Ionic Liquids

DOI: 10.1002/anie.200700941

How to Predict the Physical Properties of Ionic Liquids: A Volume-Based Approach**

John M. Slattery,* Corinne Daguenet, Paul J. Dyson, Thomas J. S. Schubert, and Ingo Krossing*

Ionic liquids (ILs) have captured the imagination of a large and steadily growing community of scientists due to their applications as reaction media,[1,2] in batteries and supercapacitors,[3] in solar and fuel cells,[4] for electrochemical deposition of metals and semiconductors,[5] for protein extraction and crystallization,[6] in nanoscience,[7] in physical chemistry,[8] and many others. By choosing different combinations of ions, or by modifying the chemical structures of the constituent ions, the physical properties of an IL can be significantly altered. However, the number of possible modifications is huge, and one can envisage an enormous number of salts that have the potential to form ILs—some say as many as 10^{12} to 10^{18}.[9,10] Since the vast majority of these have yet to be synthesized, it is imperative to develop methods to predict the physical properties of unknown ILs in order to facilitate the design of new materials and reduce the need for time-consuming trial-and-error syntheses. The "Holy Grail" is the full characterization of an unknown IL prior to its laboratory synthesis.

Previous attempts to make quantitative predictions of the physical properties of ILs by using quantitative structure–property relationships (QSAR), molecular mechanics (MM) simulations, as well as modifying older ideas, such as the concept of "hole theory" or the "Parachor", have had some success.[10–12] However, these methods all have significant drawbacks which limit their application for predicting the properties of unknown salts. These include the need for large experimental datasets to derive correlations, time-consuming computational methods, or the need for at least some experimental data from the IL under study.

We recently showed that the relatively low melting points of ILs can be understood by a simple thermodynamic cycle based on lattice and solvation energies.[13,14] This model also allowed the prediction of the melting points (and dielectric constants) of ILs with good accuracy. Subsequently, we noticed a strong relationship between the molecular volumes V_m of ILs and their fundamental physical properties: viscosity, conductivity, and density. Herein we describe these simple relationships and show that it is possible for nonspecialists to predict the physical properties of even unknown ILs with very good accuracy from only their molecular volumes and an anion-dependent correlation.

The molecular volume V_m (or formula-unit volume) of a salt is a physical observable and is defined as the sum of the ionic volumes V_{ion} of the constituent ions. For example, for a binary IL V_m is given by Equation (1).

$$V_m = V_{ion}(A^+) + V_{ion}(X^-) \qquad (1)$$

The ionic volume is a measure of the size of an ion, similar to the traditional ionic radius.[15] However, ionic radii are poorly defined and arguably not physically meaningful for nonsymmetrical ions such as those found in many ILs. In contrast, ionic volumes are well defined and equally valid for symmetrical and nonsymmetrical ions. The ionic volume can be derived from crystal structures (e.g., the CCDC Database)[16] containing the ion of interest in combination with a reference ion of known volume (see Table 1, the Supporting

Table 1: Ionic volumes for ions found in this study.

Ion	V_{ion} [nm^3]	Ion	V_{ion} [nm^3]
$[C_2MIM]^+$ [a]	0.156 ± 0.018	$[C_4MPyr]^+$ [e]	0.221 ± 0.015
$[C_3MIM]^+$ [a]	0.178 ± 0.028	$[C_5MPyr]^+$ [f]	0.238 ± 0.018
$[C_4MIM]^+$ [a]	0.196 ± 0.021	$[C_5NEt_3]^+$ [g]	0.268 ± 0.016
$[C_5MIM]^+$ [a]	0.219 ± 0.015	$[C_4NMe_3]^+$ [h]	0.198 ± 0.013
$[C_6MIM]^+$ [a]	0.242 ± 0.015	$[SEt_3]^+$	0.177 ± 0.017
$[C_8MIM]^+$ [a]	0.288 ± 0.015	$[MeSPh_2]^+$	0.268 ± 0.015
$[C_4MMIM]^+$ [b]	0.229 ± 0.012	$[BF_4]^-$	0.073 ± 0.009
$[C_2(CN)MIM]^+$ [c]	0.167 ± 0.013	$[PF_6]^-$	0.109 ± 0.008
$[C_3(CN)MIM]^+$ [c]	0.194 ± 0.015	$[TfO]^-$	0.131 ± 0.015
$[C_4(CN)MIM]^+$ [c]	0.222 ± 0.013	$[Tf_2N]^-$	0.232 ± 0.015
$[C_4Py]^+$ [d]	0.198 ± 0.013	$[N(CN)_2]^-$	0.089 ± 0.010

