# **Ionic Liquids Today**

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- >>> Colour and Purity of Ionic Liquids
- >>> Electrodeposition of Aluminium
- >>> Weakly Coordinating Anions

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## I. Editorial

by Thomas J.S. Schubert.

Since the release of our last newsletter the ionic liquid community was vigorous mixed up. The changes regard some of pioneers of ionic liquid commercialisation.

The first announcement was that a long-term colleague, Dr. Urs Welz-Biermann from Merck KGaA, leaves the company to accept a call to become the first Director of the freshly founded China Ionic Liquid Laboratory (CHILL) at Dalian/China. This stresses clearly that China has identified the importance of ionic liquid research.

From my very personal point of view, (now) Professor Welz-Biermann is surely one of the most important and profiled players in the ionic liquid community. The build up of Merck's ionic liquid activities are definitely strongly related with his name. When I entered the scene during my job at Solvent Innovation in 2001, we both were beginners and we helped each other a lot. After the foundation of IOLITEC in 2003, I found in Welz-Biermann a good co-operation partner, who really believed in ionic liquids, but also in the power of innovation from a start-up-company named IOLITEC.

My team and I wishes all the best and a successful start at CHILL. I'm sure that will read soon something about his activities in IONIC LIQUIDS TODAY!

The second announcement is at least comparable remarkable: The pioneer of ionic liquid development & distribution, but also my diving board into the ionic liquid scene (I was the first employee!) Solvent Innovation was bought by Merck KGaA (USA: EMD) to become Merck-Solvent-Innovation. The former share-holders Dr. Claus Hilgers, ionic liquid pioneer Professor Peter Wasserscheid, and Creavis (Evonik), who joined the corporation in 2003, sold their shares completely to Merck. This



demonstrates clearly the interest of major companies in ionic liquids, and, of course, the strong interest of Merck, in particular.

To our best knowledge we became now the independent start-up-company, which acts longest in the field of ionic liquid research and distribution, and, if it wasn't the case before, presumably the largest and most experienced start-up-company in the scene.

To demonstrate this, please do not hesitate to contact us to test our experience...

Best regards,

Thomas J.S. Schubert, Managing Director, IOLITEC.



## **II** Colour Purity and Purification of Ionic Liquids

by Dr. Marco Klingele.

Ionic liquids have moved more and more into the centre of academic and industrial research in recent years with the number of publications dealing with these materials virtually exploding from only a handful per annum a few years back to thousands nowadays. This is due to the fact that ionic liquids hold great promise to revolutionize many known applications and make possible the development of new, more sustainable processes, exploiting the unique combination of properties that these materials provide. A very large number of anion-cation combinations are possible, which offers the opportunity to design new materials and tailor their physical properties, e.g. melting point, density, viscosity and miscibility with other solvents, to suit a specific application. Thorough characterisation of ionic liquids and the collection of reliable physical data are utterly important for the development of new applications.

In this context purity is one of the major issues in ionic liquids research [1]. It is well known that impurities can change the physical properties of ionic liquids considerably and in some cases cause significant variability in the physical data measured and reported. To give just one example, the melting point of 1,2-dimethyl-3-propylimidazolium chloride varies from 58–66°C [2] to 138°C [3] in the literature. Depending on the type of ionic liquid the most common impurities are organic volatiles (e.g. unreacted amine, unreacted alkylating agent or trace amounts of residual solvent), halide impurities from incomplete anion exchange, other ionic impurities originating from contaminants in the reagents used and water. All of these impurities affect the physical properties and might also affect the performance of ionic liquids in a given application. Sometimes strict exclusion of a certain contaminant is crucial for a process to work while in many cases overly strict purity requirements are unnecessary.



While there is a broad spectrum of methods available for the purification of conventional materials, the purification of ionic liquids presents some difficulties. It is exactly the otherwise advantageous properties of ionic liquids (e.g. very low vapour pressure, low melting points and good miscibility with common solvents) that render most of the traditional purification methods like distillation, recrystallisation or extraction useless. In order to obtain pure ionic liquids the use of rigorously purified starting materials and the employment of manufacturing procedures that meet the highest quality standards are essential [4]. But even then it is not always possible to produce highly pure ionic liquids simply because sometimes the synthetic pathways preclude that such high purity levels can be achieved.

Although colourlessness is generally perceived as a prime quality criterion, a yellow, orange or somewhat brownish colouration of an ionic liquid should probably be the least concern in this context. Colour is usually the result of unidentifiable trace amounts of impurities [5]. While in most cases it is possible to obtain colourless materials, certain anions (e.g. iodides, thiocyanates or dicyanamides) make it practically impossible to obtain colourless ionic liquids. For most applications of ionic liquids colour is not a crucial parameter, though. It has been reported in the literature that ionic liquids can be decolourised and hence purified using sorbents like activated charcoal [5,6,7,8], alumina [7] or silica [5]. Indeed, sorbent treatment works well with many ionic liquids and colourless or only slightly coloured materials can be obtained. However, it has been found that the use of sorbents to "purify" ionic liquids can actually lead to further contamination, for example in the case of alumina [9]. It is to be expected that other sorbents behave similarly.

