# **Ionic Liquids Today** www.iolitec.com

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# >>> Viscosities & Conductivities of ionic liquids

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### 1 Editorial

by Thomas J. S. Schubert.

As every year, we introduce in the first quarter of a year our actualized product & price list. According to the scale-up of our production and to optimized production processes, we, as a customer-dedicated company, are now in the position to let our customers participate in this development by lowering prices of a number of important ionic liquids. The scale-up is of course a consequence of the more and more increasing speed of commercialization of a couple of ionic-liquid-based technologies.

A very interesting feature is that BMIM  $BF_4$  and BMIM  $PF_6$  are still heading the list of ionic liquids in terms of publications in 2010, followed by BMIM CI and BMIM BTA (BTA also TFSI or NTf<sub>2</sub>). BMIM  $PF_6$  was named the "antichrist" (I think by Ken Seddon?) of ionic liquids technologies, which is of course right, if we just think a second about the unlikely degradation products. But it may still be an interesting material for a number of applications that are running in closed systems. Please consider that most notebook-batteries are still using Li  $PF_6$ , while rumours say that in China they are using already Li BTA.

So the first four places are taken by the 1-butyl-3-methylimidazolium-cation. On the next four places are following only 1-ethyl-3-methylimidazolium-cations (BTA, BF4, Cl, and Br). Ranked 9<sup>th</sup> is the first non-imidazolium-cation, *N*-butyl-*N*- methylpyrrolidinium bis(trifluorosulfonyl)imide, which was introduced as a fine chemical into the market 2005 by IOLITEC. On 10<sup>th</sup> place is, from my point of view, the upcoming star of ionic liquids, 1-ethyl-3-methylimidazolium acetate, which is known to be a good solvent for the dissolution of cellulose.

I tell you no secret if I inform you with a little bit of proud that all of the ionic liquids taken from the top ten of the most cited ionic liquids in 2010 are available at reduced process in our portfolio...

Best regards,

Mona, Shal

Thomas J. S. Schubert, CEO & Founder, IOLITEC.

### 2 Physico-chemical Properties of Ionic Liquids – Part I

By Maria Taige and Thomas J.S. Schubert.

**A**s mentioned already many times before there are numerous interesting applications of ionic liquids, e.g. electrolytes for lithium ion batteries,<sup>1</sup> for plating<sup>2</sup> or for dye sensitized solar cells,<sup>3</sup> for which low viscosities and high conductivities play a significant role. Models for the prediction of viscosities and conductivities of ionic liquids were described by *Kantlehner et al.*<sup>4</sup> and *Krossing et al.*<sup>5</sup> In this context, it is well known that impurities can affect the physical properties of ionic liquids.<sup>6</sup> In this article we would like to present you some viscosity and conductivity data of selected ionic liquids, available in qualities as described in our technical data sheets from our product portfolio.

### 2.1 Imidazolium-based bis(trifluorosulfonyl)imides

Due to both, their thermal *and* their electrochemical stability,<sup>7</sup> ionic liquids with bis(trifluoromethylsulfonyl)imide anions are interesting substances for organic reactions as well as for electrochemical applications.

According to a higher symmetry, 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (DiMIM BTA) has a slightly higher viscosity than 1-ethyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM BTA) (Fig. 1). Imidazolium BTAs with longer alkylsubstituents than ethyl (PMIM BTA, BMIM BTA, HMIM BTA, OMIM BTA and DecMIM BTA) are more viscous, which is due to the higher molecular mass and stronger van der Waals interactions. The methylation of the C2-position increases not only the thermal stability and the stability against bases but also the viscosity of the ionic liquids. As expected, hydrogen bonds between hydroxy-functionalized ionic liquids increase the viscosity as can be seen on the and HO-EMIM BTA. 1-Allyl-3-methylimidazolium example of EMIM BTA bis(trifluoromethylsulfonyl)imide (AllylMIM BTA) has a surprisingly low viscosity (Fig. 1), but a significantly lower conductivity at room temperature than EMIM BTA).

<sup>&</sup>lt;sup>1</sup> Moosbauer, D.; Zugmann, S.; Amereller, M.; Gores, H. J. *J. Chem. Eng. Data* **2010**, *55*, 1794–1798.

<sup>&</sup>lt;sup>2</sup> Koenig, U.; Sessler, B. *Trans. Inst. Met. Finish.* **2008**, *86*, 183–188.

<sup>&</sup>lt;sup>3</sup> Zakeeruddin, S. M.; Graetzel, M. *Adv. Funct. Mater.* **2009**, *19*, 2187–2202.

<sup>&</sup>lt;sup>4</sup> a) Bogdanov, M. G.; Kantlehner, W. *Z. Naturforsch.* **2009**, *64b*, 215 – 222. b) Bogdanov, M. G.; Iliev, B.; Kantlehner, W. *Z. Naturforsch.* **2009**, *64b*, 756 – 764.

<sup>&</sup>lt;sup>5</sup> Eiden, P.; Bulut, S.; Kochner, T.; Friedrich, C.; Schubert, T.; Krossing, I. J. Phys. Chem. B **2011**, 115, 300-309.

<sup>&</sup>lt;sup>6</sup> Endres, F. *Phys. Chem. Chem. Phys.*, **2010**, *12*, 1648.

 <sup>&</sup>lt;sup>7</sup> M. Götz, F. Ortloff, M. Taige, T. J. S. Schubert Long-term stability of ionic liquids at temperatures over 180°C, Green Solvents, October 10-13, **2010**.

EMIM BTA has the highest conductivity of all investigated imidazolium-based ionic liquids, which is followed by PMIM BTA, BMIM BTA and AllylMIM BTA. 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides possesses an electrochemical window of up to 4.9 V (measured with a platinum working electrode, a glassy carbon counter electrode and a silver/silver chloride reference electrode).