[a] $[C_nMIM]^+$ = 1-alkyl-3-methylimidazolium, where *n* is the length of the alkyl chain. [b] $[C_4MMIM]^+$ = 1-butyl-2,3-dimethylimidazolium. $[C_n(CN)MIM]^+$ = $[C_nMIM]^+$ with a terminal nitrile group in the longer alkyl chain. [d] $[C_4Py]^+$ = butylpyridinium. [e] $[C_4MPyr]^+$ = 1-butyl-4-methylpyrrolidinium. [f] $[C_5MPyr]^+$ = 1-pentyl-4-methylpyrrolidinium. [g] C_5 = pentyl. [h] C_4 = butyl.

---

[*] Dr. J. M. Slattery, Prof. Dr. I. Krossing
Institut für Anorganische und Analytische Chemie
Albert-Ludwigs-Universität Freiburg
Albertstrasse 21, 79104 Freiburg (Germany)
Fax: (+49) 761-203-6001
E-mail: john.slattery@ac.uni-freiburg.de
krossing@uni-freiburg.de

Dr. C. Daguenet, Prof. P. J. Dyson
Institut des Sciences et Ingénieries Chimiques
École Polytechnique Fédérale de Lausanne (EPFL)
1015 Lausanne (Switzerland)

Dr. T. J. S. Schubert
IoLiTec
Ferdinand-Porsche-Strasse 5/1
79211 Denzlingen (Germany)

[**] This work was supported by the EPF Lausanne, the Roche Research Foundation, the Albert-Ludwigs-Universität Freiburg, IoLiTec, and the Deutsche Forschungsgemeinschaft (DFG) priority program SPP 1191. We also thank the Alexander von Humboldt Foundation for the research fellowship of J.M.S.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Information, and references [13,17,18] for details and new ionic volumes). Moreover, it is possible to assess V_{ion} and thus V_m on the basis of extrapolation of available data or simple quantum chemical calculations of the volume for the ion in question. Thus, it is possible to establish V_m for unknown ILs with good accuracy prior to synthesis.

To establish meaningful correlations between the physical properties of ILs and their molecular volumes, accurate physical data were required for a range of ILs. Only data from highly purified ILs, synthesized by us, with experimentally determined low contents of halide and water (typically less than 100 ppm) were used in this work.[19,20]

The molecular volumes of a series of ILs based on bis(trifloromethylsulfonyl)imide ($[Tf_2N]^-$) as the anion were found to be strongly correlated ($R^2 = 0.94$) with their viscosities (Figure 1 a, ◆). The viscosity of these ILs increases exponentially with increasing V_m. Remarkably, this correlation is independent of the molecular structure of the cation, even though five different cation types (imidazolium, pyridinium, pyrrolidinium, ammonium, and sulfonium cations) were included in the dataset. When data from ILs based on different anions were included, it became clear that the correlations are strongly anion dependent. Ionic liquids based on fluorometalate ions ($[BF_4]^-$ and $[PF_6]^-$) and dicyanamide ions ($[N(CN)_2]^-$) formed separate series to those based on $[Tf_2N]^-$ ions (Figure 1 a, ▲ and ●). In these cases the correlations also appear to be independent of the cation structure, although fewer cation types were considered. When functionalized imidazolium fluorometalate ILs with a terminal nitrile group in the longer alkyl chain, that is, $[C_n(CN)MIM][MF_x]$ ILs,[21] were considered, they did not fit with the data for other fluorometalate salts, but rather formed a fourth distinct series (Figure 1 a, ■).

