Short communication

The conductivity of pyrrolidinium and sulfonylimide-based ionic liquids: A combined experimental and computational study

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ARTICLE INFO

ABSTRACT

Ionic conductivity is a fundamental property of ionic liquids with its origin and exact nature under debate. Using a specially selected system of pyrrolidinium cations (PYR_{1x}, x = 3,4) and sulfonylimide anions (FSI, TFSI, BETI, and IM14)-based ionic liquids we observe a simple and accurate connection between *ab initio* computed cation and anion volumes and measured molar ionic conductivities.

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Many proposed electrochemical applications of ionic liquids (ILs) rely on the high mobilities and the large amounts of charge carriers inherently present and the thereby resulting high ionic conductivities [1–3]. However, the nature of the diffusing species and the molecular level interactions in ILs are currently subject of vivid discussions and scientific efforts, and the observed ionic conductivity is most often seen as a product of a combination of processes. This is for example manifested in the different transport values and observations obtained by NMR and electrochemical techniques, *e.g.* expressed as Haven ratios [4–9]. Often the sizes of the diffusing species are used as a starting point for discussions of the total ionic conductivities observed, *i.e.* using Nernst and Stokes–Einstein equation-based arguments. However, IL studies often use a range of different kinds of cations and anions and thus other factors than simply the IL ion or complex sizes may affect the observations and conclusions made. To overcome such ambiguities, we here use a designed system of only six ILs; all based on pyrrolidinium cations and sulfonylimide anions (Table 1) [10]. Some of these ILs have already been shown to be highly interesting as electrolyte media for lithium battery application [11,12]. The reason for choosing this very limited specific set of ILs is that they are chemically extremely similar and therefore we suggest that for these ILs the conductivity should decrease as the IL ion sizes increase, *e.g.* from the small FSI^- to the large IM_{14}^- anion, all other things are considered being constant. In Fig. 1 we test this *Ansatz* by plotting the molar ionic conductivity, Λ, at room temperature *vs.* the sum of *ab initio* calculated cation and anion volumes, V_{tot}. As seen our data are almost perfectly fitted (R^2 = 0.9942). We stress that impurities can play a significant role in IL conductivity measurements and thus any ILs used for this kind of study must be ultra-pure [13]; the sensitivity of the present fit with respect to changes in the values is very high. The seminal work by Slattery et al. [14] used volumes obtained from crystal structures as a starting point for comparisons with the conductivity of no less than 23 ILs, which however needed separate fits for each choice of anion, while at the same time the cation dependence, shown for imidazolium, pyrrolidinium and ammonium-based ILs, was much smaller (as can be expected from the smaller chemical differences compared to changing the anions). Thus, while using a similar approach and very few ILs, the present ILs allow for a simple but so far not shown observation across different anions to be made.

One, but not the sole, prerequisite for a true picture of the simple connection observed above is that the ion–ion interactions in the ILs do not differ, otherwise the equilibrium of "free" ions *vs.* ion-pairs *vs.* higher aggregates (although neither of these concepts are unproblematic to even define for ILs) would. Not surprisingly, as all the presently used anions are free to coordinate with the pyrrolidinium cations via the same two oxygen atoms of the SO_2 groups, the ILs used have almost identical cation–anion interac-
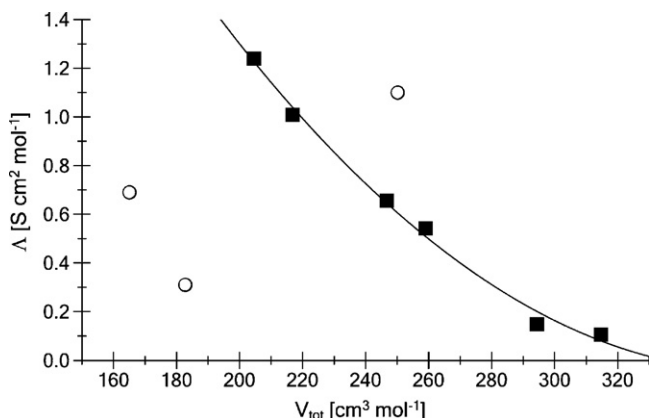
Table 1
Computed and experimental data for the ionic liquids.