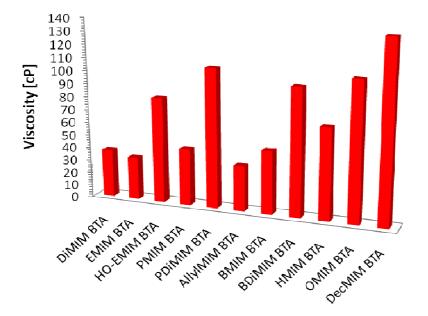
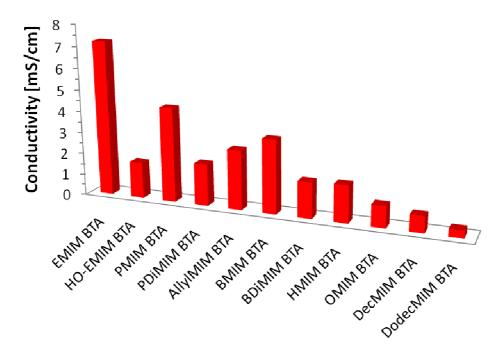


Fig. 1. Viscosities of selected imidazolium-based bis(trifluoromethylsulfonyl)imides at r.t.



**Fig. 2.** Conductivities of selected imidazolium-based bis(trifluoromethylsulfonyl)imides at r.t. (measured with platinum electrodes).

### 2.2 Pyrrolidinium-based bis(trifluorosulfonyl)imides

wider electrochemical window 5.9 V) 1-alkyl-1-Due to their (up to methylpyrrolidinium bis(trifluoromethylsulfonyl)imides are an even more interesting class of ionic liquids for electrochemical applications. Unfortunately the viscosity of these ionic liquids is only lower than 100 cP for 1-propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (PMPyrr BTA) and for 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyrr BTA). The viscosities of the investigated 1alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imides are altogether slightly higher than the according imidazolium-based ionic liquids (Fig. 1 and Fig. 3).

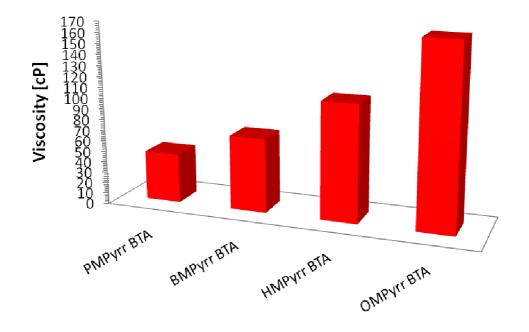
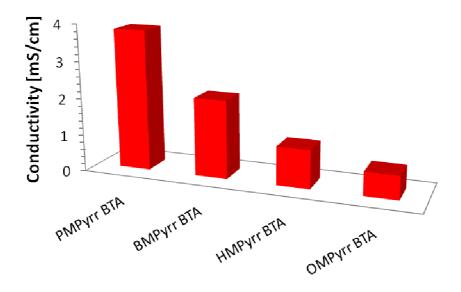


Fig. 3. Viscosities of selected 1-Alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imides at r.t.

A remarkable fact is, that the conductivity of 1-propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Fig. 7) is only slightly smaller than the conductivity of the corresponding imidazolium-based ionic liquids (but has nearly the double conductivity of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. Longer chains are following the general trend of lowering the conductivity (Fig. 4).



**Fig. 4.** Conductivities of selected pyrrolidinium-based bis(trifluoromethylsulfonyl)imides at room temperature (measured with platinum electrodes).

#### 2.3 Pyridinium-based bis(trifluorosulfonyl)imides

Another interesting result is that 3-Picolinium- (Alkyl<sub>3</sub>Pic) and 4-picolinium-based (Alkyl<sub>4</sub>Pic) bis(trifluoromethyl-sulfonyl)imides show a lower viscosity than the corresponding 2-picolinium-based bis(trifluoromethyl-sulfonyl)imides (Fig. 5). 1-Butylpyridnium bis(trifluoromethyl-sulfonyl)imide (BuPy BTA) is slightly higher viscous than the Bu<sub>4</sub>Pic BTA and the Bu<sub>3</sub>Pic BTA, but significantly lower viscous than Bu<sub>2</sub>Pic BTA. So among the investigated pyridinium bis(trifluoromethylsulfonyl)imides Et<sub>4</sub>Pic BTA has the lowest viscosity.

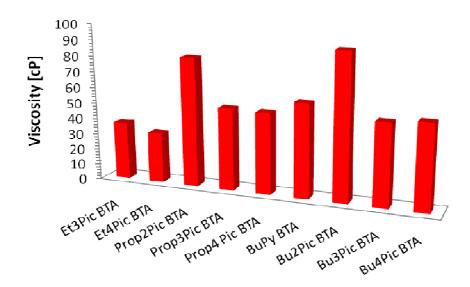
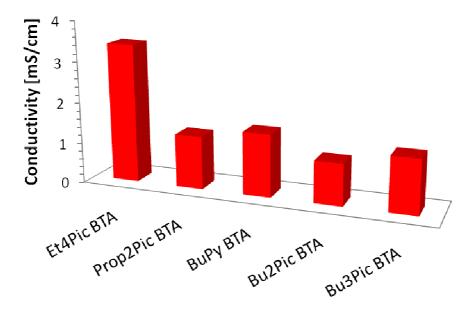


Fig. 5. Viscosities of selected pyridinium-based bis(trifluoromethylsulfonyl)imides at r.t.

Et₄Pic BTA has also a high conductivity of over 3 mS·cm<sup>-1</sup> at room temperature. But the conductivity of EMIM BTA is more than twice as big, while both substances have a similar electrochemical stability. Therefore, we recommend using EMIM BTA for electrochemical applications.