The viscosity correlations shown in Figure 1 a give empirical equations that have an Arrhenius (or perhaps more appropriately Vogel–Fulcher–Tammann) form [Eq. (2)][22] where a is the empirical pre-exponential factor (in cP), b is an empirical constant (in nm^{-3}), and V_m is the molecular volume (in nm^3). Empirical constants for each series are given in Table 2.

$$\eta = a\,e^{b\,V_m} \tag{2}$$

For particles (here ions) in a fluid to move in response to an applied force they must overcome the attractive (Coulomb) interactions with their neighbors. Thus, for a particle to move it must have a minimum energy E_a. The probability of a particle having energy E_a is given by a Boltzmann distribution and thus is proportional to $e^{-E_a/RT}$. Since the viscosity of a fluid is inversely proportional to the mobility of the particles within it, the viscosity is related to E_a according to Equation (3).

$$\eta \propto e^{E_a/RT} \tag{3}$$

When this is compared to Equation (2) it becomes clear that the molecular volume of the IL is incorporated in the E_a term of Equation (3). Such a hypothesis is reasonable, since the volume of the particles in a fluid is clearly related to the minimum energy required for them to move. The empirical equations shown in Figure 1 each contain a constant b, which is multiplied by V_m. These constants contain the temperature-

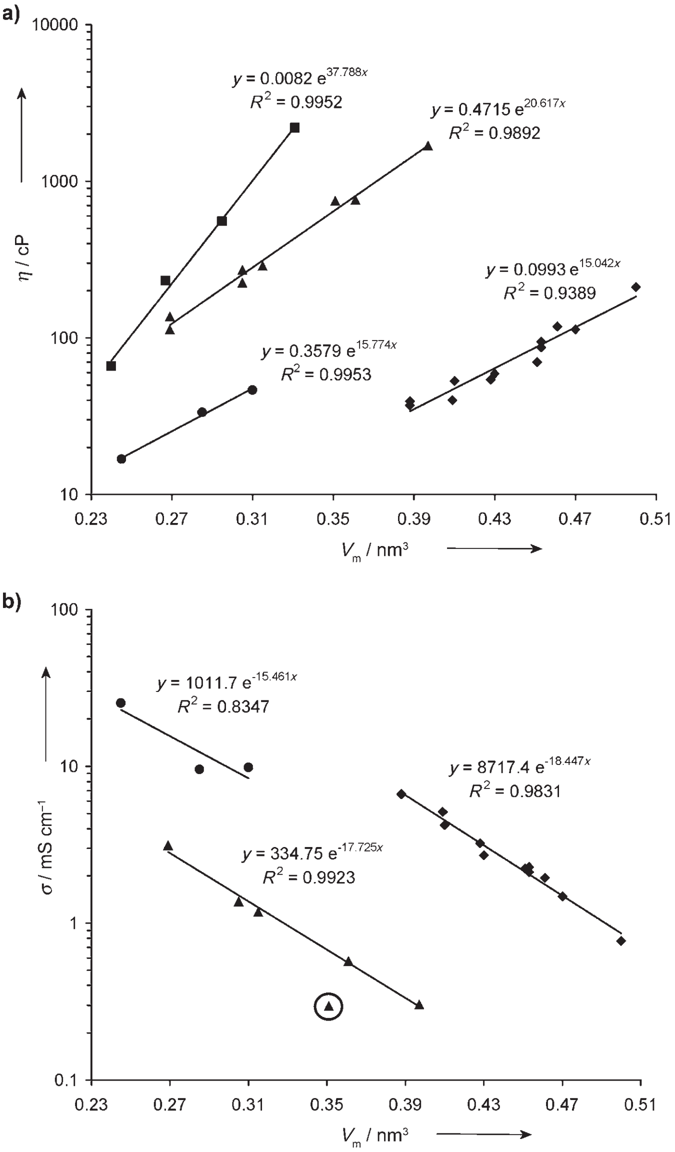

Figure 1. Correlations between a) molecular volume and viscosity and b) molecular volume and conductivity, both at 20–22 °C. ■ $[C_n(CN)MIM][MF_x]$ salts, ▲ $[MF_n]^-$ salts, ● $[N(CN)_2]^-$ salts, ◆ $[Tf_2N]^-$ salts. A suspected outlier in the $[MF_n]^-$ data is circled; this point was not included when determining the regression line. Viscosities and conductivities are plotted on logarithmic axes; x and y in the regression equations are V_m and η or σ, respectively. $[MF_n]^-$ is either $[BF_4]^-$ or $[PF_6]^-$. The cations used for ▲, ●, and ◆ can be found in the Supporting Information.

Table 2: Summary of empirical constants for $T = 20$–$22\,°C$ [see Eqs. (2), (4), and (5)].