Another aspect of ionic liquid purification or the manufacturing of ultra-pure ionic liquids, respectively, is the fact that every additional step during the production process directly correlates to the cost of the material. Therefore, a reasonable compromise between purity requirements and economic considerations in commercial ionic liquid production and use is necessary. Ionic liquids users need to be aware that some impurities do not matter for certain applications and that some materials are hard or even impossible to manufacture at the highest purity levels or at acceptable cost.

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At IoLiTec we always try to meet our customers needs and provide the best solution to a problem. Our ionic liquids are produced to the highest purity level that can be achieved in an economical way. However, if you have specific needs, e.g. require colourless materials for spectroscopy or ionic liquids free of certain impurities, please do not hesitate to discuss your need with us. We will be glad to make the possible happen!

- [1] K. R. Seddon, A. Stark, M.-J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275.
- [2] H. L. Ngo, K. LeCompte, L. Hargens, A. B. McEwen, *Thermochim. Acta* 2000, 357–358, 97.
- [3] J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.* **1982**, *21*, 1263.
- [4] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, 2nd edition, Wiley-VCH, Weinheim, **2008**.
- [5] M. J. Earle, C. M. Gordon, N. V. Plechkova, K. R. Seddon, T. Welton, *Anal. Chem.* 2007, *79*,758.
- [6] P. Nockemann, K. Binnemans, K. Driesen, *Chem. Phys. Lett.* **2005**, *415*, 131.
- [7] G. B. Appetecchi, S. Scaccia, C. Tizzani, F. Alessandrini, S. Passerini, *J. Electrochem. Soc.* **2006**, *153*, A1685.
- [8] A. K. Burrell, R. E. Del Sesto, S. N. Baker, T. M. McCleskey, G. A. Baker, *Green Chem.* 2007, *9*, 449.
- [9] F. Endres, S. Zein El Abedin, N. Borissenko, Z. Phys. Chem. 2006, 220, 1377.



### **III** Electrodeposition of Aluminium from Ionic liquids

by Andreas Reisinger.

To improve either the appearance or the corrosion resistance of work pieces, coatings are today of outstanding importance for many applications. The most commonly used way to apply coatings certainly is electrodeposition of metals. Even though there do exist other techniques such as PVD or CVD, they are expensive and only used for special applications. One metal with excellent properties as coating layer is aluminium. However, this metal is not acceible via classical electroplating technologies due to its base character and the comparably narrow electrochemical window of water. In other words: one would rather decompose water than deposit aluminium from an aqueous electrolyte.

Therefore, numerous attempts have been made to deposit aluminium from a nonaqueous electrolyte systems.<sup>[i]</sup> These systems often consist organic solvents in combination with organoaluminium compounds. Today, this method is even available on a commercial basis, however, the combination of highly flammable organic solvents and pyrophoric compounds is dangerous and requires special precautions.

Parallel to the development of the organic electrolyte systems, the possibility of aluminium electrodeposition from room temperature molten salts could be shown. These salts consist of chloroaluminate anions in combination with electrochemically stable organic cations such as imidazolium, pyridinium or pyrrolidinium.<sup>[1]</sup> One of the major advantages of this approach is that the electrolyte is due to its salt-like character not flammable and therefore much safer in use. Within the past 5 to 10 years, the development showed a tendency even to air and waterstable electrolytes, mostly based on hydrophobic NTf<sub>2</sub>-salts.<sup>[ii]</sup>

Within the governmentally funded NEMESIS Project, one task of IOLITEC consisted in the demonstration of AI electrodeposition from different electrolytes and onto different substrates.

Since possible deposition rates are rather low for the nowadays very popular air- and waterstable ionic liquid based electrolyte systems such as  $BMPyrr^+N(Tf)_2^-$  /  $AlCl_3$ ,



IOLITEC concentrated its work on the older but well known tetrachloroaluminate based electrolytes. With these imidazolium salt based systems several and different metallic substrates could be coated reproducably and with good adherence. Furthermore it could be shown that an electrolyte can be used over a longer period and for several depositions before it has to be replaced. Within this research work, also the influence of different additives and deposition parameters has been investigated.



**Figure 1.** Cross section (left) and REM picture (right) of a deposited Al-layer on a Cu substrate (10.000 s duration of deposition).

