Direct Evidence of Ion-dipole Interaction between Imidazolium Cations and Polar Molecules in Ionic Liquid Solutions by Means of Mass Spectrometric Analysis of Clusters

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The mass spectrometric analyses of clusters in solutions composed of hydrophobic 1-alkyl-3-methylimidazolium hexafluorophosphates and various polar organic solvents demonstrate that the Coulomb-dipole interaction between the imidazolium cations and polar molecules is relatively strong.

Room temperature ionic liquids (ILs) have gained much attention as a promising class of "green" alternatives for volatile organic solvents in a variety of applications such as syntheses, catalyses, separations, and electrochemistry,[1] because ILs have unique and important properties. They are thermally stable liquid over a wide temperature range and their vapor pressures are negligibly small. In order to promote the application of ILs into the chemical processes, it is of great importance to know how the ILs interact with chemical species in solution. As for the properties of ILs, the solvatochromic effect and the Kamlet–Taft parameters of ILs have been compared with those of organic solvents.[2,3] Welton et al.[3] determined the Kamlet–Taft parameters of the hydrogen bond acidity (α), the hydrogen bond basicity (β), and the dipolarity/polarizability effects (π^*) in a wide range of ILs. It was found that α and β are generally moderate, whereas π^* is much higher than usual organic solvents, which suggests strong ion-probe Coulombic interactions. From these results, the properties of ILs in solution can be predicted qualitatively. Nevertheless, more direct experimental approach should be necessary to obtain the molecular-level information. For this purpose, here we perform mass spectrometric analyses of clusters in IL solutions. It has been reported that IL solutions showed several peaks arising from parent ions and their aggregates in mass spectra;[4] however, there has been no attempt so far to observe the clusters of solvated species. In this study, we present mass spectra of solvated species and discuss intermolecular interactions in binary IL solutions consisting of hydrophobic 1-alkyl-3-methylimidazolium hexafluorophosphates and organic solvents.

The molecular clusters in IL solutions were measured by a specially designed mass spectrometer, whose details have already been described elsewhere.[5,6] Figures 1a and 1b show typical mass spectra of positively charged species generated from 2 mg cm^{-3} ($\approx$6 mmol dm^{-3}) 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) in *N*,*N*-dimethylformamide (DMF) and methanol (MeOH). In both the polar solvents, the solvated species of $[C_4MIM]^+(\text{solvent})_n$ with n up to 2 or 3 were observed appreciably. The signal intensities of the $[C_4MIM]^+(\text{solvent})_n$ relative to that of the bare $[C_4MIM]^+$ cation are obviously dependent on a kind of solvent; DMF > MeOH in this case. We also observed another peak of $[C_4MIM]^+([C_4MIM]^+[PF_6]^-)$ at $m/z \approx 423$, originated from the ion-pair species. The measurements were carried out in the same manner for several polar solvents: dimethyl sulfoxide (DMSO), acetonitrile (AN), pyridine (PY), and tetrahydrofuran (THF). It was practically impossible, however, to observe clear signals of solvated species in apolar solvents. This is attributable to the fact that ILs form ion-pairs in low dielectric constant media.[7]

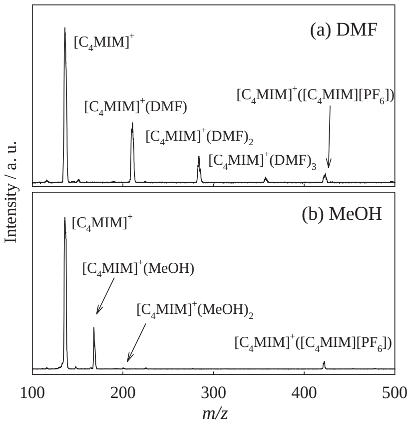

Figure 1. Mass spectra of positively charged species generated from (a) DMF and (b) MeOH solutions of $[C_4MIM][PF_6]$.

The signal intensities of solvated and ion-pair species are normalized by that of the bare $[C_4MIM]^+$ cation so as to compare with the clustering structures in different solutions. In Figure 2, the left and middle bars in each solution stand for the normalized intensities of solvated cations of $[C_4MIM]^+(\text{solvent})_n$ with $n = 1$ and 2, respectively. The normalized intensities of $[C_4MIM]^+(\text{solvent})$ in different solutions are well correlated with those of $[C_4MIM]^+(\text{solvent})_2$. On the other hand, the normalized intensities of the ion-pair species, as represented by the right bars, seem to increase with decreasing those of the solvated species. We focus on the solvent-dependent normalized intensity of the singly-solvated cation in the following discussion because it should reflect most sensitively the microscopic environment around the cation in solution. According to the recent results of solvatochromic probes,[2,3] the ion–solvent Coulombic interaction is the predominate factor in the solvation structure around the cation. If such a kind of interaction is of great importance, the normalized signal intensity should increase with the dipole moment (μ) of solvent molecule. Surely the normalized intensities in highly polar solvents such as DMF, DMSO, and AN are very large, whereas those in less polar solvents of PY, THF and MeOH are small. The plot of the normalized intensity vs the dipole moment in Figure 3a, more directly, indicates that this is the case in spite of slightly scattered data points, where the correlation coefficient is $\approx$0.84. One may consider another possibility that the solvent-dependent normalized intensity is related to the dielectric constant of solvent because

