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Molecular structure, reorientational dynamics, and intermolecular interactions in the neat ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate*

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Abstract: Results on the molecular and liquid structure and the reorientational dynamics are reported for the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]). In quantum-chemical calculations for [BMIM][PF_6] in the gas phase, hydrogen bonding between the proton at carbon 2 in the aromatic ring and the fluorine atoms of the hexafluorophosphate anion was found. From the analysis of ^{13}C relaxation data, the reorientational motions were evaluated, and the Vogel–Fulcher–Tammann and Arrhenius activation energies for the overall and internal reorientational motions, respectively, of the different ^{13}C–^{1}H vectors are given as well as correlation times at 300 K. By performing molecular dynamics (MD) simulations, pair-distribution functions between moieties in the cation and the phosphorous atom in the anion were determined. The pair-distribution function for the proton at carbon 2 exhibits a particular sharp and strong maximum indicating a strong interaction with the anion. The quantum-chemical calculations, the motional parameters, and the results from the MD simulations support the existence of hydrogen bonding and the formation of ion pairs in the ionic liquid.

INTRODUCTION

The introduction of ionic liquids [1], which are room-temperature molten salts, as potential green solvents led to a quickly growing number of publications on these systems. They are actually investigated in many synthetic as well as nonsynthetic applications in industry and academia because of the broad variability of their solvent properties. One very important feature of ionic liquids is their apparently vanishing vapor pressure, which makes them practically nonvolatile. However, compared to the amount of literature published about their preparation and possible applications, little is known about their physical and physicochemical properties, and particularly the molecular and liquid structure, and molecular dynamics in these liquids. To understand the relation between molecular and macroscopic properties of

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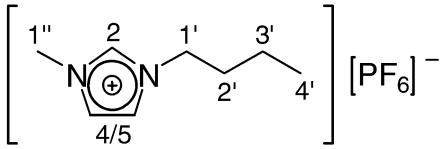
ionic liquids and thus the route of chemical reactions in them, their molecular structure and dynamics have to be known.

1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6], **1**) is a prominent example of non-chloroaluminate ionic liquids (Scheme 1). The structure of the ion pair **1** in the gas phase was studied by Meng et al. [2], thermodynamic properties were calculated from Monte Carlo simulations of the neat liquid **1** [3], translational diffusion in the system methanol/**1** was measured by Richter et al. [4]. Antony et al. [5] and Dölle and Carper [6] investigated the reorientational dynamics in neat **1**. Potential parameters for the simulation of the neat liquids dimethyl and ethylmethylimidazolium chloride and hexafluorophosphate were developed by Hanke et al. [7a], and for ethylmethylimidazolium tetrachloroaluminate by de Andrade et al. [7b]. The potential parameters were then used to calculate pair-distribution functions [7], self-diffusion constants, and reorientational correlation times of cations and anions [7a].



Scheme 1

It is the aim of this investigation to present results on the molecular and liquid structure, and the molecular reorientational dynamics in the ionic liquid [BMIM][PF_6], which should serve as a model for other ionic liquids. These molecular properties will be discussed with respect to the intermolecular interactions in ionic liquids. The present study will hopefully help to understand the specific properties of ionic liquids, which make them suited for the many different applications in chemistry.

RESULTS AND DISCUSSION

Molecular structure

The molecular structure of [BMIM][PF_6] ion pairs has already been published in a previous paper [2], and it is shown in Fig. 1 for the optimized geometry of one ion pair. The structural data of the ion pair **1** clearly show the occurrence of hydrogen bonding between the fluorine atoms of the $[PF_6]^-$ anion and the $[BMIM]^+$ cation [2]. Particularly strong hydrogen bonds were observed to the hydrogen at carbon 2 in the aromatic ring. As a consequence, the bond distance between C2 and the attached proton is elongated from 110 ppm in the naked cation to 113 pm in the ion pair. The distances between fluorine atoms in the anion and protons in the cation become shorter than the sum of the van der Waals radii of 267 pm. These findings were corroborated by changes in the charges from 0.24 *e* and 0.12 *e* to 0.35 *e* and –0.01 *e* at the hydrogen and carbon atom in the naked cation and the ion pair, respectively [2].