Figure 1 shows a REM picture as well as a cross section of a deposited aluminium layer. Especially the cross section shows the the layer is rather homogeneous and well interconnected with the substratesone.

Furthermore it could be shown that the thickness of the coating layer may be improved by prolongued deposition time (Figure 2).





**Figure 2.** Cross section of Al layers received at different deposition times: 10.000s (left), 20.000s (middle) and 30.000s electrolyte with different additives. (right).

Additives are commonly used in conventional electrodeposition to optimise parameters such as deposition rates or the morphologies of the surfaces. These techniques have been also applied for the ionic liquid based aluminium test electrolytes, which led to very homogeneous and glossy aluminium layers with good interconnection to the substrate.

These examples as well as numerous scientific articles<sup>[1]</sup> demonstrate that it is possible to obtain high quality aluminium layers not only from organic but also from ionic liquid based electrolyte systems. With its continuous micro reactor production lines, IOLITEC is in the position to produce ionic liquid based electrolytes for pilot plant applications (100 kg scale). Upon request, the production capacity can also be expanded to a ton scale. If you are interested in electodeposition of base metals from ionic liquids, please do not hesitate and contact us.

<sup>[1]</sup> Yuguang Zhao, T. J. VanderNoot *Electrochim. Acta*, **1997**, *42*, 3.

S. Zein El Abedin, E.M. Moustafa, R. Hempelmann, H. Natter, F. Endres *Electrochem. Commun.*, 2005, 7, 1111; F. Endres, S. Zein El Abedin *Phys. Chem. Chem. Phys.*, 2006, *8*, 2101.



## IV Weakly coordinating anions for the synthesis of ionic liquids

Weakly coordinating anions (WCAs) have gained a lot of interest in chemistry in recent years.<sup>1</sup> Popular classes of WCAs are based on highlyfluorinated alkoxyaluminates or borates. Extensive studies on fluorinated alkoxyaluminates have been performed by Krossing *et al.*<sup>2</sup> WCAs play an important role in i.e. catalysis since they are able to stabilize highly reactive cationic species due to their low basicity.

*Krossing et al.*<sup>3</sup> were able to stabilize a large number of reactive cations such as  $PX_4^+$ ,  $P_2X_5^+$  and  $P_5X_2^+$  (X=Br, I) in the presence of the  $[Al(pftb)_4]^-$  anion (pftb=  $OC(CF_3)_3$ ).

They were also able to isolate complexes cations such as  $Ag(P_4S_3)^+$  and  $Ag(P_4S_3)_2^+$  in combination with the the  $[Al(pftb)_4]^-$  anion.<sup>4,5</sup> In addition, RT stable salts of the tris(ethene)silver-cation were obtained by stabilization with the  $[Al(pftb)_4]$ -anion.<sup>6</sup> Krossing *et al.* also synthesized and characterized various cationic Bronsted acid complexes of the perfluorinated alkoxyaluminates.<sup>7</sup>

Recently *Mudring et al.* reported on the synthesis of ionic liquids containing a  $[Al(hfip)_4]$ -anion (hfip= OCH(CF<sub>3</sub>)<sub>2</sub>) by metathesis reaction of Li  $[Al(hfip)_4]$  and BMIM Cl or BMPyrr Cl.<sup>8</sup> It was show that BMIM  $[Al(hfip)_4]$  has a melting point of 34°C whereas BMPyrr  $[Al(hfip)_4]$  melts at 47°C. The viscosities at 60°C where 7.85 mm<sup>2</sup>/s for the BMIM species and 12.92 mm<sup>2</sup>/s for the BMPyrr species. Which are lower than the viscosities of ionic loiquids such as BMIM PF<sub>6</sub> or BMIM BF<sub>4</sub> at the same temperature. High electrochemical windows of 8V were determined for both compounds.

However, a major draw back of ionic liquids with  $[Al(hfip)_4]$  anions is the decomposotion of the anion in the presence of water. The attempt to synthesis water stable ionic liquids with BMIM or BMPyrr cations and an  $[Al(pftb)_4]$  anion lead to salts with meltingpoints >100°C.

<sup>&</sup>lt;sup>1</sup> I. Krossing, I Raabe, *Angew. Chem. Int. Ed.* **2004**, *43*, 2066.

<sup>&</sup>lt;sup>2</sup> I. Krossing, A. Reisinger, *Coord. Chem. Rev.* **2006**, *250*, 2721.

<sup>&</sup>lt;sup>3</sup> M. Gonsior, I. Krossing, L. Müller, I. Raabe, *Chem. Eur. J.* **2002**, 4475-4492.

<sup>&</sup>lt;sup>4</sup> I. Krossing, A. Adolf, M. Gonsior, *J. Am. Chem. Soc.* **2002**, 7111-7116.