IL anion/type	a	b	c	d	g	h
$[Tf_2N]^-$	0.0993	15.042	8717.4	18.447	1.4684	1.0026
$[MF_x]^-$	0.4715	20.617	334.75	17.725	1.4684	1.0026
$[N(CN)_2]^-$	0.3579	15.774	1011.7	15.461	1.4684	1.0026
$[C_n(CN)MIM][MF_x]$	0.0082	37.788	–	–	–	–

dependent part of Equation (3), which should allow one to extrapolate these correlations to different temperature regimes and predict the viscosities of ILs at different temperatures. The b constants also contain the remaining part of the E_a term, and the magnitude of this constant is related to the strength of the intermolecular interactions in the IL. Stronger intermolecular interactions make it more difficult for a particle to overcome the interactions with its neighbors and thus increase E_a.

The magnitudes of the b constants (see Table 2) help to explain why separate series are seen for different anion types and for the functionalized cations. In ILs containing the relatively weakly coordinating $[Tf_2N]^-$ ion, b is 15.042.[23] For the more strongly coordinating fluorometalate anions a larger b value of 20.617 is found, and the viscosity of these ILs increases more rapidly with increasing V_m. Functionalization of the imidazolium cations leads to a b value of 37.788. Clearly, incorporation of the Lewis basic and relatively polar nitrile group in the cation strengthens the intermolecular interactions in these ILs.

Similar anion-dependent correlations were found for the conductivities of the ILs (Figure 1b).[24] Good correlations were found for the $[Tf_2N]^-$ ILs (◆) and the fluorometalate ILs (▲). Correlation for the $[N(CN)_2]^-$ ILs is poorer (●), although, due to the small number of data points, it is not clear whether this is due to an outlier or to uncertainties in the measurements.[25]

The conductivity of the ILs decreases exponentially with increasing V_m [Eq. (4)] where c and d are empirical constants of best fit (in $\mathrm{mS\,cm^{-1}}$ and $\mathrm{nm^{-3}}$, respectively). Empirical constants for each series are given in Table 2. This exponential relationship can also be understood in terms of ion mobility, as conductivity is proportional to the mobility of charge carriers in the fluid and thus it has an inverse form relative to the viscosity equation [Eq. (2)].

$$\sigma = c\,e^{-d V_m} \tag{4}$$

All ion volumes V_{ion} used herein were derived from the unit-cell volumes V_{cell} of X-ray crystal structures. Since the density of a solid is directly related to the volume and contents of the unit cell, it is reasonable to estimate the density of a solid IL directly from the volumes of the ions involved. However, as most of the applications of ILs involve the salt in the liquid state, it is more useful to estimate the density of the IL. This was possible by using the good correlation between V_m and the experimentally determined densities ρ of the above ILs (see the Supporting Information). These correlations are anion-dependent. However, when the molar mass M_r of the ILs was taken into account and V_m was plotted against the molar concentration of the ILs (given by ρ/M_r, in $\mathrm{mol\,dm^{-3}}$) a correlation involving all salts, except the nitrile-functionalized ILs, was found (Figure 2).

The molar concentration of these ILs is related to V_m by a power series, which leads to the relationship between V_m and the density of an IL (in $\mathrm{g\,dm^{-3}}$) shown in Equation (5) with M_r

$$\rho = M_r\,g\,V_m^{-h} \tag{5}$$

being the molar mass; g and h are empirical constants of best fit (g in $\mathrm{mol\,dm^{-3}}$ and h is dimensionless), and are listed in Table 2. This relationship is especially useful, as it incorporates nearly all of the salts that were studied and suggests that this correlation is applicable to a wide variety of ILs. However, the molar concentrations of the nitrile-functionalized salts do not fit with the data from the other salts. It is likely that functionalization significantly changes the intermolecular interactions in the IL, an effect that is also seen in the viscosity data, and that this strongly affects the density changes that occur in the salts with temperature changes and during phase transitions. Note that a very recent independent study also relates the densities of ILs with the ionic volumes of their constituent ions.[26]