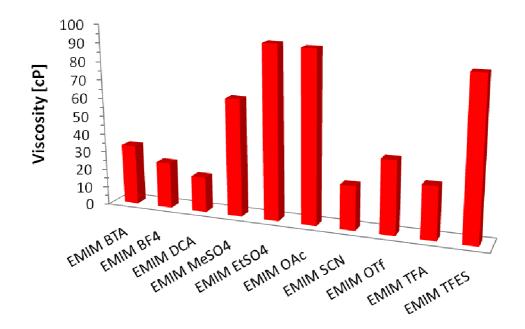


**Fig. 6.** Conductivities of selected pyridinium-based bis(trifluoromethylsulfonyl)imides at r.t. (measured with platinum electrodes).

### 2.3 Variation of anions of 1-Ethyl-3-methylimidazolium-based ILs

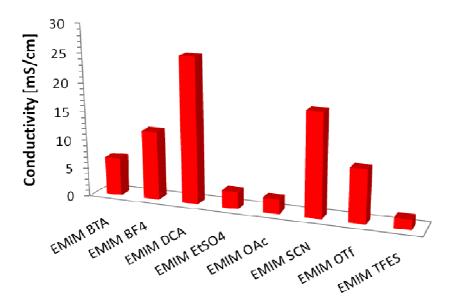
The influence of different anions on the viscosity of 1-ethyl-3-methylimidazoliumbased ionic liquids is demonstrated in Fig. 7. The dicyanamide (EMIM DCA, 19.4 cP) possesses the lowest viscosity of these ionic liquids, followed by 1-ethyl-3methylimidazolium thiocyanate with 24 cP. Viscosities below 30 cP showed also 1ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF<sub>4</sub>) and the corresponding trifluoroacetate (EMIM TFA). The major disadvantage of all tetrafluoroborates is of course their sensibility against hydrolysis, but if water-free conditions can be guaranteed, this ionic liquid may be a good compromise.

The ionic liquid with the best electrochemical stability in combination with the lowest viscosity is EMIM BTA (33 cP) followed by EMIM OTf (1-ethyl-3-methylimidazolium triflate, 39.8 cP). 1-Ethyl-3-methylimidazolium ethylsulfate (EMIM EtSO<sub>4</sub>), 1-ethyl-3-methylimidazolium acetate (EMIM OAc) and 1-ethyl-3-methylimidazolium tetrafluoroethanesulfante (EMIM TFES) are in this group the ionic liquids with the highest viscosity (Fig. 7).



**Fig. 7.** Influence of the anion on the viscosity on the example of ionic liquids with 1-ethyl-3-methylimidazolium cations.

As expected, EMIM DCA and EMIM SCN show high conductivities of 25.3 mS·cm<sup>-1</sup> and 17.9 mS·cm<sup>-1</sup>, respectively (Fig. 8). The conductivities of EMIM BF<sub>4</sub>, EMIM OTf and EMIM BTA are with approximately 6 and 12 mS·cm<sup>-1</sup> comparable good for pure ionic liquids. It's no surprise that EMIM EtSO<sub>4</sub>, EMIM OAc and EMIM TFES exhibit very poor conductivities, all clearly below 5 mS·cm<sup>-1</sup>.



**Fig. 8.** Influence of the anion on the conductivity on the example of ionic liquids with 1-ethyl-3-methylimidazolium cations (measured with platinum electrodes).

### 2.4 Summary

In conclusion, among the studied ionic liquids, 1-ethyl-3-methylimidazolium dicyanamide and the corresponding thiocyanate showed the lowest viscosities and highest conductivities. Both physical properties are of course controlled by the ion-diffusivity, leading to the assumption that the anions should first of all be small and should also delocalize the negative charge over larger parts of the molecule.

If electrochemical stability is taken also into considerations, *N*,*N*-dialkyl-pyrrolidiniumbased bis(trifluormethylsulfonyl)amides are surely good candidates, with slightly better values for viscosity and conductivity in the case of PMPyrr BTA, but with a lower melting point in the case of the BMPyrr BTA.

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide is a compromise between the highly stable PMPyrr BTA and the highly conductive and low viscous EMIM DCA, which shows only a poor stability.

Finally, EMIM  $BF_4$  might not be a bad choice, since the conductivity of the tetrafluoroborate-anion is nearly two times higher compared to the BTA. In this case one has to look carefully if the electrochemical window of approx. 4 V (at Pt) is enough.