Ionic liquid	ΔE [kJ mol^{-1}]	V_{cation} [cm^3 mol^{-1}]	V_{anion} [cm^3 mol^{-1}]	V_{tot} [cm^3 mol^{-1}]	σ at 20 °C[a] [mS cm^{-1}]	M_w [g mol^{-1}]	ρ at 20 °C[b] [g cm^{-3}]	Λ at 20 °C [S cm^2 mol^{-1}]	η at 20 °C[c] [mPas]
PYR$_{13}$FSI	−299.6	118.7	85.9	204.6	5.4	308.36	1.343	1.24	45.3
PYR$_{14}$FSI	−292.2	130.9	85.9	216.8	4.1	322.39	1.310	1.01	65.9
PYR$_{13}$TFSI	−304.7	118.7	128.1	246.8	2.3	408.37	1.432	0.66	72.5
PYR$_{14}$TFSI	−302.7	130.9	128.1	259.0	1.8	422.41	1.399	0.54	95.1
PYR$_{14}$BETI	−299.6	130.9	163.4	294.3	0.42	522.32	1.481	0.15	347.5
PYR$_{14}$IM$_{14}$	−296.4	130.9	183.8	314.7	0.28	572.43	1.512	0.11	556.0

[a] Ref. [31].
[b] Ref. [32].
[c] Ref. [33].

Fig. 1. The molar ionic conductivity at 20 °C vs. the sum of the cation and anion volumes for the six pyrrolidinium-based ILs (■) and the three imidazolium-based ILs (○).

tion energies (ΔE): 298.5 ± 6 kJ mol^{-1} (Table 1) [15–19]. Due to the very complex potential energy surfaces of these 1:1 ion-pairs, the interaction energies were recently computed for the PYR$_{14}$TFSI IL to have a range of *ca.* 15 kJ mol^{-1}, but the ion-pairs used here approximately correspond to the minimum energy configuration obtained in Ref. [9] (ion-pair 6). The numeric value of the interaction energy, *i.e.* the relative strength of interaction, is on the lower end for ILs previously reported by different groups [9,20–26] and thus supports the high ionic conductivities observed. In Fig. 2 the
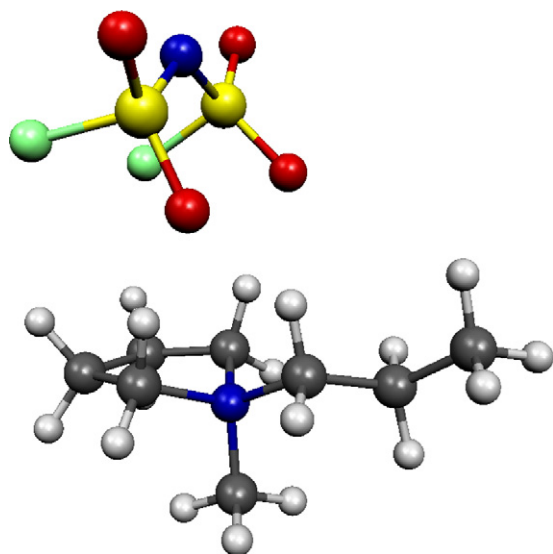
Fig. 2. The most stable Pyr$_{13}$FSI ion-pair as obtained from the B3LYP/6-311+G* calculations.

