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Water-induced Acceleration of Transport Properties in Hydrophobic 1-Butyl-3-methylimidazolium Hexafluorophosphate Ionic Liquid

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The electric conductivities and self-diffusion coefficients in dried and water-saturated 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF$_6$], were measured at 25 and 40 °C. Although the presence of water can remarkably induce acceleration of transport properties in the ionic liquid, the ionic dissociation remains almost unchanged.

Room temperature ionic liquids (ILs) have attracted much attention as a promising class of environmentally-benign alternatives for volatile organic solvents in a variety of applications such as reactions, separations, and electrochemical devices.[1] Typical ILs have a stable liquid range over 300 °C, negligible vapor pressure, wide electrochemical windows, and excellent thermal and chemical stability. Recently, it has been found that transport properties in highly viscous [BMIM][PF$_6$] can be remarkably improved by a small amount of substance[2–4] as well as dissolution of carbon dioxide.[5] Although several researchers[6] pointed out that the addition of water to ILs does not affect solvatochromic parameters significantly, the mechanism has still remained unrevealed. Here, we report the effects of water, which could be one of the most practically vital issues in many applications, on transport phenomena in hydrophobic [BMIM][PF$_6$] in relation to intermolecular interactions between water and IL species.

The electric conductivities in dried and water-saturated [BMIM][PF$_6$][7] were measured with a 4-terminal conductometer (Fuso, Model 369). As shown in Figure 1, the molar electric conductivity (Λ)[8] remarkably increased up to three times or more due to the presence of water. The increase in Λ is mainly attributed to a drastic decrease in the macroscopic viscosity of solution.[2] In this work, nevertheless, we further investigate how water molecules accelerate the transport properties in the IL solutions at the molecular level by means of NMR (Varian, Inova 300) spectroscopy.

^{1}H and ^{19}F NMR spectra of dried and water-saturated [BMIM][PF$_6$] gave the average signals even if the chemical equilibria exist between free and ion-pair species.[9] In the water-saturated samples, only a signal of water appeared at $\delta_\mathrm{w} \approx 2.5$ (Table 1). The solubility of water in IL can be determined from the signal integrals. The mole fractions (x_w) of water in the water-saturated samples are 0.25 and 0.28 at 25 and 40 °C, respectively, corresponding to 2.11 and 2.47 w/w %, which are in a good agreement with the literature values.[2,10] Although the solubility of water in the hydrophobic IL is rather high, the relatively small values of δ_w show that water molecules are present mostly in the free state without self-association. It was also found that the presence of water brings about little change in the ^{1}H chemical shifts of IL except for the acidic C2 proton in the imidazolium cation (δ_IL(H2)), where a slight downfield shift of ≈0.5 was observed (Table 1). In accordance with the previous NMR studies of ILs,[11] this is interpreted by the formation of weak hydrogen bonding between the C2 proton and water oxygen.

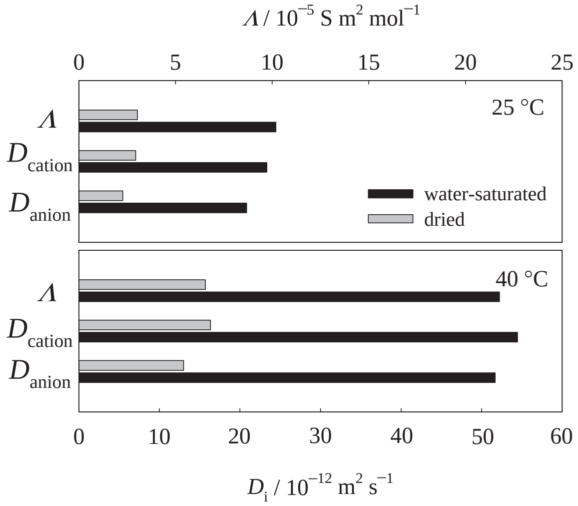

Figure 1. Effects of water on D_cation, D_anion, and Λ in dried and water-saturated [BMIM][PF$_6$].