$\frac{25 \text{ g}}{50 \text{ g}} \frac{65.00 \text{ f}}{86.00 \text{ f}}{100 \text{ g}} \frac{130.00 \text{ f}}{130.00 \text{ f}}{250 \text{ g}} \frac{255.00 \text{ f}}{295.00 \text{ f}}{900 \text{ g}} \frac{150.00 \text{ f}}{115.00 \text{ f}}{250 \text{ g}} \frac{255.00 \text{ f}}{255.00 \text{ f}}{900 \text{ g}} \frac{155.00 \text{ f}}{900 \text{ g}} \frac{100 \text{ g}}{925.00 \text{ f}}{115.00 \text{ f}}{150.00 \text{ f}}{250 \text{ g}} \frac{255.00 \text{ f}}{900 \text{ g}}{100 \text{ g}} \frac{150.00 \text{ f}}{95.00 \text{ f}}{115.00 \text{ f}}{250 \text{ g}}{255.00 \text{ f}}{116 \text{ g}}{945.00 \text{ f}}{116 \text{ g}}{95.00 \text{ f}}{116 \text{ g}}{2780.00 \text{ f}}{16 0.00 \text{ f}}{10 0$	1-Ethyl-3-methylimidazoliun tetrafluoroborate, >98% IL-0006-HP [143314-16-3]	$\mathbf{n}$ $C_6H_{11}BF_4N_2$	<b>Reduced</b> MW 197.97		- <b>propylpyrrolidir</b> pmethylsulfonyl [223437-05-6]		<b>Reduced</b> MW 408.38
bis(trifluoromethylsulfonyl)imide, 99%dicyanamide, >98%ReducedIL-0023-HP[174899-82-2] $C_8H_{11}F_6N_3O_4S_2$ MW 391.31IL-0003-HP[370865-89-7] $C_8H_{11}N_5$ MW 177.21 $\bigvee_{N \ \forall \oplus}$ $(CF_3SO_2)_2N^{\odot}$ $100 \text{ g}$ $120.00 \in$ $50 \text{ g}$ $75.00 \in$ $50 \text{ g}$ $95.00 \in$ $\bigvee_{N \ \forall \oplus}$ $(CF_3SO_2)_2N^{\odot}$ $100 \text{ g}$ $120.00 \in$ $100 \text{ g}$ $120.00 \in$ $500 \text{ g}$ $95.00 \in$ $\bigvee_{N \ \forall \oplus}$ $00 \text{ g}$ $120.00 \in$ $100 \text{ g}$ $120.00 \in$ $100 \text{ g}$ $160.00 \in$ $\bigvee_{M \ \oplus}$ $00 \text{ g}$ $120.00 \in$ $100 \text{ g}$ $160.00 \in$ $\bigvee_{M \ \oplus}$ $1 \text{ kg}$ $745.00 \in$ $1 \text{ kg}$ $995.00 \in$	N S N S S S S S S S S S S S S S	50 g 100 g 250 g 500 g 1 kg	86.00 € 130.00 € 295.00 € 525.00 € 945.00 €		(CF <sub>3</sub> SO <sub>2</sub> )₂	50 g 100 g 250 g 500 g 1 kg	69.00 € 115.00 € 235.00 € 385.00 € 695.00 €
bis(trifluoromethylsulfonyl)imide, 99%dicyanamide, >98%ReducedIL-0023-HP[174899-82-2] $C_8H_{11}F_6N_3O_4S_2$ MW 391.31IL-0003-HP[370865-89-7] $C_8H_{11}N_5$ MW 177.21 $\bigvee_{N \ \ensuremath{\sim} \ensuremath{\mathbb{N}}}^{N}$ $(CF_3SO_2)_2N^{\odot}$ $100 \ g$ $120.00 \ \in$ $50 \ g$ $75.00 \ \in$ $50 \ g$ $95.00 \ \in$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $(CF_3SO_2)_2N^{\odot}$ $100 \ g$ $120.00 \ \in$ $100 \ g$ $120.00 \ \in$ $50 \ g$ $95.00 \ \in$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $120.00 \ \in$ $100 \ g$ $100 \ g$ $160.00 \ \in$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $120.00 \ \in$ $100 \ g$ $160.00 \ \in$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $120.00 \ \in$ $100 \ g$ $160.00 \ \in$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $120.00 \ \in$ $100 \ g$ $160.00 \ \in$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $160.00 \ \in$ $100 \ g$ $500 \ g$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $160.00 \ \in$ $100 \ g$ $500 \ g$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $100 \ g$ $160.00 \ \in$ $100 \ g$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $100 \ g$ $100 \ g$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $100 \ g$ $100 \ g$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $100 \ g$ $100 \ g$ $\bigvee_{N \ \ensuremath{\mathbb{N}}}^{N}$ $100 \ g$ $100 \$							
$ \begin{array}{c} 25 \text{ g} & 55.00 \in \\ 50 \text{ g} & 75.00 \in \\ 50 \text{ g} & 75.00 \in \\ N \swarrow \mathbb{B}^{N} & 250 \text{ g} & 260.00 \in \\ 500 \text{ g} & 440.00 \in \\ 1 \text{ kg} & 745.00 \in \end{array} \begin{array}{c} 25 \text{ g} & 71.00 \in \\ 500 \text{ g} & 95.00 \in \\ N \swarrow \mathbb{B}^{N} & 250 \text{ g} & 260.00 \in \\ 500 \text{ g} & 500 \text{ g} & 440.00 \in \\ 1 \text{ kg} & 745.00 \in \end{array} $							
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						m	Reduced
	bis(trifluoromethylsulfonyl)i	mide, 99%	MW 391.31	dicyanamid	e, >98%		

### **3** Selected Applications of Ionic Liquids

By Boyan Iliev (BI), Sven Sauer (SS), Maria Taige (MT), Marcin Smiglak (MS), Frank M. Stiemke (FS), and Thomas J. S. Schubert (TS).

### Liquid-Liquid Extraction of Toluene from Heptane Using 1-Alkyl-3methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids (BI)

S. Garcia, M. Larriba, J. Garcia, J. Torrecilla, and F. Rodriguez, *J. Chem. Eng. Data.*, **2011**, 113-118.

The qood stability suitable polarity of the 1-alkyl-3-methyl and bis(trifluoromethylsulfonyl)imide ionic liquids have prompted their use as solvents for the extraction of mixtures of aromatic and aliphatic hydrocarbons. The solubility of toluene and heptane are higher as it grows the length of the alkyl chain in the imidazolium ring by increasing the distribution ratios and decreasing the selectivity in the extraction of toluene. The experiments with [mmim][Tf2N] and [emim][Tf2N] ionic liquids have shown good results in the separation of toluene from heptane comparing with the distribution ratios and separation factor of sulfolane in the whole range of composition. Moreover, the no detection of ionic liquid in the raffinate phase may improve the liquid-liquid extraction process by removing the purification step for recovering the solvent from the raffinate phase.