<sup>&</sup>lt;sup>5</sup> I. Krossing, L. van Wüllen, *Chem. Eur. J.* **2002**, 700-711.

<sup>&</sup>lt;sup>6</sup> I. Krossing, A. Reisinger, *Angew. Chem.*. **2003**, 5903.

<sup>&</sup>lt;sup>7</sup> I. Krossing, A. Reisinger, *Eur. J. Inorg. Chem.* **2005**, 1979-1989.

<sup>&</sup>lt;sup>8</sup> T. Timofte, S. Pitula, A.-V. Mudring, *Inorg. Chem.* **2007**, *46*, 10938.



According to personal information Krossing *et al.* will soon report on the synthesis and properties of tetraalkylammonium salts with different Al-based WCA anions.

In co-operation with **Prof. Krossing** from the University of Freiburg/Germany, IOLITEC expanded its portfolio by 4 salts of weakly-coordinating anions (WCAs), namely salts of the tetrakis(perfluoro-t-butoxy)aluminate-anion  $[Al(OC(CF_3)_3)_4]^-$ . Especially the lithium and silver salts are useful precursors for the synthesis of ionic liquids according to the well known procedures from literature.

#### Lithium tetrakis(perfluoro-*tert*-butoxy)aluminate: Li [Al(pftb)<sub>4</sub>]



The salt Li[Al(pftb)<sub>4</sub>] is a useful precursor for the introducing of the [Al(pftb)<sub>4</sub>]-anion into various other salts by metathesis. Li-Salts of WCAs are used as substitute for LiClO<sub>4</sub> in Li-catalysed Diels-Alder-reactions, 1,4-conjugate-additions and pericyclic rearrangement-reactions.<sup>9,10,11</sup> Also radical polymerisations have been catalysed by these kind of salts.

The use of Li  $[Al(pftb)_4]$  as electrolyte support in the Li-ion-batteries is limited since the mobility of large ions are insufficient for this application. However, a good performance has been achieved in polymer-based Li-ion-batteries using a Poly(ethylenoxide)-matrix.<sup>12</sup>

<sup>&</sup>lt;sup>9</sup> R. Braun, J. Sauer, *Chem. Ber.*, **1986**, *119*, 1269.

<sup>&</sup>lt;sup>10</sup> P. A. Grieco, J. J. Nunes, M. D. Gaul, *J. Am. Chem. Soc.*, **1990**, *112*, 4595.

<sup>&</sup>lt;sup>11</sup> A. Flohr, H. Waldmann, *J. Prakt. Chem.*, **1995**, *337*, 609

<sup>&</sup>lt;sup>12</sup> H. Tokuda, S. Tabata, M. A. B. H. Susan, H. Hayamizu, M. Watanabe, *J. Phys. Chem. B*, 2004.



#### Our special offer:\*

#### Li [Al(pftb)<sub>4</sub>] (98%):

| KI-018-1 g  | 55,00 €  |
|-------------|----------|
| KI-018-5 g  | 247,50 € |
| KI-018-10 g | 445,50 € |

#### Silver tetrakis(perfluoro-*tert*-butoxy)aluminate: Ag [Al(pftb)<sub>4</sub>]



This silver salt is facile starting material to introduce the  $[Al(pftb)_4]$  anion and it can be used in most chlorinated alkanes. It has also been described to catalyse i.e. a variety of hetero-Diels-Alder-reactions.<sup>13,14</sup>

If combined with various alkyl iodides synthetic useful alkyl-cations can be generated *in situ* by precipitation of AgI.

 $R-I + Ag [Al(pftb)_4] \rightarrow R^+ [Al(pftb)_4]^- + Ag-I$ 

Gonsior<sup>15</sup> used this silver-complex among others to stabilize a large number of reactive phosphenium- and arsenium-intermediates during his PhD-studies.

<sup>&</sup>lt;sup>13</sup> S. Saitoin, *Lewis Acids in Organic Synthesis*, *Ed.* H. Yamamoto, Wiley-VCH Weinheim, Germany, **2000**, 9.

<sup>&</sup>lt;sup>14</sup> N. J. Patmore, C. Hague, J. H. Cotgreave, M. F. Mahon, C. G. Frost, A. S. Weller, *Chem. Eur. J.*, **2002**, *8*, 2088.

<sup>&</sup>lt;sup>15</sup> M. Gonsior, " From cationic silver complexes to reactive Phosphenium- and Arsenium-intermediates stabilized by weakly coordinating anions", Dissertation, Göttingen: Cuvillier, **2005**, ISBN 3-86537-583-9.