obtained stable cation–anion 1:1 ion-pair structure is shown for PYR$_{13}$FSI. In order to test the importance of the interaction energy *vs.* other factors we include also data for EMI$^+$-based ILs with different ΔE; EMI$^+$-BF$_4^-$ (351 kJ mol^{-1}), EMI$^+$-PF$_6^-$ (326 kJ mol^{-1}), and EMI$^+$-TFSI$^-$ (320 kJ mol^{-1}) [15]. Our values are qualitatively comparable to previous studies, with BF$_4^-$ being significantly stronger bound and TFSI$^-$ and PF$_6^-$ approximately equal [20]. We also use the Λ values from Table 4 in Ref. [20] (25 °C), but note, however, that those data are for the corresponding BMI$^+$-based ILs and thus we use a V_{tot} based on a BMI$^+$ volume (122.1 cm^3 mol^{-1}) rather than EMI$^+$ (96.6 cm^3 mol^{-1}) [15]. For BF$_4^-$ and PF$_6^-$ the volumes are 43.0 and 60.7 cm^3 mol^{-1}, respectively [15]. It is clear from Fig. 1 that no simple correlation can be found for these ILs (changing from BMI$^+$ to EMI$^+$ volume would simply translate the data points along the *x*-axis). The reasons can be various and we here outline a few possibilities. One is that the ion–ion interaction energy indeed is the determining factor for the differences, but that the use of 1:1 ion-pair models fails to correctly describe the difference between the interactions between the IL cations and an isotropic PF$_6^-$ and an anisotropic TFSI$^-$, respectively (as the obtained relative energy difference is only 6 kJ mol^{-1}). Another possibility is that the well-known intra-molecular flexibility of the TFSI$^-$ anion is responsible for the higher molar conductivity of EMITFSI—but this does not explain the higher molar conductivity observed compared to the pyrrolidinium ILs. Yet another possibility is that other aspects like ion–ion distances or the different possibilities for "sliding" of ions with respect to each other [27,28] are more important prerequisites for unambiguous comparisons. In any case there indeed seems to be more to a general correlation of conductivity *vs.* ion volume than an interaction energy based on 1:1 ion-pair calculations. However, as exemplified here, with an appropriate choice of ILs such differences can be avoided. For proof or counter-proof another set of ILs, with the volumes of the ions being approximately identical, but where the interaction strength varies significantly would be needed—but we envisage such a set to be very difficult, if not impossible, to obtain. A further extension of the model also to varying (descriptions and/or modeling of) ion–ion interactions, ion types and shapes, as for the imidazolium-based ILs above is obviously then much more elaborate—but realistic using the current model as a first stepping stone. This would perhaps finally allow *a priori* prediction of the conductivity of most simple aprotic ILs, at least for ILs where the alkyl chains of the cations do not entangle or create any nano-phase separation. Note that the present observations as such do not discriminate between different amounts or types of diffusing species: "free" ions, ion-pairs, *etc.*, but rather provide a common baseline for the six ILs, which in passing also is supported by IR and Raman data, with no significant differences seen for the anion bands sensitive to ion-pair formation [29,30]. Thus we do not here speculate about the roles of "friction" or ion-pairing/aggregation in the ILs and avoid the difficulties with the interpretation of these phenomena and their influence on the ion conductivity.