1,3-Dimethylimidazolium bis(trifluoromethylsulfonyl)imide, 99%							
IL-0198-HP	[174899-81-1]	$C_7H_9F_6N_3O_4S_2$	MW 377.28				
N	\ N (CF₃SO₂)₂N <sup>⊖</sup>	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	$67.50 \in$ 90.00 € 150.00 € 320.00 € 545.00 € 925.00 € 3'930.00 €				

# Where are ionic liquid strategies most suited in the pursuit of chemicals and energy from lignocellulosic biomass?

N. Sun, H. Rodriguez, M. Rahmana and R. Rogers, *Chem. Commun.*, **2011**, 1405–1421.

Certain ionic liquids have been shown to dissolve cellulose, other biopolymers, and even raw biomass (e.g., wood) under relatively mild conditions. This particular ability of some ionic liquids, accompanied by a series of concurrent advantages, among which is the least partial separation of the major constituent biopolymers,

enables the development of improved processing strategies for the manufacturing of many biopolymer-based advanced materials. The solubility of some of those materials in IIs is surprisingly high, e.g. for Cellulose (MMC) up to 28%, for starch 15%, for chitin 20% and silk fibroin 23%.

Although these technologies are in the early laboratory stages, they are promising and offer better pathways, less energy intensive processes, and significantly improved health and environmental benefits when compared to current processes

1-Ethyl-3-m chloride, >9	ethylimidazolium 95%			1-Butyl-3-m chloride, 99	ethylimidazolium %		
IL-0093-TG	[65039-09-0]	$C_6H_{11}CIN_2$	MW 146.62	IL-0014-HP	[79917-90-1]	$C_8H_{15}CIN_2$	MW 174.67
~	, ⊂, ci <sup>⊝</sup> , N , S ⊕ , Ci <sup>⊝</sup>	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	$\begin{array}{c} 60.00 \in \\ 75.00 \in \\ 105.00 \in \\ 165.00 \in \\ 260.00 \in \\ 495.00 \in \\ 2'095.00 \in \end{array}$	$\sim$	, ⊂\ Cl <sup>⊝</sup> ∼∕N, ∽N, Cl <sup>⊝</sup>	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	$\begin{array}{c} 47.50 \in \\ 65.00 \in \\ 85.00 \in \\ 150.00 \in \\ 207.50 \in \\ 290.00 \in \\ 1'015.00 \in \end{array}$
Filled in as n	melt!						

### An efficient activity ionic liquid-enzyme system for biodiesel production

Teresa De Diego, Arturo Manj´on, Pedro Lozano, Michel Vaultier and Jos´e L. Iborra\*, *Green Chem.* **2011**, *13*, 444-451

Biodiesel is one of the most important alternative fuels in the near future. Therefore new opportunities to produce biodiesel in a efficient and environmentally friendly ways are investigated. Iborra lately described the use of enzyme systems together with ionic liquids for the production of biodiesel. He showed that the use of long alkyl chain ionic liquids based on imidazolium cations ( $C_{10}$ MIM up to  $C_{18}$ MIM) and BF<sub>4</sub>, PF<sub>6</sub> and BTA anions increased the efficiency of the production process. The use of these ionic liquids produces a homogeneous at the start of the reaction but at the end of the reaction a three phase system is generated which allows the extraction of the product with common techniques. The enzyme ionic liquid mixture could then be reused. The highest synthetic activity showed 1-Hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide together with Novocym 435. The activity is here more than three times higher than in an solvent free system. Also the conversion after 3h in the IL system was much higher than in the solvent free case (90% vs. 27%).

The combination of ionic liquids and enzyme delivered new unique possibilities in biodiesel processing and extraction techniques.

1-Hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, >98%								
IL-0103-HP	[404001-50-9]	C <sub>22</sub> H <sub>39</sub> F	$_6N_3O_4S_2$	MW 578.69				
	√── N_ <u>&gt;N</u> ⊕ (CF <sub>3</sub> S	O₂)₂N <sup>⊖</sup>	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	112.50 € 150.00 € 252.50 € 537.50 € 912.50 € 1′550.00 € 6′200.00 €				

# The effect of coordinating and non-coordinating additives on the transport properties in ionic liquid electrolytes for lithium batteries (SS)

P. M. Bayley, A. S. Best, D. R. MacFarlane, M. Forsyth\*, *Phys. Chem. Chem. Phys.*, **2011**, *13*, 4632-4640

Forsyth described in this article the influence of different additives, namely toluene and THF on ionic liquid electrolytes in lithium ion batteries. As battery electrolyte ionic liquid 1-Propyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide with Lithium bis(trifluoromethylsulfoyl)imide salt was used together with the additive toluene and THF respectively. He performed different measurements like Multinuclear Pulsed-Field Gradient NMR, spin-lattice relaxation times and conductivity over a wide temperature range to determine the transport properties of the liquid.

He showed that the conductivity of the two different samples is in general increased at low temperatures where THF is slightly more efficient than toluene. The anion and Lithium self-diffusivity is also more enhanced by THF. In contrast the pyrrolidinum cation is only marginally influenced. THF clearly showed an interaction with Lithium ion whereas toluene showed no appreciable interaction with the ions at all.

Lithium batteries with ionic liquid electrolytes may be further improved by using ether oxygen containing additives.

1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 99% Reduced							
IL-0044-HP	[223	437-05-6]	C <sub>10</sub> H	${}_{18}F_6N_2O_4S_2$	MW 408.38		
	N +	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	N⊖	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	52.00 € 69.00 € 115.00 € 235.00 € 385.00 € 695.00 € 2'780.00 €		

## Electrochemical performance of electrospun poly(vinylidene fluoride-cohexafluoropropylene)-based nanocomposite polymer electrolytes incorporating ceramic fillers and room temperature ionic liquid (TS)

P. Raghavan, X. Zhao, J. Manuel, G. S. Chauhan, J.-H. Ahn, H.-S. Ryu, H.-J. Ahn, K.-W. Kim, Changwoon Nah, *Electrochimica Acta* **2010**, *55*, 1347.