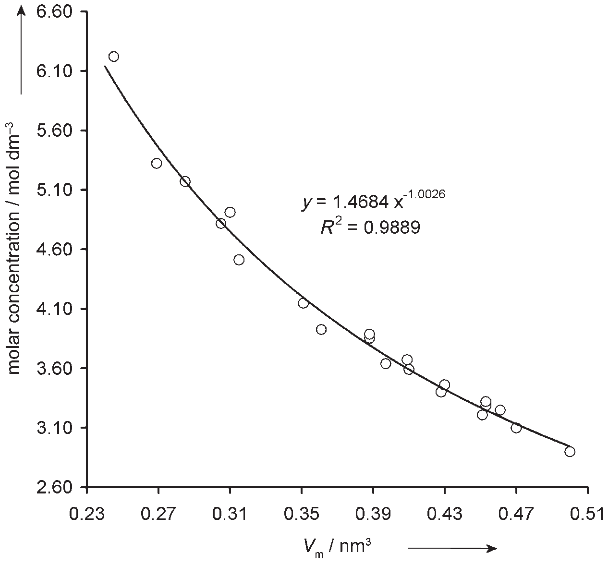

Figure 2. Correlation between molecular volume and molar concentration at 20–22 °C. All ILs, except the nitrile-functionalized fluorometalate ILs, are included.

During this work we found only two ILs that did not fit the correlations described above ($[SMePh_2][Tf_2N]$ and $[C_4NMe_3][Tf_2N]$). The reasons for this are not entirely clear and are still under investigation. It may be due to improper measurements of their physical properties. However, at this point we reiterate that the above correlations work well for a variety of IL cation types with the usual aliphatic residues; these represent a large proportion of known and potential ILs.

To predict the physical properties of an unknown IL using Equations (2), (4), and (5) one must establish V_m for the IL from the sum of the V_{ion} values for the constituent ions. An explicit instruction of how this can easily be achieved is deposited in the Supporting Information. The derived V_m value of the unknown IL must then be substituted into Equations (2), (4), and (5) by using the correct empirical constants from Table 1, and this leads to very good estimates for the viscosities, conductivities, or densities of unknown ILs, provided that they incorporate anions for which constants have been established. Currently the anions for the IL in question can be $[N(CN)_2]^-$, $[BF_4]^-$, $[PF_6]^-$, and $[N(SO_2CF_3)_2]^-$; further work intended to broaden this range is in progress. This procedure is remarkably simple and when applied to the 23 ILs investigated in this study, the predicted physical properties are in excellent agreement with the experimentally determined values (Figure 3; for plots of conductivity and density, see the Supporting Information).

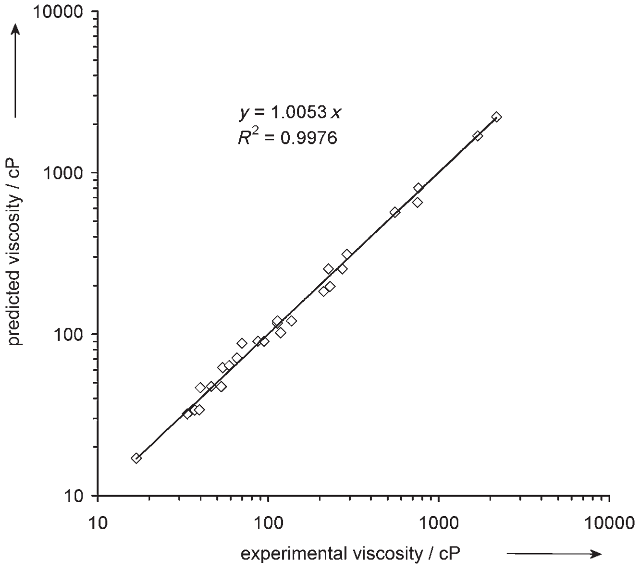

Figure 3. Experimental versus predicted viscosities for all ionic liquids in the current study.

The experimental and predicted viscosities, conductivities, and densities are highly correlated in all cases ($R^2 = 0.9976$, 0.9871, and 0.9702, respectively) and the standard error of the estimate (s_{est}) statistics, which give an estimate of the average absolute error of the predictions, are also very good (26 cP, $0.2\,\mathrm{mS\,cm^{-1}}$, and $27\,\mathrm{g\,dm^{-3}}$ respectively). As the viscosity data covers a very large range of values (from 17 to 2181 cP) the s_{est} value is not a good estimate of the error in the predictions at the extremes of this range. In this case the average of the percentage errors for the predictions (9 %) may also be used to assess the accuracy of the predictions.