#### Our special offer:\*

### Ag [Al(pftb)<sub>4</sub>] (98%):

| KI-019-1 g  | 65,00 €  |
|-------------|----------|
| KI-019-5 g  | 297,50 € |
| KI-019-10 g | 540,00 € |

## Triphenylcarbenium tetrakis(perfluoro-*tert*-butoxy)aluminate: Ph<sub>3</sub>C [Al(pftb)<sub>4</sub>]



This compound is of great interest in homogenous catalysis. Metallocenes of the formula  $[(Cp)2M(CH_3)]^+$  that are active catalysts, require a stable weekly coordinating anion, which is very important for the activity and selectivity of i.e. the polymerization. Ph<sub>3</sub>C [Al(pftb)<sub>4</sub>] generates very reactive catalysts of a well defined composition<sup>16</sup>:

$$(Cp)_2 Zr(CH_3)_2 + Ph_3 C \left[Al(pftb)_4\right] \rightarrow (Cp)_2 Zr(CH_3)^+ \left[Al(pftb)_4\right]^- + MeCPh_3$$

<sup>&</sup>lt;sup>16</sup> E. Y.-X. Chen, T. J. Marks, *Chem. Rev.*, **2000**, *100*, 1391.



#### Our special offer:\*

## Ph<sub>3</sub>C [Al(pftb)<sub>4</sub>] (98%):

| KI-020-1 g  | 65,00 €  |
|-------------|----------|
| KI-020-5 g  | 297,50 € |
| KI-020-10 g | 540,00 € |

## Diethyloxonium tetrakis(perfluoro-tert.-butoxy)aluminate monoetherate: H(OEt<sub>2</sub>)<sub>2</sub> [Al(pftb)<sub>4</sub>]



This protonated ether can be usen as a facile  $H^+$ -source since the reaction byproduct diethylether can easily be removed from the reaction mixture. With this compound the [Al(pftb)<sub>4</sub>] anion can easily be introduced to carboxylate salts.

## Our special offer:\*

#### H(OEt<sub>2</sub>)<sub>2</sub> [Al(pftb)<sub>4</sub>] (98%):

| KI-021-1 g  | 95,00 €  |
|-------------|----------|
| KI-021-5 g  | 427,50 € |
| KI-021-10 g | 769,50 € |



## V Applications of Ionic Liquids

## **Material Science**

#### Magnetite-embedded Cellulose Fibers prepared from Ionic Liquid

N. Sun, R. P. Swatloski, M. L. Maxim, M. Rahman, A. G. Harland, A. Haque, S. K. Spear, D. T. Daly, R. D. Rogers, *J. Mater. Chem.* **2008**, *18*, 283-290.

*Rogers et al.* described a dry-jet wet spinning process for making magnetically active cellulose fibers. They used the common ionic liquid 1-ethyl-3-methyl-imidazolium chloride to dissolve cellulose from different sources with various degrees of polymerization. The magnetite particles were dispersed in the solution, and then coagulated in a water bath. Furthermore, they reported that the texture was related to the concentration of magnetite particles, the concentration of cellulose, and the molecular weight in the spinning solution.

Rogers and co-workers already discovered the high solubility of cellulose in ionic liquids in 2002 (R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974-4975.), which became one of the most important examples for the innovative power of ionic liquids in the field of solvents, since they are able to dissolve more cellulose than other common solvents such as  $CS_2$  or NMMO.

#### 1-Ethyl-3-methyl-imidazolium chloride (>98%):

#### EMIM Cl (>98%):

| IL-0093-HP-50 g  | 115,00 €   |
|------------------|------------|
| IL-0093-HP-100 g | 150,00 €   |
| IL-0093-HP-250 g | 320,00 €   |
| IL-0093-HP-500 g | 542,50€    |
| IL-0093-HP-1 kg  | 920,00 €   |
| IL-0093-HP-5 kg  | 3.680,00 € |

## **Inorganic Synthesis**

Studies on the synthesis of nano-alumina in air and water stable ionic liquids

H. K. Farag, F. Endres, J. Mater. Chem. 2008, 18, 442-449.



In the first years of the new century the use of air and water stable ionic liquids in organic synthesis dominated strongly over inorganic synthesis. However, over the past three years ionic liquids were discovered as suitable reaction media for inorganic synthesis as well (see also Ionic Liquids Today 01-07: Ionic Liquids and Nano-technology – A useful Symbiosis?).

Recently, *Endres* and *Farag* published another interesting example in the Journal of Material Chemistry, where they reported the synthesis of nano-alumina using the air and water stable ionic liquids *N*-Butyl-*N*-methyl-pyrrolidinium bis(trifluoromethyl-sulfonyl)imide (BMPyrr NTf<sub>2</sub>) and 1-ethyl-3-methyl-imidazolium imidazolium bis(trifluoromethylsulfonyl)imide (EMIM NTf<sub>2</sub>). The nano-alumina was synthesized by hydrolysis of AlCl<sub>3</sub>, which shows a biphasic behaviour with both ionic liquids at concentrations of 1.6 mol·L<sup>-1</sup> (BMPyrr NTf<sub>2</sub>) 2.5 mol·L<sup>-1</sup> (EMIM NTf<sub>2</sub>).