In terms of safety next to the separator membrane the electrolyte is surely one of the weakest parts in high-energy-density lithium batteries. In this context, ionic liquids were already discussed in many papers before.

In this paper, *Ahn et al.* reported a highly performing poly(viniylidene fluoride-cohexafluoropropylene)-baed nanocomposite for Lithium polymer battery (LPB, Li/LiFePO<sub>4</sub>-cell), using ceramic fillers together with the room temperature ionic liquid 1-butyl-3-methyl-imidazolium bis(trifluorosulfonylmethyl)amide (BMIM BTA). The ceramic fillers such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or BaTiO<sub>3</sub> can affect mechanical strength and ion conductivity. Among these three materials, which showed all a better conductivity of the membrane than the neat polymer, BaTiO<sub>3</sub> showed the best results, followed by SiO<sub>2</sub>. The membranes were activated with a 0.5 M solution of Lithium bis(trifluoromethylsulfonyl)amide.

The addition of BMIM BTA into the porous structure of the membrane led to an improvement of the ionic conductivity by acting as an ion reservoir.

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99% <i>Reduced</i>							
IL-0029-HP	[174899-83-3]	$C_{10}H_{15}F_6N_3O_4S_2$	MW 419.37				
	/──\ N <mark>◇ 例</mark> \ ♥	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	54.00 € 72.00 € 122.00 € 260.00 € 440.00 € 750.00 € 3'000.00 €				

### Safe and easy handling of nanoparticles due to ionic liquidbased dispersions (FS)

T.J.S. Schubert, F.M. Stiemke, A. Willm, M. Zellner, *Green Chemistry* **2011**, *submitted*.

Using Ionic liquids for the dispersion of nanoparticles, in particular carbon-nanotubes (CNTs) in water, leads to stable and safe-to-handle dispersions. This method provides a non-dusty, non-volatile, non-inflammable solution for a safer handling that enables new applications. The dispersions were obtained by mixing the dry CNT-powder (0.1 - 0.5 wt%) with the required amount of IL and addition to water followed by 15-30 min treatment with ultrasound. Good results can be obtained by 1-hexadecyl-3-methylimidazolium chloride as dispersing agent. Furthermore, several different MWCNTs (0.1 wt%) can be dispersed in several neat room temperature liquid ionic liquids. No bucky gel, - as it was observed for SWCNTs by Watanabe<sup>i</sup> – was formed, while dispersing the MWCNTs in 1-benzyl-3-methyl-imidazolium dicyanamide or *N*-methyl-trioctylammonium bis(trifluoromethylsulfonyl)imide.

<sup>i</sup> T. Katakabe, T. Kaneko, M. Watanabe, T. Fukushima, T. Aida, *J. Electrochem. Soc.* 2005, **152**, A1913. S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, Y. Mita, A. Usami, N.Terada, M. Watanabe, *Electrochem. Solid-State Lett.*, **2005**, *8*, A577-A578.

	1-Hexadecyl-3-methylimidazolium chloride, >98%			Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide, 99%
IL-0115-HP	[61546-01-8]	$C_{20}H_{39}CIN_2$	MW 343.00	$IL-0017-HP  [375395-33-8]  C_{27}H_{54}F_6N_2O_4S_2  MW \; 648.85$
	∽∽∽ N~S⊕ CI <sup>⊖</sup>	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	60.00 € 79.00 € 125.00 € 255.00 € 405.00 € 650.00 € 2'600.00 €	$(CF_{3}SO_{2})_{2}N^{\bigcirc} $ $\begin{array}{c} 25 \text{ g} & 75.00 \in \\ 50 \text{ g} & 97.50 \in \\ 100 \text{ g} & 165.00 \in \\ 250 \text{ g} & 340.00 \in \\ 500 \text{ g} & 555.00 \in \\ 1 \text{ kg} & 995.00 \in \\ 5 \text{ kg} & 4'230.00 \in \end{array}$
1-Benzyl-3- dicyanamid	methylimidazolium e, >98%			
IL-0242-HP	[958445-60-8]	$C_{13}H_{13}N_5$	MW 239.28	
	∕─∖ <sup>⊖</sup> N(CN)₂ ∕ N ∕∕ ⊕ ∕	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	75.00 € 100.00 € 170.00 € 365.00 € 620.00 € 1'050.00 € 4'465.00 €	

### **Crystalline vs. Ionic Liquid Salt Forms of Active Pharmaceutical Ingredients: A Position Paper (MS)**

J. Stoimenovski, D. R. MacFarlane, K. Bica, R. D. Rogers, *Pharmaceutical Research*, **2010**, *27*, 521-526.

"Why not consider liquid salt forms of active pharmaceutical ingredients (APIs) as an alternative versatile tool in the pharmaceutical industry?..." With these words Professor Robin Rogers and Professor Dough MacFarlane start their paper entitled "Crystalline vs. Ionic Liquid Salt Forms of Active Pharmaceutical Ingredients: A Position Paper" (*Pharmaceutical Research* **2010**, *27*, 521). But really, why not consider using liquid salt forms of APIs; Ionic Liquid APIs (IL-APIs)? As it was already shown in recent publications ionic liquids can not only be used as solvent for pharmaceutical agents but by proper modifications APIs can become ionic liquids themselves. Such conversion may positively influence not only physical properties of APIs (solubility, dissolution rate, lack of polymorphism) but also, through the introduction of pharmaceutically active counter-ion, produce liquids possessing dual functionality.