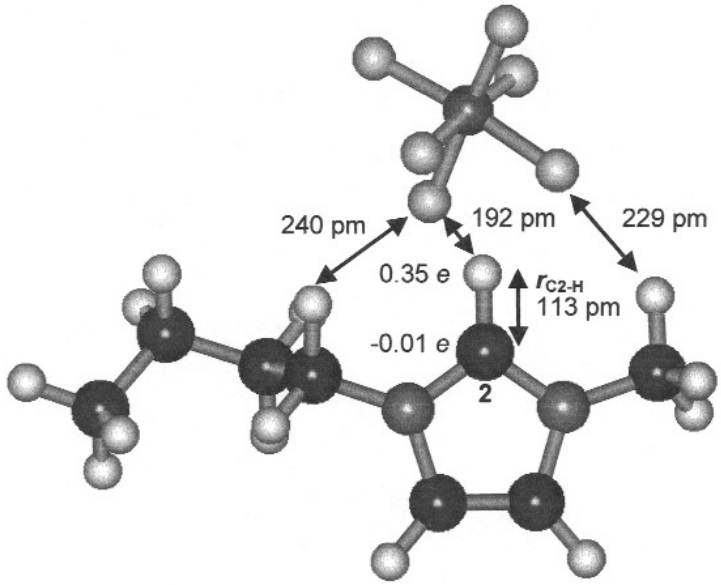


Fig. 1 Optimized AM1 minimum structure of one ion pair of [BMIM][PF$_6$].

Molecular reorientational dynamics

The total ^{13}C spin–lattice relaxation rates $1/T_1$ and NOE factors η were measured at a resonance frequency of 62.89 MHz in a temperature range from 250 to 357 K for the neat liquid [BMIM][PF$_6$] [5]. The models used for fitting parameters of reorientational motion to the experimental data were already introduced in ref. [5].

From the fits, values for the activation energies of reorientational motion were obtained which are presented in Fig. 2. The temperature dependence of the reorientational correlation times for the overall motion was described by a Vogel–Fulcher–Tammann equation

$$\tau_M = \tau_{VFT} \exp\left(\frac{E_{VFT}}{R(T - T_0)}\right) \quad , \tag{1}$$

in which the parameter T_0 is of the order of the glass transition temperature T_g, and R is the gas constant. The quantity E_{VFT} is often called apparent activation energy. From the overall motion an internal reorientational motion could be separated using the approach by Lipari and Szabo [8]. The internal correlation times, however, obey an Arrhenius equation

$$\tau_i = \tau_A \exp(E_A/RT) \tag{2}$$

with the activation energy E_A. The activation energies are interpreted as fit parameters representing a measure for the hindrance of the corresponding reorientational process. All ^{13}C–^{1}H vectors show more or less the same VFT activation energy for the overall motion, except maybe the methyl group in the butyl chain, for which it is less. The Arrhenius activation energy of the internal motion is of the order of the usual activation barriers in alkyl chains.

When the fit parameters are used to calculate effective reorientational correlation times τ_c, the results in Fig. 3 are obtained. All values for the aromatic ^{13}C–^{1}H vectors are of the same order of magnitude and exhibit clearly the slowest reorientational motion, whereas the values for the ^{13}C nuclei in the butyl chain are significantly smaller and decrease toward the methyl group because the alkyl chain becomes more and more flexible toward the end. The internal rotation of the methyl group 1″ is so fast

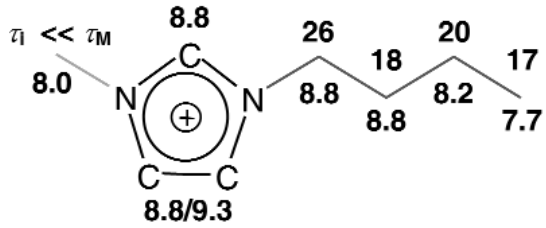


Fig. 2 Activation energies E_{VFT} and E_A (values below and above the carbons in the alkyl chain, respectively) of the overall and internal reorientational motion of the $^{13}C–^{1}H$ vectors in [BMIM][PF_6] in kJ·mol^{-1}.

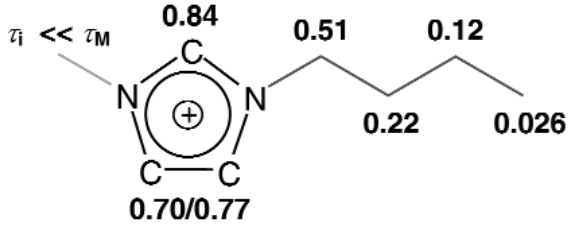


Fig. 3 Reorientational correlation times τ_c of the $^{13}C–^{1}H$ vectors in [BMIM][PF_6] at 300 K in ns.

that no effective correlation time could be calculated. The values for the aromatic carbons reflect the velocity of the overall reorientational motion of the cation, which is even at room temperature already relatively slow.