The authors demonstrated also a structure directing effect: depending on the ionic liquid and the temperature they observed different modifications of  $Al_2O_3$ . A generalized principle concerning ionic liquids and nano-structures was summarized in a review from *Anonietti et al.* in 2004 (M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem.* **2004**, *116*, 5096-5100.).

## *N*-Butyl-*N*-methyl-pyrrolidinium bis(trifluoromethyl-sulfonyl)imide (99%): BMPyrr NTf<sub>2</sub> (99%):

| TL-0035-HP-50 a  | 99 50 <i>E</i> |
|------------------|----------------|
| IL-0055-HF-50 g  | 99,50 E        |
| IL-0035-HP-100 g | 166,50 €       |
| IL-0035-HP-250 g | 340,00 €       |
| IL-0035-HP-500 g | 555,50€        |
| IL-0035-HP-1 kg  | 997,50 €       |
| IL-0035-HP-5 kg  | 3.990,00 €     |

1-Ethyl-3-methyl-imidazolium imidazolium bis(trifluoromethylsulfonyl) imide (99%):

#### EMIM NTf<sub>2</sub> (99%):

| 85,00 €    |
|------------|
| 143,50€    |
| 305,00 €   |
| 515,00€    |
| 875,00€    |
| 3.065,00 € |
|            |



## **Properties of Ionic Liquids**

## Understanding Ionic Liquids at the Molecular Level: Facts, Problems, and Controversies

H. Weingärtner, Angew. Chem., Int. Ed., 2008, 47, 654-670.

*Weingärtner's* article sheds light on some ionic liquid myths concerning their properties by understanding them from the molecular level. A "must" for everybody who works with ionic liquids!

## **Green Chemistry**

## Hydrogenation of Carbon Dioxide is Promoted by a Task-Specific Ionic Liquid

Z. Zhang, Y. Xie, W. Li, S. Hu, J. Song, T. Jiang, B. Han\*, *Angew. Chem., Int. Ed.*, **2008**, *47*, 1143-1145.

Today it is surely not necessary to tell anything about the problems caused by  $CO_2$ . To get rid of this unlikely greenhouse gas is certainly one of the major challenges for the beginning  $21^{st}$  century.

One of the most interesting strategies is the use of  $CO_2$  as a C1-source, e.g. by direct hydrogenation to form formic acid. Though there have been already described several methods, the reuse of the necessary bases and catalysts, but also the recovery of the formic acid remains a certain problem.

*Han et. al* described a new method, using a task specific ionic liquid (1-(N,N-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethansulfonate) that enables the recovery of the product and the catalyst:



The separation process can be conducted without any VOC and the authors reported good selectivities.



## Nano-Technology / Catalysis

## Palladium nanoparticles supported onto ionic carbon nanotubes as robust recyclable catalysts in an ionic liquid

Y. S. Chun, J. Y. Chin, C. E. Song, S. Lee\*, *Chem. Comm.* **2008**, 942-944.

Ionic Liquids are well-known as useful and environmental friendly reaction media in organic synthesis and catalysis. The immobilization of catalysts on solid phases like silica was also reported before.

*Lee et al.* presented a method to immobilize Palladium nanoparticles onto ionic liquid functionalized multiwall carbon nanotubes (MCWNTs).



The catalytic system led to complete conversions and could be recycled up to 50 times.



## **VI** Community

by Tom F. Beyersdorff, Andreas E. Reisinger & Thomas J.S. Schubert.

#### Seminar announcement (Germany, Switzerland and Austria only)

In cooperation with our partner Deutsche Metrohm IoLiTec organizes a one day seminar concerning "Applications and Analytics of Ionic Liquids" in Filderstadt/Germany on June 10<sup>th</sup>, 2008.

Experts from Deutsche Metrohm and IoLiTec will guide through the seminar which is devided into in a lecture part and a practical part. The main topics of the lectures are a general introduction to ionic liquids, ion-chromatography of ionic liquids, volumetric and coulometric Karl-Fischer titration of ionic liquids and aspects of cyclovoltatry of ionic liquids.

The practical part is devided into 5 selected experiments including ionchromatography, cyclovoltametry, Karl-Fischer titration and determination of physical parameters such as viscosity, conductivity and density.