As argued by authors, also control over solubility (increase of hydrophobicity or decreased dissolution rate) may bring new options for the APIs delivery; e.g. extended API release times. Or, through proper selection of counter-ions for the APIs, induction of ion-pair based membrane transport (e.g. API delivery through skin). Potential seems to be great, and here at IoLiTec we realize that. Therefore, we are ready to work with you through collaboration projects and design dual functional ILs that may suit your needs.

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# Influence of solvation layers of ionic liquids on electrochemical reactions (MT)

Frank Endres, Oliver Höfft, Natalia Borisenko, Luiz Henrique Gasparotto, Alexandra Prowald, Rihab Al-Salman, Timo Carstens, Rob Atkin, Andreas Bund and Sherif Zein El Abedin *Phys. Chem. Chem. Phys.* **2010**, *12*, 1724-1732.

Due to their wide electrochemical window ionic liquids are excellent media for electrochemical reactions. Enders et al. recently published a very interesting discussion paper on the influence of different ionic liquids on the electrodepo-sition of aluminium, tantalum as well as of a mixture of silicium and germanium. Their recent results showed that the deposition of these metals and semiconductors is strongly influenced by the ionic liquids. During the electrodeposition of aluminium in 1-butyl-1-methylpyrrolidinium bis(trifluoro-methylsulfonyl)imide (BMPyrr BTA) a nanocrystalline aluminium surface is obtained while under the same conditions in 1ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM BTA) the deposited aluminium is microcrystalline. Also interesting is the fact that tantalum can be deposited from BMPyrr BTA, while no tantalum deposition is observed from EMIM BTA. In addition, the authors discussed that the number of solvation layers formed on Au(III) electrodes strongly depends on the structure of the cation of the ionic liquid and on the electrode potential. Therefore, they presume that the solvation layer influence the electrocatalytic performance of metal electrodes. In their opinion a better understanding of the interface reactions in ionic liquids is of utmost importance.

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99%				nethylpyrrolidiniu omethylsulfonyl)i		Reduced
IL-0023-HP [174899-82-2] C	$_{3}H_{11}F_{6}N_{3}O_{4}S_{2}$	MW 391.31	IL-0035-HP	[223437-11-4]	$C_{11}H_{20}F_6N_2O_4S_2$	MW 422.41
$\bigvee_{N} \bigvee_{\oplus}^{N} (CF_3SO_2)_2 N^{\ominus}$	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	55.00 € 75.00 € 120.00 € 260.00 € 440.00 € 745.00 € 2'980.00 €	~~	$\bigvee_{\oplus}$ (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	52.00 € 69.00 € 115.00 € 235.00 € 385.00 € 695.00 € 2'780.00 €

### Melting Behavior of Pyrroldinium-Based Ionic Liquids and Their Binary Mixtures (MT)

M. Kunze, S. Jeong, E. Paillard, M. Winter, S. Passerini *J. Phys. Chem. C* **2010**, *114*, 12364.

*Passerini et al.* recently published a very interesting paper about the low temperature behavior of pyrrolidinium-based ionic liquids. They used among other things 1propyl-1-methylpyrrolidinium- (PMPyrr) and 1-butyl-1-methylpyrrolidinium- (BMPyrr) cations in combination with bis(trifluoromethanesulfonyl)imide (BTA), bis(fluorosulfonyl)imide (FSI) or bis(pentafluoroethanesulfonyl)imide (BETI) anions as ionic liquids. The low temperature behavior was investigated by differential scanning calorimetry (DSC). The lowest melting points of the pure substances is observed for the BMPyrr FSI (-18 °C). PMPyrr FSI has a slightly higher melting point of -9 °C. The ionic liquids with BTA-anions have a slightly higher melting point of -7 °C (BMPyrr BTA) or 10 °C (PMPyrr BTA), while the melting point of the ionic liquids with BETI anion is higher in the case of BMPyrr (7 °C) and lower in the case of PMPyrr (5 °C). The authors explain these observations with the size of the ions. The melting point is higher for those ionic liquids which consist of anions and cations with a similar size.

The authors investigated the melting behavior of the binary 50 mol% mixtures PMPyrr BTA + PMPyrr FSI, BMPyrr BTA + BMPyrr FSI, BMPyrr BTA + PMPyrr FSI and BMPyrr FSI + PMPyrr BTA. They observed reduced melting points (below -40 °C) and enhanced liquidus ranges for the mixtures. The crystallization process of the investigated mixtures is strongly determined by the anion.

1-Methyl-1-propylpyrrolidini bis(trifluoromethylsulfonyl)i		Reduced		nethylpyrrolidiniu methylsulfonyl)i		Reduced
IL-0044-HP [223437-05-6]	$C_{10}H_{18}F_6N_2O_4S_2$	MW 408.38	IL-0035-HP	[223437-11-4]	$C_{11}H_{20}F_6N_2O_4S_2$	MW 422.41
$(CF_3SO_2)_2N$	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	52.00 € 69.00 € 115.00 € 235.00 € 385.00 € 695.00 € 2′780.00 €	~~	$\langle N \\ \oplus \rangle$ (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	25 g 50 g 100 g 250 g 500 g 1 kg 5 kg	$52.00 \in$ 69.00 € 115.00 € 235.00 € 385.00 € 695.00 € 2'780.00 €

# A 3.6 V lithium-based fluorosulphate insertion positive electrode for lithium-ion batteries (TS)

N. Recham, J.-N. Chotard, L. Dupont, C. Delacourt, W. Walker, M. Armand, J.-M. Tarascon, *Nature Materials* **2009**, *9*, 68.

What happened here? The term "ionic liquid" is not used in the headline? Yes, but the authors used an ionic liquid to synthesize the inorganic material LiFeSO<sub>4</sub>F by using the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (EMIM BTA). LiFeSO<sub>4</sub>F is an interesting new cathode material, challenging more established materials like LiFePO4 or Lithium cobalt oxides. So the authors presented a novel example in which way ionic liquids have also an impact in the synthesis of inorganic materials.

