**
- **are thermally stable,**
- **have moderate to good heat storage densities,**
- **the activity for water is tuneable.**

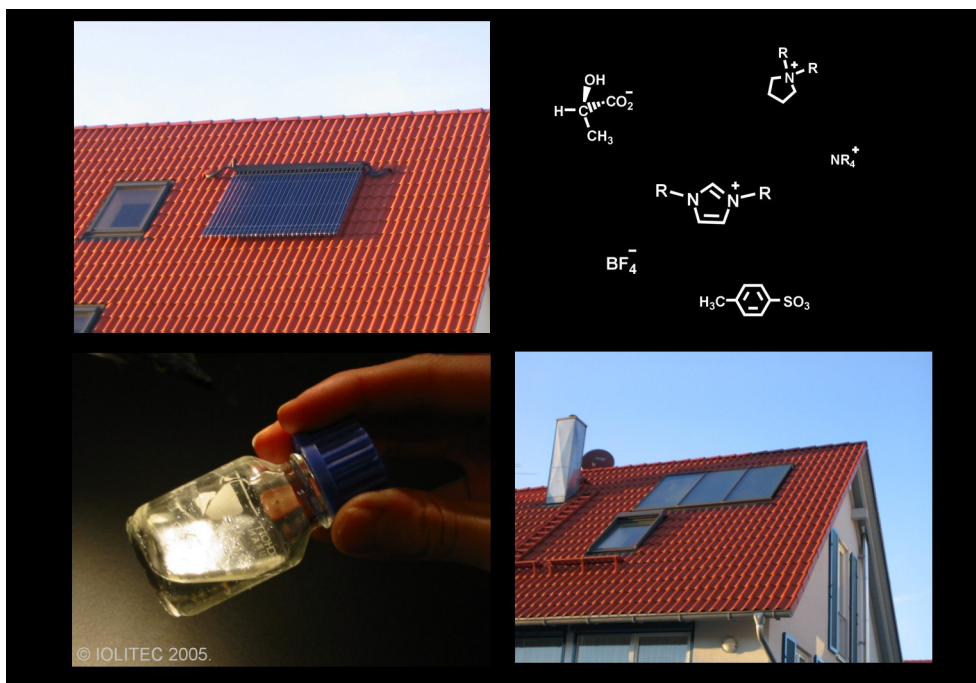
Thermal Fluids

In 2001 *Rogers et al.* from the University of Alabama were the first who suggested during the **Solar Forum 2001** the use of ionic liquids as thermal fluids for solar thermal installations.⁴ Though initially published thermal stabilities from up to 480°C have been corrected after a couple of different reinvestigations (today selected

⁴ B. Wu, R.G. Reddy, R.D. Rogers, *Proceedings of Solar Forum 2001*.

Ionic Liquids Today, Issue 1/06

materials show long-term-stabilities from about 250°C),⁵ the unique mix of physical/thermodynamic properties opens the door for their use as thermal fluids.

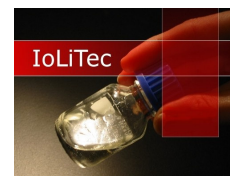


IOLITEC explores since 2003 the potential of using ionic liquids as thermal fluids. In 2005 we widened up our research activities together with our partners from the Fraunhofer Institute for Solar Energy Systems (FhG ISE, Freiburg), from Tyforop Chemie (Hamburg) and from the Centre for Environmental Research and – Technology (UFT Bremen) from the potential use of ionic liquids in solar thermal house installations. This project is funded by the **Deutsche Bundesstiftung Umwelt e.V.**

With this issue, we would like to introduce our first IOLI**Therm**[®] Test-Kit “Thermal Fluids”, which is designed for research on high-end applications, where an extreme technical performance is needed.

Furthermore, we’re in the position to produce bulk-quantities up to 100 kg. Together with our partners, we’re in the position to offer suitable materials even on a ton’s scale.

⁵ K.J. Baranyai, G.B. Deacon, D.R. MacFarlane, J.M. Pringle, J.L. Scott, *Aust. J. Chem.* **2004**, 57, 145-147.



Ionic Liquids Today, Issue 1/06

Cooling technology

Not only heating, but also cooling of buildings by using solar power is an interesting feature: To transform heat into cooling energy heat pumps have to be used. In this context, ionic liquids could play another important role as working media in **sorption cooling technology**.

Today sorption cooling technology produces cooling energy by evaporation using combinations of e.g. water - lithium bromide as working media. To regenerate the lithium bromide it has to be pumped heated.