For further information on the seminar please visit the homepage of Deutsche Metrohm at:

http://www.metrohm.de/templates/PDF/ion liquids seminar 2008.pdf

## IOLITEC's nano materials activities separated from core company – <u>www.nanomaterials.iolitec.com</u> launched

In recent years Ionic Liquids have been widely used not only as alternative solvent for organic chemistry but also in the synthesis of inorganic materials as detailed in "Ionic Liquids Today" 01/07. Their great synthetic potential particularly in the preparation of microporous structures and synthesis of metal, oxide and composite particles has been shown by a number of different academic groups such as the Feldmann group at the university of Karlsruhe or the Antonietti group in Potsdam. Next to synthesis of inorganic nanomaterials, also the dispersability and desagglomeration of nanopowders, two crucial points in using nanostructured materials, can be significantly improved as shown in "Ionic Liquids Today" 02/07. This may be attributed mainly to the surface active properties of ionic liquids.



These two links between ionic liquids and nano materials caused IOLITEC to start own activities in the field of nanomaterials. As a consequence, IOLITEC has spent a lot of research work in the production and dispersion of nanomaterials in combination with ionic liquids. To complement these activities and to be in the position to offer a broad selection of nanomaterials, IOLITEC started its nanomaterials sale in co-operation with selected manufacturing partners.

Very soon after launching our nanomaterials catalogue, the number of requests, either for powders or for dispersions increased significantly. Due to this dynamic evolution, IOLITEC decided to separate the nanomaterial activities. The resulting Division is called "IOLITEC Nanomaterials" and got its own internet site <u>www.nanomaterials.iolitec.com</u> (english) <u>www.nanomaterials.iolitec.de</u> (german).





Next to IOLITEC's high quality nano materials and dispersion, also the electroplating activities, which are closely related, have been added to this division and included in the new homepage.

For requests and orders related to nanomaterials, dispersions and coatings, a couple of new email adresses leading directly to the right people has been created. These are in detail:

info@nanomaterials.iolitec.com and info@nanomaterials.iolitec.de as well as

order@nanomaterials.iolitec.com and order@nanomaterials.iolitec.de.

## Meet IOLITEC @ the Chemspec Europe, Munich, Germany 18<sup>th</sup> + 19<sup>th</sup> June 2008.

IOLITEC is proud to announce to attend for the first time at the Chemspec Europe 2008 at Munich.

Please do not hesitate to contact us to arrange a meeting – Your welcome!

### **Upcoming Exhibitions and Conferences:**

August 17<sup>th</sup>-21<sup>st</sup>: 236th ACS National Meeting & Exposition, Philadelphia, USA.

Join the "Ionic Liquids: From Knowledge to Application" symposium during the 236<sup>th</sup> ACS National meeting and meet the IoLiTec team.

August 24<sup>th</sup>-29<sup>th</sup>: EUCHEM 2008, Conference on Molten Salts and Ionic Liquids, Copenhagen, Denmark

**September 14<sup>th</sup>-20<sup>th</sup>: 2<sup>nd</sup> International Conference on Green Chemistry,** Moskow – St. Petersburg, Russia.

September 28<sup>th</sup> – October 1<sup>st</sup>: Green Solvents – Progress in Science and Application, Friedrichshafen, Germany.

IOLITEC will attend at the ACS National Meeting, the EUCHEM 2008, and the Green Solvents Conference. We were glad to arrange a meeting with you!



## **VII** Special Offers\* from our Portfolio:

With the beginning of 2008 IoLiTec extended its portfolio to more than 180 ionic liquids. A large number of new imidazolium, piperidinium, pyridinium, pyrrolidinium based ionic liquids as well as alkylimidazoles and useful precursors were added to our catalogue. All catalogue products are also available in pilot plant and bulk quantities.

In case that you have not yet received our new extended catalogue, please order it at: <u>info@iolitec.de</u>.

In addition to our standard portfolio IoLiTec offers custom synthesis of every patent free ionic liquid on a scale from 50 g to 100 kg. If you are interested in this service please contact us.

## Temporary price reductions for the following products:

#### Ethylimidazole: EtIm



#### EtIm (>98%):

| KI-0003-HP-1 kg   | 135,00€   |
|-------------------|-----------|
| KI-0003-HP-2,5 kg | 312,50€   |
| KI-0003-HP-5 kg   | 575,00€   |
| KI-0003-HP-10 kg  | 950,00€   |
| KI-0003-HP-25 kg  | 1.750,00€ |
| KI-0003-HP-50 kg  | 3.000,00€ |
| KI-0003-HP-100 kg | 5.000,00€ |



## 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide: EMIM NTf<sub>2</sub>

 $\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$ 

### EMIM NTf<sub>2</sub> (99%):

| IL-0023-HP-50 g  | 85,00 €    |
|------------------|------------|
| IL-0023-HP-100 g | 143,50 €   |
| IL-0023-HP-250 g | 305,00 €   |
| IL-0023-HP-500 g | 515,00 €   |
| IL-0023-HP-1 kg  | 875,00 €   |
| IL-0023-HP-5 kg  | 3.065,00 € |
|                  |            |