 $FeSO_4 \cdot H_2O_{(s)} + LiF \longrightarrow LiFeSO_4F_{(S)} + H_2O$ 

As they mentioned, the combination of hydrophobicity and thermal stability enables a synthesis under water-poor conditions: The hydrophobic ionic liquids encapsulates the reacting powder and leads to a delayed release of the crystal water from the FeSO4. In addition, the reaction was carried out at elevated temperatures, which is of course only possible in a thermally stable, non-evaporating material.

In the outlook they suggested that it might be possible to discover other interesting materials by using this technique. We at IOLITEC believe that pyrrolidinium-based materials, which are thermally even more stable and also more hydrophobic, might be also interesting in this context.

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, 99%	Reduced	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 99%	
IL-0035-HP [223437-11-4] $C_{11}H_{20}F_6N_2O_4S_2$	MW 422.41	IL-0023-HP [174899-82-2] $C_8H_{11}F_6N_3O_4S_2$	MW 391.31
$(CF_{3}SO_{2})_{2}N^{\bigcirc} (CF_{3}SO_{2})_{2}N^{\bigcirc} $	52.00 € 69.00 € 115.00 € 235.00 € 385.00 € 695.00 € 2′780.00 €	$\begin{array}{c} 25 \text{ g} \\ 50 \text{ g} \\ 100 \text{ g} \\ \swarrow N \swarrow N (\text{CF}_3 \text{SO}_2)_2 \text{N}^{\bigcirc} 250 \text{ g} \\ \swarrow N \swarrow M (\text{CF}_3 \text{SO}_2)_2 \text{N}^{\bigcirc} 1 \text{ kg} \\ 1 \text{ kg} \\ 5 \text{ kg} \end{array}$	55.00 € 75.00 € 120.00 € 260.00 € 440.00 € 745.00 € 2′980.00 €

### 4 Community

### **IOLITEC@ Social Media**



Please follow IOLITEC at Facebook or connect yourself with IOLITEC's team at LinkedIn!

We invite you to become a member of the Ionic Liquids group on Facebook. Researchers, students, professionals from industry are welcome! From time to time we'll inform about latest publications on Facebook or we are open for any type of discussions!

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

### **Deadlines Approaching for COIL-4**

In our last issue of "Ionic Liquids Today" in 2010 we announced the COIL-4 conference which will be held from June 15-18, 2011 in Washington DC. Dr. Robin Rogers and the organizing committee from ACS are eagerly working on setting up an exciting conference program and accompanying exhibition.

Deadlines for this conference are approaching, and we encourage everybody who is interested in attending this exciting event to take advantage of the early bird registration.

# Deadline for the **early bird registration** is **March 15<sup>th</sup>, 2011**. **Abstract submission** also closes on **March 15<sup>th</sup>, 2011**.

Companies that are interested in sponsoring the event or exhibit during the event are always invited to contact Dr. Tom Beyersdorff (<u>beyersdorff@iolitec.com</u>) for further information.

Additional information on COIL-4 can be found at <u>www.COIL-4.org</u>.

# Bunsenkolloquium: Grenzflächen in Lithium(ionen)batterien, Goslar, Germany, March 24-25, 2011

http://www.efzn.de/veranstaltungen/bunsen-2011/

This year's Bunsenkolloquium will take place at the "Energie-Forschungszentrum Niedersachen" in Goslar and will focus on **Interfaces in Lithium (ion) batteries.** Dr. Maria Taige will give a talk on our recent developments in ionic liquid-based electrolytes for Lithium-Ion-Batteries.

## European Coating Show 2011, Nürnberg, Germany, March 29-31, 2011 http://www.european-coatings-show.com/de/default.ashx

IOLITEC will visit the European Coating Show. Talk to our CEO Dr. Schubert at the meeting area at "Münzing Chemie GmbH"'s booth 215, Hall 10.0.

## STLE 66th Annual Meeting & Exhibition, Atlanta/USA, May 21-25, 2010 http://www.stle.org/news/news.aspx?nid=71

Meet IOLITEC Inc. at the 66th Annual Meeting of the "Society of Tribologists and Lubrication Engineers". Dr. Tom Beyersdorff, President of our US-subsidiary Iolitec Inc, will give a talk at the Nanotribology session about "Ionic Liquids – Versatile Materials for Lubrication"

#### International Symposium on Ionic Liquid Crystals, Stuttgart, Germany

#### May 25-27, 2011

IOLITEC will support the International Symposium on Ionic Liquid Crystals in Stuttgart. This Symposium will bring leading researchers in the field of ionic liquidcrystals together, e.g. Laurent Douce and Bertrand Donnio (Straßburg), Andrea Pace and Ivana Pibiri (Palermo), Duncan Bruce and John Slattery (York), Joaquin Barbera (Zaragossa), Frank Giesselmann (Stuttgart), Ludger Harnau and Christian Holm (MPI Stuttgart), Andreas Taubert (Potsdam), Joachim Stumpe (Fraunhofer Institut für Angewandte Polymerforschung). Dr. Thomas Schubert and Dr. Sven Sauer will give a talk on their recent results in this research field.

# September 4-7, 2011: 1<sup>st</sup> International Conference on Ionic Liquids in Separation and Purification Technology, Sitges, Spain (<u>www.ilsept.com</u>)

IOLITEC's CEO Thomas J. S. Schubert is part of the organizing committee. Further information will follow in the next issue.

November 27<sup>th</sup> – December 1<sup>st</sup>, 2011: International Symposium on Molten Salts and Ionic Liquids, Cancun, Mexico (<u>www.flogen.com</u>)

Pease keep us informed about other interesting events we could highlight in Ionic Liquids Today.

### <u>Imprint</u>

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