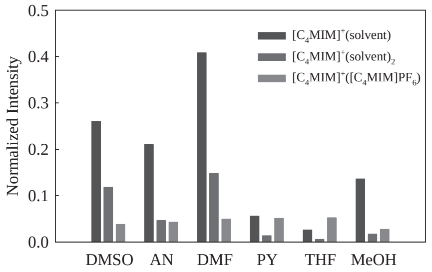

Figure 2. Normalized intensities of solvated and ion-pair species of $[C_4MIM]^+$ generated from different solutions. The concentration was fixed at $2\,mg\,cm^{-3}$.

it may primarily determine the ion-pair equilibrium in solution. However, the relationship between the normalized intensity and the inverse ($1/\varepsilon_r$) of the relative dielectric constant remains unclear even though it looks like that the normalized intensity decreases asymptotically with increasing $1/\varepsilon_r$ (Figure 3b). Therefore, we conclude that the microscopic environment around the cation is mainly controlled by the dipole moment of solvent molecule rather than the macroscopic property of dielectric constant.

Several researchers[2c,2d,8] pointed out the presence of strong hydrogen-bonding-type interactions involving the acidic C2 proton of the imidazolium cation. Certainly, in view of the relatively small dipole moment, MeOH gives the large signal intensity of the solvated cation (Figure 3a). The present results in different solutions can be explained most reasonably by the ion-dipole interaction; however, the increase in the intensity in MeOH with hydrogen bonding ability would possibly suggest such a kind of specific interaction.

To know the effect of the alkyl group in the cations, we measured mass spectra for a series of 1-alkyl-3-methylimidazolium hexafluorophosphates with different alkyl chains from C_2 to C_8 in methanol. Although it seemed that $[C_6MIM]^+$ gave relatively larger signals of solvated species, the mass spectra remained almost unchanged irrespective of the alkyl chain length. This suggests that the ionic nature of the imidazolium cations will not be significantly affected by the alkyl side chain. Moreover, we investigated the concentration dependence of mass spectra in $[C_4MIM][PF_6]$–methanol solutions. It was observed that all the signal intensities tended to become much weaker as the concentration of $[C_4MIM][PF_6]$ increased. In contrast, however, the normalized signal intensity of $[C_4MIM]^+$-$([C_4MIM]^+[PF_6]^-)$ arising from the ion-pair species remarkably increased at higher concentrations beyond $\approx 50\,mmol\,dm^{-3}$. At such concentrations, the signals of the solvated species were much smaller than that of the ion-pair species. This result shows that the ion-pair formation should promote at higher concentrations. In solutions containing IL as the main component, hence, we should pay much attention to intermolecular interactions with the ion-pair species as well as the individual ionic species.

It has become apparent, in this study, that the mass spectrometric analysis of clusters is a very powerful tool to provide significant and direct information on intermolecular interactions in rather complicated IL systems even though neat ILs are extremely non-volatile. It was found that the Coulomb-dipole interaction between the imidazolium cations and polar molecules is of primary importance in IL solutions. Further investigations in combination with other experimental techniques such as electric conductometry lead to more reliable picture of intermolecular interactions in IL solutions.

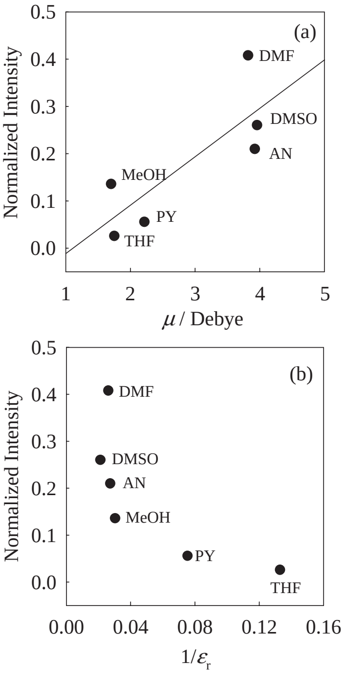

Figure 3. Plots of normalized intensity of singly-solvated cation, $[C_4MIM]^+$ (solvent), vs μ (a) and $1/\varepsilon_r$ (b). The straight line in (a) represents a linear least-square fit of the experimental data.

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References and Notes

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