## 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide: BMIM NTf<sub>2</sub>

 $\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$ 

#### BMIM NTf<sub>2</sub> (99%):

| IL-0029-HP-50 g  | 95,00€     |
|------------------|------------|
| IL-0029-HP-100 g | 155,00 €   |
| IL-0029-HP-250 g | 330,00 €   |
| IL-0029-HP-500 g | 560,00€    |
| IL-0029-HP-1 kg  | 950,00 €   |
| IL-0029-HP-5 kg  | 3.325,00 € |



## 1-Butyl-3-methylimidazolium dicyanamide: BMIM N(CN)<sub>2</sub>



### BMIM N(CN)<sub>2</sub> (>98%):

| 157,50€   |
|-----------|
| 347,50€   |
| 630,00 €  |
| 1.135,00€ |
|           |

#### Potassium hexafluorophosphate: KPF<sub>6</sub>

$$\begin{array}{c} \mathsf{F} & \mathsf{F} \\ \mathsf{F} & \mathsf{F} \\ \mathsf{F} & \mathsf{F} \\ \mathsf{F} \\ \mathsf{F} \\ \mathsf{F} \end{array} \\ \mathsf{F} \\ \mathsf{F} \end{array}$$

#### KPF<sub>6</sub> (99%):

| KI-0031-HP-1 kg   | 121,50 € |
|-------------------|----------|
| KI-0031-HP-2,5 kg | 272,50 € |
| KI-0031-HP-5 kg   | 495,00 € |



#### Bis(trifluoromethylsulfonyl)imide, 80% aqueous solution: HNTf<sub>2</sub>



In contrast to our price list 2008 the quality of this material increased from a 70% to an 80% aqueous solution. In conclusion price adjustments had to be made.

#### HNTf<sub>2</sub> (>98%):

| KI-0029-HP-1 kg   | 575,00€    |
|-------------------|------------|
| KI-0029-HP-2,5 kg | 1.295,00 € |
| KI-0029-HP-5 kg   | 2.300,00 € |

\* All special offers are valid until April 30<sup>th</sup>, 2008.

All prices are EXW Denzlingen/Germany, costs for shipping and handling and custom charges are not included in the prices.





#### Temporary promotion prices for the following nano-products!\*

Iolitec supports you exploring the incredible properties of nanomaterials in your applications. Please, have a look at our current special offers and find the product you need for your new research ideas.

#### **Fullerene C60**

#### C60 (99.5%)

| CP-0001-HP-01g | 77,70€     |
|----------------|------------|
| CP-0001-HP-02g | 133,20€    |
| CP-0001-HP-05g | 277,50€    |
| CP-0001-HP-10g | 444,00 €   |
| CP-0001-HP-25g | 1.059,00 € |

Fullerenes and/or their derivatives are used in different applications fields like organic solar cells, pharmaceuticals or biomedicine.

#### Silver - Ag

#### Ag, 100 nm, 99.9%

| NM-0022-HP-10g  | 107,10 €   |
|-----------------|------------|
| NM-0022-HP-50g  | 382,50 €   |
| NM-0022-HP-100g | 612,00 €   |
| NM-0022-HP-500g | 1.368,00 € |

The antimicrobial effect of silver nanopowder is of great interest for research. The thermal and electric conductivity of Silver nanopowders also make it a very interesting additive in different applications like conductive paste or inks.



#### Yttrium(III)oxide - Y<sub>2</sub>O<sub>3</sub>

#### Y<sub>2</sub>O<sub>3</sub>, 30-50 nm, 99.5%

| NO-0030-HP-100g | 81,00 €    |
|-----------------|------------|
| NO-0030-HP-500g | 289,40 €   |
| NO-0030-HP-1kg  | 463,00 €   |
| NO-0030-HP-5kg  | 1.097,10 € |

Yttrium oxide is widely used as an additive for inorganic composite materials, e.g. sintering additives for cermaic materials, stabilizing additives for zirconia, for optical coatings, high temperature super conductors and many more.

#### Silicon carbide - SiC

| SiC, 60 nm, 99% |          |
|-----------------|----------|
| NC-0002-HP-50g  | 63,30€   |
| NC-0002-HP-100g | 110,80 € |
| NC-0002-HP-500g | 395,80 € |
| NC-0002-HP-1kg  | 633,30€  |

Due to its high melting point and hardness, SiC is used as abrasive and grinding material. Furthermore Silicon carbide is used as semiconducting material for high temperature applications (up to 600 °C).

#### \* All special offers are valid until April 30<sup>st</sup>, 2008.

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



#### <u>Imprint</u>

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