Liquid structure

In a supporting molecular dynamics (MD) simulation study, the liquid structure was investigated. In Figs. 4 to 6, the pair-distribution functions $g(r)$ between a carbon atom in the cation or the proton bound to it, and the phosphorous atom in the anion are plotted. The pair-distribution functions are thus a measure of the probability to find the anion near the carbon or the proton bound to it. In the figures the functions for carbons 2, 5, and 2′ and the corresponding protons are compared to each other. The $g(r)$ functions for carbon 2 exhibit sharp maxima with large maximum values, the peak for the corresponding proton being even higher. The coordination numbers, which are also given in the figures, have a value of two. Compared to that, the maxima and coordination numbers for carbon 5, which is also situated in the aromatic ring, are smaller. The pair-distribution function for C2′ is almost featureless and has only a small maximum value.

The interpretation of these results is straightforward: The intermolecular interactions between the cation and anion are quite strong at C2 and especially at the proton bound to it. It becomes obvious that the hydrogen bonding found also in the quantum-chemical study between the proton at C2 and the fluorine atoms in the anion is effective in the MD simulation of the liquid. This is confirmed by the fact that the distance at the maximum for the distribution function of the proton at C2 is shorter than that of C2 itself. The anion is not just situated somewhere below or above the imidazolium ring but interacts specifically with the proton at C2. Since the interaction between the proton at C5 and the anion is not as strong as to the proton at C2, the maxima in the distribution functions become less pronounced. For C2′, the maximum has almost disappeared because of the flexibility of the alkyl chain. This interpretation finds further confirmation in the MD simulation study by Hanke et al. [7a], who observed that the largest probability for finding an anion is near the C2 below and above the ring.

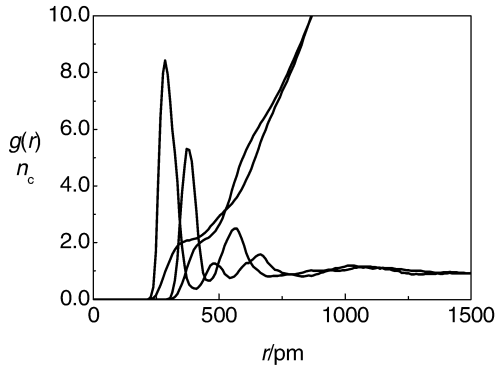


Fig. 4 Pair-distribution functions $g(r)$ and coordination numbers n_c for C2 of the $[BMIM]^+$ cation and the proton at C2, respectively, and the phosphorus of the anion $[PF_6]^-$.

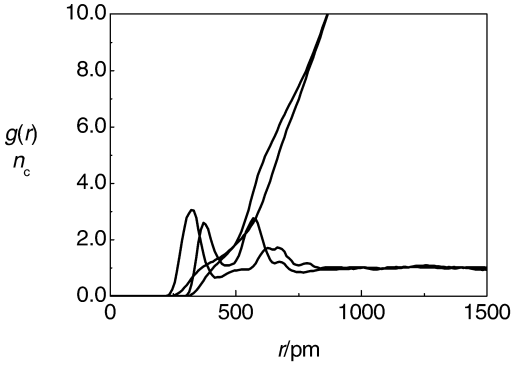


Fig. 5 Pair-distribution functions $g(r)$ and coordination numbers n_c for C5 of the $[BMIM]^+$ cation and the proton at C5, respectively, and the phosphorus of the anion $[PF_6]^-$.

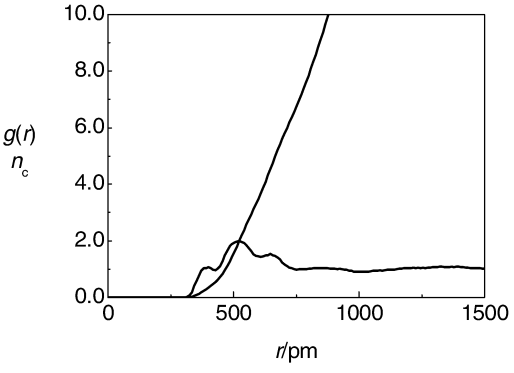


Fig. 6 Pair-distribution functions $g(r)$ and coordination numbers n_c for C2′ of the $[BMIM]^+$ cation and the phosphorus of the anion $[PF_6]^-$.

CONCLUSIONS

Meng et al. [2] observed in their quantum-mechanical study of $[BMIM][PF_6]$ ion pairs in vacuo hydrogen bonding between the $[PF_6]^-$ anion and the hydrogen atom at C2 in the aromatic ring of the $[BMIM]^+$ cation. The most important result of the present investigation is that this finding is supported

by the evaluation of the molecular dynamics by means of NMR relaxation measurements and MD simulations.