Ionic liquids seem to be ideal media since they have three very important properties: They are liquid, they have just a negligible vapour pressure and some of them are very hygroscopic!

Since October 2005 IOLITEC explores the use of ionic liquids as new media in sorption-cooling-technology in another project funded by the **Deutsche Bundesstiftung Umwelt e.V.** together with our partners from the Institut für Technische Thermodynamik in Karlsruhe and from company Berndt KG.

IV. Community

By Thomas Schubert.

Preview: IOLITEC at exhibitions and conferences.

If you like to meet us at one of the upcoming exhibitions and conferences, please contact us at info@iolitec.de or by phone +49 (0) 7666 913929.

March, 23rd-24th: **Deutsche Bunsentagung**, Clausthal-Zellerfeld.

Meet us at our stand and ask Dr. Tom Beyersdorff and Dr. Thomas Schubert about high purity and ultra high purity materials for reasonable prices!

May, 15th-18th: **ACHEMA**, Frankfurt.

Meet us at the stand from the Centre for Environmental Research and –Technology (UFT), Bremen. We present our latest developments from the NEMESIS-project (funded by the BMBF).

May, 15th-18th: **Smart Coatings**, Berlin.

Andreas Bösmann, was invited as speaker about applications of ionic liquids in coating technology.



Ionic Liquids Today, Issue 1/06

Interesting articles:

Application: Capacitors

Solvent-free double-layer capacitors with polymer electrolytes based on 1-ethyl-3-methyl-imidazolium triflate ionic liquid

A. Lewandowski, A. Świdorska, *Appl. Phys A: Mater. Sci. & Process.*, **2006**, *82*, 579 – 584.

Application: Batteries

Reversibility of Lithium Secondary Batteries Using a Room-Temperature Ionic Liquid Mixture and Lithium Metal

S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, Y. Mita, A. Usami, N. Terada, M. Watanabe, *Electrochem. Solid-State Lett.*, **2005**, *8*, A577-A578

Application: Hydroformylation/Catalysis

Stability and Kinetic Studies of Supported Ionic Liquid Phase Catalysts for Hydroformylation of Propene

A. Riisager, R. Fehrmann, M. Haumann, B.S.K. Gorle, P. Wasserscheid, *Ind. Eng. Chem. Res.* **2005**, *44*, 9853-9859.

Physical Data: Vapor pressure

Vapor pressure and thermal stability of ionic liquid 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide

Y.U. Paulechka*, Dz. H. Zaitsau, G.J. Kabo, A.A. Strechan, *Thermochimica Acta* **2005**, *439*, 158-160.

Physical Data: Polarity

How Polar Are Ionic Liquids? Determination of the Static Dielectric Constant of an Imidazolium-based Ionic Liquid by Microwave Dielectric Spectroscopy

C. Wakai, A. Oleinikova, M. Ott, H. Weingärtner, *J. Phys. Chem. B* **2005**, *109*, 17028-17030.

Review (German Language):

Dr. Thomas Schubert, *Nachrichten aus der Chemie* **2005**, *53*, 1222-1225-
Short review about applications of ionic liquids (German language).



Ionic Liquids Today, Issue 1/06

V. Interesting New Materials

By Tom Beyersdorff.

Applications for Ionic Liquids

In the context of IOLITEC's general R&D in the manifold area of ionic liquids we identified several new applications for ionic liquids. Two innovative applications are presented below.

Ionic Liquids as Solvents for Karl-Fischer-Titration

The determination of water in a broad variety of different samples is of great importance in many areas of industrial analytics such as food-industry, pharmaceuticals and fine-chemicals. One of the most powerful tools is the so called *Karl-Fischer-Titration* (KFT). This method allows to determine the water content very precisely, in some case below 50 ppm. The equipment for the titration process includes an automatic titrator, special reagents for the titration and a water-free solvent that is able to dissolve many different substances completely.

IOLITEC developed (patent pending)^[1] a method that takes advantage of the manifold solvent-properties of ionic liquids in matters of Karl-Fischer-titration, especially to enable the determination of water content of materials that are almost insoluble in classic solvents. Even though classic solvents cover a wide range of materials, there are still a number problems in the food-, pharmaceutical- and polymer-areas.

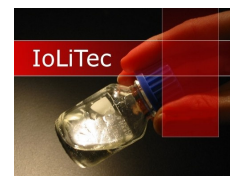
As we demonstrated in a couple of examples (e.g. for cheese, nuts or some polymers), some materials could be dissolved in our new Karl-Fischer-solvents completely. As a consequence, it's now possible to determine the water-content directly without an extensive preparation-procedure of the specimen.