Acknowledgements

References

[1] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Nat. Mater. 8 (2009) 621.
[2] A. Fernicola, B. Scrosati, H. Ohno, Ionics 12 (2006) 95.
[3] H. Ohno, Electrochemical Aspects of Ionic Liquids, Wiley, 2005.
[4] A. Noda, K. Hayamizu, M. Watanabe, J. Phys. Chem. B 105 (2001) 4603.
[5] H. Tokuda, K. Hayamizu, K. Ishii, A.B.H. Susan, M. Watanabe, J. Phys. Chem. B 109 (2005) 6103.
[6] A. Wulf, R. Ludwig, P. Sasisanker, H. Weingärtner, Chem. Phys. Lett. 439 (2007) 323.
[7] N.A. Stolwijk, Sh. Obeidi, Electrochim. Acta 54 (2009) 1645.
[8] H. Jin, B. O'Hare, J. Dong, S. Arzhantsev, G.A. Baker, J.F. Wishart, A.J. Benesi, M. Maroncelli, J. Phys. Chem. B 112 (2008) 81.
[9] F. Castiglione, M. Moreno, G. Raos, A. Famulari, A. Mele, G.B. Appetecchi, S. Passerini, J. Phys. Chem. B 113 (2009) 10750.
[10] G.B. Appetecchi, S. Scaccia, C. Tizzani, F. Alessandrini, S. Passerini, J. Electrochem. Soc. 153 (2006) A1685.
[11] J.-H. Shin, W.H. Henderson, G.B. Appetecchi, F. Alessandrini, S. Passerini, Electrochim. Acta 50 (2005) 3859.
[12] C. Tizzani, G.B. Appetecchi, M. Carewska, G.-T. Kim, S. Passerini, Aust. J. Chem. 60 (2007) 47.
[13] S. Randström, M. Montanino, G.B. Appetecchi, C. Lagergren, A. Moreno, S. Passerini, Electrochim. Acta 53 (2008) 6397.
[14] J.M. Slattery, C. Daguenet, P.J. Dyson, T.J.S. Schubert, I. Krossing, Angew. Chem. 119 (2007) 5480.
[15] The calculations for the free ions and the ion-pairs have been performed using the B3LYP functional [16–18] as implemented in GAUSSIAN 03 [19]. The interaction energy is the difference between the sum of the free ions' energies and the energy of the corresponding most stable 1:1 ion-pair. The volumes were obtained using a Monte-Carlo-based algorithm defining the space occupied with more than 0.001 electron/bohr^3 as the volume.
[16] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[17] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[18] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.
[19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.
[20] S. Tsuzuki, H. Tokuda, K. Hayamizu, M. Watanabe, J. Phys. Chem. B 109 (2005) 16474.
[21] E.A. Turner, C.C. Pye, R.D. Singer, J. Phys. Chem. A 107 (2003) 2277.
[22] S.A. Katsyuba, P.J. Dyson, E.E. Vandyukova, A. Chernova, A. Vidis, Helv. Chim. Acta 87 (2004) 2556.
[23] M.G. Del Popolo, G.A. Voth, J. Phys. Chem. B 108 (2004) 1744.
[24] R. Holomb, A. Martinelli, I. Albinsson, J.C. Lassègues, P. Johansson, P. Jacobsson, J. Raman Spectrosc. 39 (2008) 793.
[25] E.I. Izgorodina, M. Forsyth, D.R. MacFarlane, Aust. J. Chem. 60 (2007) 15.
[26] J. Scheers, P. Johansson, P. Jacobsson, J. Electrochem. Soc. 155 (2008) A628.
[27] S. Zahn, G. Bruns, J. Thar, B. Kirchner, Phys. Chem. Chem. Phys. 10 (2008) 6921.
[28] S. Zahn, F. Uhlig, J. Thar, C. Spickermann, B. Kirchner, Angew. Chem. Int. Ed. 47 (2008) 3639.
[29] M. Herstedt, M. Smirnov, P. Johansson, M. Chami, J. Grondin, L. Servant, J.C. Lassègues, J. Raman Spectrosc. 36 (2005) 762.
[30] A. Matic, L.E. Fast, P. Johansson, S. Passerini, G.B. Appetecchi, unpublished data.
[31] The ionic conductivity measurements were performed at ENEA: the samples were placed in sealed glass conductivity cells (AMEL 192/K1) equipped with two porous platinum electrodes (cell constant of 1.0 ± 0.1 cm). The cells were assembled in the dry room. The samples were then held at $-40\,^{\circ}$C overnight (18 h). The measurement was run by performing a $1\,^{\circ}$C h^{-1} heating scan from $-40\,^{\circ}$C to $100\,^{\circ}$C using an AMEL 160 conductivity meter and a climatic test chamber (Binder GmbH MK53) located in the dry room. The entire setup was controlled by software developed at ENEA.
[32] The viscosity measurements performed at ENEA were conducted using a HAAKE Rheostress 600 rheometer located in the dry room. The tests were performed from 20 to $80\,^{\circ}$C with a $1\,^{\circ}$C min^{-1} heating rate in the 100 to 2000 s^{-1} rotation speed range. Measurements were taken after $10\,^{\circ}$C steps.
[33] The density measurements were performed at ENEA from $80\,^{\circ}$C to $20\,^{\circ}$C by $10\,^{\circ}$C step using a density meter (Mettler Toledo DE40) in the dry-room. The samples were previously degassed under vacuum at $50\,^{\circ}$C overnight to avoid bubble formation during the cooling scan tests.