Further evidence is found in the detailed analysis of ref. [5], in which the values of the generalized order parameters by Lipari and Szabo [8] for the different $^{13}C–^{1}H$ vectors were analyzed: All values for the order parameter S^2 are rather large when compared to those found for molecular systems interacting mainly by van der Waals forces [9]. This finding shows that the order parameter is resulting mainly from ultrafast stretching and bending vibrations. The "inter" term, being a consequence of librational motions of the whole molecule in the cage of the surrounding liquid molecules is obviously almost vanishing. This observation was also made for other liquid systems interacting by strong intermolecular interactions like hydrogen bonds [10,11]. The order parameter S^2, which was observed for the ^{13}C nuclei 2 and 1′ to be unity, is an indicator for a missing very fast overall *and* also internal motion. The model of hydrogen bonding between the cation and anion of [BMIM][PF_6] was additionally confirmed in a study by Headley and Jackson [12] by measurements of ^{1}H NMR chemical shifts.

It is well known that hydrogen bonding intensifies the formation of ion pairs in electrolyte solutions significantly when compared to systems without specific interactions [13]. Thus, it is assumed for the ionic liquid **1** that the hydrogen bonding leads to the formation of ion pairs or even higher aggregates. It can now be speculated that in ionic liquids not only ion pairs are formed, but also higher aggregates with a kind of layer structure, in which the anions are located mainly above and below the aromatic ring near C2. The occurrence of the hydrogen bonding in addition to the Coulombic interactions between the ions might explain the high viscosity and some of the other specific macroscopic properties of the ionic liquid **1**.

METHODS

The relaxation data measurements and their detailed analysis were described previously in ref. [5]. The MD simulations were performed with the simulation program MOSCITO 4.0 by D. Paschek (Dortmund University, Germany). The atomic distances, charges, and torsion potential parameters were obtained from RHF/6-311G** ab initio calculations, the intermolecular potentials from MOSCITO. The simulation temperature was 300 K, the density of the liquid 1.370 g cm^{-3}. The time step during simulation periods of 50 to 300 ps was 1.5 fs. The number of ion pairs in the simulation box was 216.

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REFERENCES

1. (a) J. D. Holbrey and K. R. Seddon. *Clean Products Processes* **1**, 223 (1999); (b) T. Welton. *Chem. Rev.* **99**, 2071 (1999); (c) P. Wasserscheid and W. Keim. *Angew. Chem. Int. Ed.* **39**, 3772 (2000); (d) *Ionic Liquids in Synthesis*, P. Wasserscheid and T. Welton (Eds.), Wiley-VCH, Weinheim (2002).
2. Z. Meng, A. Dölle, W. R. Carper. *J. Mol. Struct. (THEOCHEM)* **585**, 119 (2002).
3. J. K. Shah, J. F. Brennecke, E. J. Maginn. *Green Chem.* **4**, 112 (2002).
4. J. Richter, A. Leuchter, G. Palmer. In *Ionic Liquids in Synthesis*, P. Wasserscheid and T. Welton (Eds.), p. 162, Wiley-VCH, Weinheim (2002).
5. J. H. Antony, D. Mertens, A. Dölle, P. Wasserscheid, W. R. Carper. *ChemPhysChem* **4**, 588 (2003).
6. A. Dölle and W. R. Carper. In *Ionic Liquids in Synthesis*, P. Wasserscheid and T. Welton (Eds.), p. 168, Wiley-VCH, Weinheim (2002).

7. (a) C. G. Hanke, S. L. Price, R. M. Lynden-Bell. *Mol. Phys.* **99**, 801 (2001); (b) J. de Andrade, E. S. Böes, H. Stassen. *J. Chem. Phys. B* **106**, 3546 (2002).
8. G. Lipari and A. Szabo. *J. Am. Chem. Soc.* **104**, 4546 (1982).
9. A. Dölle. *J. Phys. Chem. A* **106**, 11683 (2002).
10. A. Friedrich, A. Dölle, M. D. Zeidler. *Magn. Reson. Chem.* **41**, 813 (2003).
11. C. Baraguey, D. Mertens, A. Dölle. *J. Phys. Chem. B* **106**, 6331 (2002).
12. A. D. Headley and N. M. Jackson. *J. Phys. Org. Chem.* **15**, 52 (2002).
13. C. A. Krauss. *J. Phys. Chem.* **60**, 129 (1956).