To extent the number of applications and tritration methods, we co-operate with the leading manufacturer of KFT Metrohm.

Our special offer:*

KF-HydroPro-010(500 g)	380,00 €
KF-HydroPro-011(1 kg)	700,00 €

¹ D. K. Magnuson et.al., J.Solution Chem. 1984, 13,583-587.



Ionic Liquids Today, Issue 1/06

KF-HydroPro-020(500 g)	520,00 €
KF-HydroPro-021(1 kg)	950,00 €
KF-HydroPro-030(500 g)	710,00 €
KF-HydroPro-031(1 kg)	1300,00 €

Ionic Liquids for Stabilization and Crystallisation of Proteins

The crystallisation of enzymes and membrane proteins is the most popular tool for their structure determination by X-ray-measurements in biochemistry, biotechnology and medicine. The results from these measurements enable a deeper insight in the activity and selectivity of for example enzymes or membrane-proteins which are important factors in the field of biotechnology or relevant factors in the conception of new drugs in the pharmaceutical industry.

In recent years many publications described the application of Ionic Liquids in biocatalysis and their effects on proteins.

An early study by *Magnusson et al.* revealed the influence of Ethylammonium nitrate $[\text{EtNH}_3]^+ \text{NO}_3^-$, which is the oldest Ionic Liquid on record, on the alkaline phosphatase from *E. coli*.^[2] It was shown that low concentrations of this Ionic Liquid had an activating effect on the enzyme. In 2001 *Iborra et. al.* determined the stability and synthetic reactivity of α -Chymotrypsin in five different Ionic Liquids in a transesterification reaction.^[3] Later the same group used fluorescence and CD-spectroscopy to verify the previously made conclusions.^[4]

Lange et.al. used Ionic Liquids as refolding additives for two model proteins.^[5] All tested Ionic Liquids acted as refolding enhancers, with varying efficacies and efficiencies.

Recently *MacFarlane et.al.* reported a group of biocompatible Ionic Liquids which are able to dissolve and stabilize significant amounts of proteins such as cytochrome c.^[6]

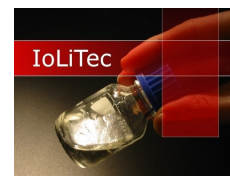
² D. K. Magnuson et.al., J.Solution Chem. 1984, 13,583-587.

³ J. L. Iborra et.al., Biotechnology and Bioengineering 2001, 75, 563-569.

⁴ J. L. Iborra et.al., Biotechnology and Bioengineering 2004, 88, 916-924.

⁵ C. Lange et.al., Protein Science 2005, 14, 2693-2701.

⁶ D. r. MacFarlane et.al., Chem. Comm. 2005, 4804-4806.



Ionic Liquids Today, Issue 1/06

IOLITEC's own research focused on the stabilization and crystallization of lysozyme as a model protein from different Ionic Liquids. The fascinating results from these experiments finally led to a patent application in 2004.^[7]

With the beginning of 2006 IOLITEC offers a **protein-crystallisation-kit** which contains 10 different ionic liquids. It's now available in two package-sizes (10x 10 g and 10x 25g).

The Protein-Kit contains the following Ionic Liquids:

- Triethylsulfonium bis(trifluoromethylsulfonyl)imide, 99%**
- 1-Butyl-3-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide, 99%**
- 1-Butyl-3-methyl-imidazolium dicyanamide, 98%**
- Triisobutylmethylphosphonium tosylate, 98%**
- 1-Ethyl-3-methyl-imidazolium trifluoromethanesulfonate, 99%**
- N-Butyl-N-trimethylammonium bis(trifluoromethylsulfonyl)imide, 99%**
- Cholin dihydrogenphosphate, 99%, 90% aqueous solution H2O**
- Ethanolammonium formiate, 98%**
- Ethylammonium nitrate, 98%**
- 1-Ethyl-3-methyl-imidazolium ethylsulfate, 99%**

Our special offer:*

small Kit : IL-Protein-Kit-10	249,50 €
large Kit : IL-Protein-Kit-25	499,00 €

CYPHOS®-IL now available from IOLITEC

With the beginning of 2006 IOLITEC expanded its Ionic Liquids-portfolio by various phosphonium IL produced by Cytec Industries Inc.