The predictions herein show that these empirical relationships are powerful tools which enable the prediction of fundamental physical properties of ILs for some of the most common anion types. However, a final caveat must be taken into account: the above correlations were derived from highly pure ILs that are liquid at the temperature at which measurements were made (20–22 °C). They are not applicable to impure ILs or materials that have significant long-range order at this temperature, that is, liquid-crystalline or solid phases. For example, $[\mathrm{C_2MIM}][\mathrm{PF_6}]$ melts at 58.3 °C (synthesized and measured in the Dyson laboratory). If the above equations are used to predict the properties of this solid salt ($V_{\mathrm{m}} = 0.265\,\mathrm{nm^3}$) under ambient conditions they predict a fairly fluid material ($\eta = 111$ cP), which is clearly not the case. Thus, when investigating previously unknown ILs it may be useful to combine this technique with a method to predict the melting point of the IL.[10,12,13]

Extrapolation of the V_{m} correlations to different temperature regimes is in progress by analysis of temperature-dependent physical data for a variety of ILs. Moreover, we are currently assessing other physical properties of ILs in dependence on V_{m}, for example, surface tension, refractive index, and heat capacity.

Received: March 2, 2007

Keywords: ionic liquids · molecular volumes · physical properties · predictive methods · sustainable chemistry

---

[1] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.

[2] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, **2003**.

[3] a) H. Shobukawa, H. Tokuda, A. B. H. Susan, M. Watanabe, *Electrochim. Acta* **2005**, *50*, 3872; b) H. Shobukawa, H. Tokuda, S.-i. Tabata, M. Watanabe, *Electrochim. Acta* **2004**, *50*, 305; S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, A. Usami, Y. Mita, M. Watanabe, N. Terada, *Chem. Commun.* **2006**, 544; c) M. C. Buzzeo, R. G. Evans, R. G. Compton, *ChemPhysChem* **2004**, *5*, 1106; d) A. Lewandowski, M. Galinski, *J. Phys. Chem. Solids* **2004**, *65*, 281.

[4] a) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737; b) P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar, M. Grätzel, *J. Am. Chem. Soc.* **2003**, *125*, 1166; c) P. Wang, S. M. Zakeeruddin, J.-E. Moser, M. Grätzel, *J. Phys. Chem. B* **2003**, *107*, 13280; d) P. Wang, S. M. Zakeeruddin, M. Shaik, R. Humphry-Baker, M. Grätzel, *Chem. Mater.* **2004**, *16*, 2694; e) C. A. Angell, W. Xu, *Science* **2003**, *302*, 422; f) F. Mazille, Z. Fei, D. Kuang, D. Zhao, S. M. Zakeeruddin, M. Grätzel, P. J. Dyson, *Inorg. Chem.* **2006**, *45*, 1585.

[5] S. Z. El Abedin, F. Endres, *ChemPhysChem* **2006**, *7*, 58.

[6] a) A. Bösemann, T. J. S. Schubert, Germany, **2004**, patent pending; b) Z. Du, Y.-L. Yu, J.-H. Wang, *Chem. Eur. J.* **2007**, *13*, 2130.

[7] a) H. Itoh, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* **2004**, *126*, 3026; b) B. S. Lee, Y. S. Chi, J. K. Lee, I. S. Choi, C. E. Song, S. K. Namgoong, S.-g. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 480; c) M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem.* **2004**, *116*, 5096; *Angew. Chem. Int. Ed.* **2004**, *43*, 4988.

[8] F. Endres, S. Z. El Abedin, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101.

[9] K. R. Seddon in *The International George Papatheodorou Symposium* (Ed.: S. Boghosian), Institute of Chemical Engineering and High Temperature Chemical Processes, Patras, Greece, **1999**, p. 131.

[10] A. R. Katritzky, R. Jain, A. Lomaka, R. Petrukhin, M. Karelson, A. E. Visser, R. D. Rogers, *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 225.

[11] a) I. Krossing, J. M. Slattery, *Z. Phys. Chem. (Muenchen Ger.)* **2006**, *220*, 1343; b) A. P. Abbott, *ChemPhysChem* **2004**, *5*, 1242; c) A. P. Abbott, *ChemPhysChem* **2005**, *6*, 2502; d) K. R. Seddon, M. Deetlefs, M. Shara, *Phys. Chem. Chem. Phys.* **2006**, *8*, 642.