Table 1. Values of x_w, ρ, c_IL, δ_w, δ_IL, Λ, D_w, D_cation, D_anion, and Λ_D for dry and water-saturated [BMIM][PF$_6$] at 25 (upper row) and 40 (lower row) °C

Sample	x_w	ρ / g cm^{-3}	c_IL / mol dm^{-3}	δ_w[b]	δ_IL(H2)[b]	$10^5\Lambda$ / S m^2 mol^{-1}	$10^{12}D_\mathrm{w}$[c] / m^2 s^{-1}	$10^{12}D_\mathrm{cation}$[c] / m^2 s^{-1}	$10^{12}D_\mathrm{anion}$[c] / m^2 s^{-1}	$10^5\Lambda_D$ / S m^2 mol^{-1}	Λ/Λ_D
dry	—	1.368[a]	4.81	—	8.16	3.03	—	7.06(8)	5.46(6)	4.70	0.65
	—	1.357[a]	4.78	—	8.14	6.55	—	16.4(1)	13.0(1)	10.5	0.62
water-saturated	0.25	1.35	4.65	2.50	8.21	10.19	348(4)	23.4(1)	20.8(1)	16.6	0.61
	0.28	1.33	4.57	2.44	8.20	21.76	630(3)	54.5(1)	51.7(1)	38.0	0.57

[a] Cited from Ref. 18. [b] vs the signal of residual ^{1}H (7.27 ppm) of CDCl$_3$ in an outer tube. [c] The 95% confidence limit is given in parentheses.

With the pulsed-field gradient sin-echo NMR technique, the self-diffusion coefficients of the cation (D_{cation}) and anion (D_{anion}) species in dried and water-saturated [BMIM][PF_6] were independently determined at 25 and 40 °C by measuring the ^{1}H and ^{19}F signals. In a similar manner to the molar electric conductivity, the significant increase was observed for both D_{cation} and D_{anion} in the water-saturated samples (Figure 1). It is very interesting, in particular, that the self-diffusion of the anion can be accelerated more effectively than that of the cation (Table 1). This fact suggests that water molecules favorably interact with the anion species in contrast to the weak hydrogen bonding between the cation and water, which was implied by the slight downfield shift of δ_{IL}(H2).

One may consider whether water promotes the ionic dissociation in ILs or not. In order to elucidate such an essential question, Λ is compared with the molar electric conductivity (Λ_D) calculated from D_{cation} and D_{anion} on the basis of the Nernst–Einstein equation:[12]

$$\Lambda_D = (|z_{\mathrm{cation}}|D_{\mathrm{cation}} + |z_{\mathrm{anion}}|D_{\mathrm{anion}})F^2/RT \qquad (1)$$

where z_{cation} and z_{anion} are charge numbers of cation and anion, respectively. Λ and Λ_D should be identical within the theoretical framework if each ion has the activity of unity without any ionic association. In practice, Λ_D is not interpreted straightforwardly because there are free and ion-pair species in IL solutions and NMR cannot distinguish them. However, the ratio of Λ/Λ_D can be a good indicator of the ionic association in ILs.[13,14] As is seen from Table 1, the presence of water decreases Λ/Λ_D very slightly. This indicates that the situation remains virtually unchanged in the water-saturated IL solutions.

The transport properties in [BMIM][PF_6] can be remarkably enhanced by the presence of water. Water molecules can weaken Coulombic cation–anion interaction, whereas they are not tightly bound to any species in view of its own large self-diffusion coefficients (D_{w} in Table 1). It was found that water did not affect the ionic dissociation; however, water can accelerate the self-diffusion of the anion more remarkably. It has been reported that Coulomb–dipole interaction is of primary importance between imidazolium cations and polar molecules in IL solutions;[15] however, less polar molecules can interact with anion species more preferably.[16,17] According to Kazarian et al.,[16] in fact, most of water molecules in ILs at relatively low concentrations exist in 1:2 type hydrogen bonded complexes of anion···HOH···anion. This is in harmony with the present results of rather enhancement in the self-diffusion of the anion in the water-saturated IL solutions. Because the system of IL solutions are very complicated, it is difficult to derive a simple explanation of intermolecular interactions. However, the downfield shift of δ_{IL}(H2) suggests that amphoteric water molecules can interact with the cation as well. It is considered, thus, that water-separated ion-pairs exist in the water-saturated IL solutions instead of contact ion-pairs in the neat IL. This conclusion is supported by the almost unchanged Λ/Λ_D. Further studies on a series of ILs consisting of various combinations of cation and anion species can lead to a reliable picture in complicated IL systems.

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8 The molar electric conductivity (Λ) was obtained by dividing the experimental electric conductivity by the molarity (c_{IL}) of [BMIM][PF_6]. The c_{IL} value was calculated from the mole fraction of water (x_{w}) and the density (ρ) of solution: $c_{\mathrm{IL}} = \rho/\{M_{\mathrm{IL}} + M_{\mathrm{w}}x_{\mathrm{w}}/(1 - x_{\mathrm{w}})\}$, where M_{IL} and M_{w} represent the molar mass of [BMIM][PF_6] and water, respectively. The density of water-saturated solution was estimated at each temperature with an oscillating density meter (Anton Paar, DMA 35n).

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