A complete list of CYPHOS®-IL which can be purchased by IOLITEC is now available at www.iolitec.de. All products are also available in multi-ton-scale on request.

If you need a quotation or more information on these IL, don't hesitate to contact us:

Phone: +49 (0)7666 9129591

Email: order@iolitec.de

⁷ A. Bösmann, T.J.S Schubert, DE102004027196.



Ionic Liquids Today, Issue 1/06

Special offers from our portfolio:

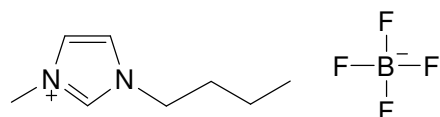
All following products are also available in multi-kg-scale.

For a quotation contact us:

Phone: +49 7666 9129591

Email: order@iolitec.de

1-Butyl-3-methyl-imidazolium tetrafluoroborate: [BMIM] BF₄

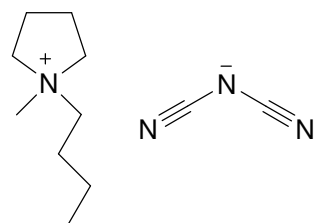


This "2nd-generation" Ionic Liquid can be used in manifold applications such as catalysis or electrochemistry.

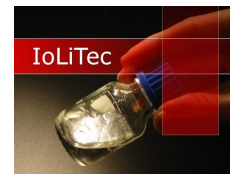
Our special offer:*

[BMIM] BF₄ (99%):	IL-012-100 g	112,50 €
	IL-012-250 g	243,00 €
	IL-012-500 g	400,00 €

1-Butyl-1-methyl-pyrrolidinium dicyanamide: [BMPyrr] N(CN)₂



This is a new Ionic Liquid in our portfolio. It is characterized by a viscosity of 45cP (20°C) and a conductivity of 10 mS/cm (20°C). Like many other dicyanamides we expect [BMPyrr] N(CN)₂ to be a good solvent for many biopolymers like for example cellulose.



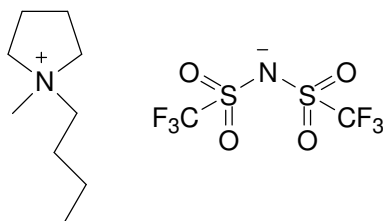
Ionic Liquids Today, Issue 1/06

Our special offer:*

[BMPyrr] N(CN)₂ (98%):	IL-041-100 g	450,00 €
	IL-041-250 g	1055,00 €
	IL-041-500 g	2000,00 €

1-Butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide:

[BMPyrr] NTf₂

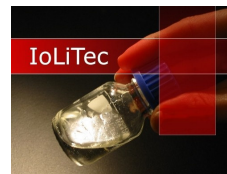


The thermal and electrochemical stability of this ionic liquid qualify it to be the perfect solvent for electrochemical applications. IOLITEc supplies this IL in two grades of purity.

Our special offer:*

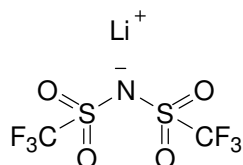
[BMPyrr] NTf₂ (99%):	IL-035-100 g	170,00 €
	IL-035-250 g	380,00 €
	IL-035-500 g	650,00 €

[BMPyrr] NTf₂ (99+%):	IL-035+100 g	180,00 €
	IL-035+250 g	425,00 €
	IL-035+500 g	820,00 €



Ionic Liquids Today, Issue 1/06

Lithium bis(trifluoromethylsulfonyl)imide: Li NTf₂



Li NTf₂ is a widely used Li-source for Lithium-ion-batteries as well as a NTf₂-source for Ionic Liquids, which are characterized by in most cases high thermal and electrochemical stability combined with a relatively high conductivity.

Our special offer:*

Li NTf₂ (98%):	KI-001-100 g	150,00 €
	KI-001-250 g	230,00 €
	KI-001-500 g	380,00 €
	KI-001-1 kg	720,00 €

* All special offers are valid until April 30st, 2006.

Impressum

© Ionic Liquids Technologies GmbH & Co. KG.
Ionic Liquids Today will be released 4 times a year.

Contact:

IoLiTec

Ionic Liquids Technologies GmbH & Co. KG

Ferdinand-Porsche-Strasse 5/1

D-79211 Denzlingen, Germany

phone: +49 (0) 7666 913929

fax: +49 (0) 7666 9129345

info@iolitec.de

www.iolitec.com

If you don't like to receive the upcoming issues, please send an e-mail to info@iolitec.de containing "Unsubscribe".