[12] a) A. R. Katritzky, A. Lomaka, R. Petrukhin, R. Jain, M. Karelson, A. E. Visser, R. D. Rogers, *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 71; b) A. R. Katritzky, R. Jain, A. Lomaka, R. Petrukhin, M. Karelson, A. E. Visser, R. D. Rogers, *J. Chem. Inf. Comput. Sci.* **2005**, *45*, 533; c) S. Trohalaki, R. Pachter, *QSAR Comb. Sci.* **2005**, *24*, 485; d) S. Trohalaki, R. Pachter, S. R. Drake, T. Hawkins, *Energy Fuels* **2005**, *19*, 279; e) D. M. Eike, J. F. Brennecke, E. J. Maginn, *Green Chem.* **2003**, *5*, 323; f) S. Alavi, D. L. Thompson, *J. Chem. Phys.* **2005**, *122*, 154704.

[13] C. Daguenet, P. Dyson, I. Krossing, A. Oleinikova, J. M. Slattery, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427

[14] News features: J. S. Yeston, *Science* **2006**, *314*, 19b; *Anal. Chem.* **2006**, *78*, 7906.

[15] R. D. Shannon, C. T. Prewitt, *Acta. Crystallogr. Sect. B* **1969**, *25*, 925; R. D. Shannon, *Acta Crystallogr.Sect. A* **1976**, *32*, 751.

[16] F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380.

[17] a) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* **1999**, *38*, 3609; b) H. D. B. Jenkins, J. F. Liebman, *Inorg. Chem.* **2005**, *44*, 6359.

[18] a) Hofmann recently determined the average atomic volumes for a number of common elements.[18b] This permits a simple additive method for the estimation of V_m, where V_m for a salt (or indeed any molecule or molecular fragment) is given by the sum of the atomic volumes of the constituent atoms. While this approach is simpler to apply, we found that molecular volumes derived directly from crystal structures (as shown herein) give better correlations, particularly when comparing ions with substantially different structures (see the Supporting Information). b) D. W. M. Hofmann, *Acta. Crystallogr. Sect. B* **2002**, *58*, 489.

[19] It has long been known that the observed physical properties of ILs are strongly affected by the purity of the material.[20] All ILs in this study were synthesized in our laboratories and purified to minimize halide and water content, which were determined by ion chromatography and Karl Fischer titration, respectively (see the Supporting Information for experimental details and physical data). For some ILs physical data were available from both the Dyson laboratory (at the EPFL) and the IoLiTec laboratory in Freiburg. These independent data agree very well and lend confidence to our conclusions. Physical data from the literature were not included in this study, as in many cases an IL is reported to have very different physical properties in two or more studies. The recent founding of an online database for the physical properties of ILs by the National Institute of Standards and Technology (NIST) is very interesting in the context of the work herein.[20e] As the number of ILs in the database increases it should be possible for users to derive similar correlations, for example, involving anions not included in our study, using the data in this database. Nevertheless, care should be taken only to use physical data from very pure ILs (purity information is included in the database) when deriving these correlations.

[20] a) J. A. Widegren, A. Laesecke, J. W. Magee, *Chem. Commun.* **2005**, 1610; b) K. R. Seddon, A. Stark, M.-J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275; c) J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156; d) C. F. Poole, B. R. Kersten, S. S. J. Ho, M. E. Coddens, K. G. Furton, *J. Chromatogr.* **1986**, *352*, 407; e) http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix.

[21] D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2004**, *43*, 2197.

[22] O. O. Okoturo, T. J. VanderNoot, *J. Electroanal. Chem.* **2004**, *568*, 167–181.

[23] I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116; *Angew. Chem. Int. Ed.* **2004**, *43*, 2066.

[24] The conductivity correlations do not include nitrile-functionalized ILs, as no experimental conductivity data were available.

[25] The $[\mathrm{N(CN)_2}]^-$ ILs have a higher content of chloride ions ((180 ± 10) ppm, determined by ion chromatography) than the other ILs in this study (due to chloride impurities in the commercial potassium dicyanamide starting material), which will effect the conductivity measurements.

[26] C. Ye, J. M. Shreeve, *J. Phys. Chem. A* **2007**, *111*, 1456.