Ionic Liquids

DOI: 10.1002/anie.201002393

Ionic Liquids with a Twist: New Routes to Liquid Salts**

*Ralf Giernoth**

electronic effects · fatty acids · ionic liquids · solvents · steric effect

Dedicated to Dr. John M. Brown

Within the last fifteen years ionic liquids (ILs) have evolved from lab curiosities to everyday commodities.[1] They are not only established as modern solvents for organic synthesis, but they also have numerous other applications—in particular as functionalized "task-specific" ILs.[2] These compounds display many often-praised properties, but the real advantage in using ionic liquids is the vast number available. If one decides to use an ionic liquid for a specific purpose, the biggest challenge is to find the right one. Many people falsely refer to this as "tunable properties", although, obviously, we cannot tune the properties of a specific IL. Instead, we simply choose a different ionic liquid (with different properties).

To date, the IL market is still dominated by the imidazolium cation. It seems that imidazolium is the universal motif used to generate room-temperature ionic liquids (RTILs). But there are severe limitations in the design of a liquid imidazolium-based salt: for RTILs we are restricted to alkyl chains of moderate length (approximately C_2–C_{12}, depending on the anion; cf. Table 1).[1,3] This problem is even more pronounced when functional groups are needed on the cation.

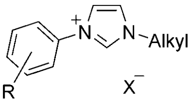
Table 1: Melting points or glass transition temperatures of 1-alkyl-3-methylimidazolium tetrafluoroborate ILs $[C_n\text{mim}]BF_4$.[3]

n[a]	M.p. [°C]	n[a]	M.p. [°C]	n[a]	M.p. [°C]
1	103.5	8	−78.5[b]	14	42.4
2	5.8[b]	10	−4.2	16	49.6
4	−71.0[b]	12	26.4	18	66.8
6	−82.4[b]				

[a] Length n of the alkyl chain in $[C_n\text{mim}]BF_4$; $[C_n\text{mim}]$ = 1-alkyl-3-methylimidazolium. [b] Glass transition temperature.

A few research groups have focused on the prediction of melting points for ILs using theoretical methods.[4] Thus the key question is: how can we design new ILs with lower melting points? Very recently the group of Strassner[5] and the groups of Davis and West[6] independently devised very practical solutions to this problem.

Strassner's idea is based on observations with ionic liquid crystals. These have proven to be easily "tunable" with variably substituted aryl substituents.[7] As students, we all learned that this "tunability" is nothing more than (+/−)-I and (+/−)-M effects, especially in aromatic substitution reactions and in linear free energy relations. The logical extension is to replace one alkyl chain in the imidazolium cation with an aryl group. Strassner et al. have termed this new group of ionic liquids "TAAILs" (tunable aryl–alkyl ionic liquids; Scheme 1).



Scheme 1. Generalized structure of TAAILs prepared by Strassner et al.[5]

In fact, the combination of inductive, mesomeric, and steric effects, and presumably π–π interactions as well, can effectively suppress crystal packing and lead to room-temperature liquid melts. The synthesis is as easy and straightforward as the synthesis of standard imidazolium ILs. Strassner and co-workers point out that the melting points of the corresponding ILs strongly depend on the (*para*-) aryl substituent: electron-donating groups lead to a lower melting point than electron-withdrawing groups. Interestingly, DFT calculations indicate that about 70% of the charge is localized on the imidazolium ring. For pure alkyl imidazolium salts the majority of the charge is localized on the alkyl groups.

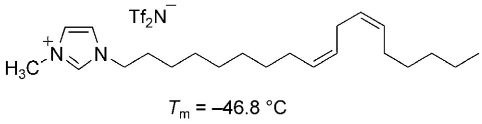
Davis and West followed a different approach to produce low-melting imidazolium ILs. Their idea is based on a model called homeoviscous adaptation (HVA),[8] which describes the change in viscosity of membrane lipids in living organisms. By studying the melting points of natural fatty acids, they realized that low-melting fats ("oils") often contain a *cis*-configured double bond in the alkyl chain. This "kink", as they call it, leads to a lower packing efficiency and thus to an increased fluidity—most probably simply an entropy-dominated effect.

In this context they synthesized a series of methylimidazolium bis(trifluoromethylsulfonyl)imide salts bearing a long fatty acid side chain (C_{16}–C_{20}; Scheme 2). And indeed: the trend in melting points closely resembles that observed for fatty acids. A strong effect is found for a *cis* double bond at C_{10}, C_{16}, and C_{18}; the effect is weaker at C_{11} and C_{12}. The viscosities are also lowered, following the same trend as the melting points.

---

[*] Priv.-Doz. Dr. R. Giernoth
Department für Chemie, Universität zu Köln
Greinstrasse 4, 50939 Köln (Germany)
Fax: (+49) 221-470-5102
E-mail: ralf.giernoth@uni-koeln.de
Homepage: http://www.ralfgiernoth.de

[**] R.G. thanks the German Science Foundation (DFG) for funding through the Emmy Noether program and the special priority programs 1166 and 1191.



Scheme 2. Example of a room-temperature ionic liquid with a long alkyl chain.[6] Tf_2N^- = bis(trifluoromethylsulfonyl)imide.

Although ionic liquids can no longer be considered novel solvents, their development continues to make progress. This is especially true for designed, task-specific ionic liquids that serve as more than just a solvent for a certain chemical transformation. The real advantage in using ILs is that there are so many different ones available. Based on the developments described in this Highlight it is apparent that much more can be expected in the near future.

Received: April 22, 2010

[1] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, **2008**.
[2] a) J. H. Davis, Jr., *Chem. Lett.* **2004**, *33*, 1072–1077; b) R. Giernoth, *Angew. Chem.* **2010**, *122*, 2896–2901; *Angew. Chem. Int. Ed.* **2010**, *49*, 2834–2839.
[3] J. Holbrey, K. Seddon, *J. Chem. Soc. Dalton Trans.* **1999**, 2133–2139.
[4] a) I. Krossing, J. M. Slattery, *Z. Phys. Chem.* **2006**, *220*, 1343–1359; b) I. Krossing, J. M. Slattery, C. Daguenet, P. J. Dyson, A. Oleinikova, H. Weingaertner, *J. Am. Chem. Soc.* **2006**, *128*, 13427–13434; c) J. M. Slattery, C. Daguenet, P. J. Dyson, T. J. S. Schubert, I. Krossing, *Angew. Chem.* **2007**, *119*, 5480–5484; *Angew. Chem. Int. Ed.* **2007**, *46*, 5384–5388.
[5] S. Ahrens, A. Peritz, T. Strassner, *Angew. Chem.* **2009**, *121*, 8048–8051; *Angew. Chem. Int. Ed.* **2009**, *48*, 7908–7910.
[6] S. M. Murray, R. A. O'Brien, K. M. Mattson, C. Ceccarelli, R. E. Sykora, K. N. West, J. H. Davis, *Angew. Chem.* **2010**, *122*, 2815–2818; *Angew. Chem. Int. Ed.* **2010**, *49*, 2755–2758.
[7] P. H. J. Kouwer, T. M. Swager, *J. Am. Chem. Soc.* **2007**, *129*, 14042–14052.
[8] M. Sinensky, *Proc. Natl. Acad. Sci. USA* **1974**, *71*, 522–525.