Absorption Spectra of Imidazolium Ionic Liquids

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The absorption spectra of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-methyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][TFSI]) were measured. The similarity of the spectra in the liquid phase with the corresponding solution spectra shows that weak electronic intermolecular interaction occurs in these ionic liquids.

Room-temperature ionic liquids are receiving considerable attention because of their remarkable properties, such as extremely low vapor pressure. Thus, ionic liquids are now used in various fields as solvents in chemical processes, such as organic synthesis, separation processes, and electrochemical processes.[1–3] Accordingly, the fundamental properties of ionic liquids, such as viscosity, solubility, and dielectric constant, have been extensively studied. To understand the characteristic properties of ionic liquids, intermolecular interaction between molecules in neat ionic liquids is important.

Absorption spectra are fundamental properties of liquids and have characteristic features that allow the determination of the type of electronic interactions that occur among molecules in the liquid. The measurement of the absorption spectra of liquid samples is not commonly attempted because of experimental difficulties. For conventional liquid samples, concentration is of the order of 10 mol dm^{-3}, and so an extremely thin optical cell (<100 nm) is required for the measurements of strong absorption peaks. Despite this difficulty, absorption spectra of liquid samples have been reported by several groups. For liquid benzene, absorption spectra are different for vapor than for solution.[4,5] For other organic liquids, such as tetramethylsilane and alkanes, absorption spectra in the liquid phase are also different from those in the vapor phase.[6] This clearly shows that the electronic structure in the liquid phase affected by intermolecular interactions can be probed by observing absorption spectra.

As we reported previously, for the alkylammonium ionic liquid, *N*,*N*,*N*-trimethylpropylammonium bis(trifluoromethanesulfonyl)imide ([TMPA][TFSI]), no absorption band is observed in the 200–400-nm wavelength range.[7] On the other hand, for imidazolium ionic liquids, it is expected that strong absorption will be observed in this wavelength range because of the presence of aromatic carbons. So far, no reliable absorption spectra in the liquid phase have been reported because of the requirement of a very thin cell. In addition to this requirement, low purity of the ionic liquids makes absorption measurements difficult. It has been pointed out that absorption spectra of imidazolium ionic liquids in the 250–300-nm range are sensitive to the purification procedure.[8,9] Paul et al. observed relatively strong absorption in this wavelength range and attributed the absorbance to intrinsic absorption due to the ionic liquids.[10]

Two imidazolium ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][TFSI]), were used in this study. The samples were purchased from Kanto Chemical Co., Inc. and were used without further purification.[11] The absorption cell for the liquid-sample measurements consisted simply of a 5-cm square with 5-mm thick optically flat ($\lambda/8$) quartz windows clamped together without any spacers. For the solution measurements, a conventional 1-cm thick quartz cell was used. Absorption spectra were measured with an absorption spectrophotometer (Shimadzu, UV-3101PC).

Figure 1 shows absorption spectra of the ionic liquids in an 1-cm quartz cell. No strong absorption signals were seen in the range of 250–300 nm, which is significantly different from the result for [bmim][PF_6] reported previously plotted together in Figure 1.[8,10] This clearly shows that the absorption tail in this wavelength range reported previously is caused by some impurities. We tentatively assign the origin of this absorption tail to degraded imidazolium cations based on its similarity to the absorption spectra after γ-ray irradiation.[12] Assuming that the absorption coefficient of the impurity is 10^4 mol^{-1} dm^3 cm^{-1} at 270 nm, the concentration of the impurity is estimated to be 10^{-4} M, which would be difficult to remove during the synthesis process. The absorption spectra of our samples show that the purity is sufficient for reliable optical measurements.

For 3×10^{-4} mol dm^{-3} [bmim][TFSI] in acetonitrile (Figure 2), the absorption peak appeared at 211 nm and we determined the absorption coefficient ε to be 5×10^3 mol^{-1} dm^3 cm^{-1}. Because the absorption due to the TFSI anion is negligibly small in this wavelength range, the absorption peak can be assigned to a π–π^* transition that originates from the C=C bond of the imidazolium cation, based on the similarity with imidazole.[13] Similar absorption spectra were obtained in water and in methanol. For [bmim][PF_6] in acetonitrile, the absorption spectrum is also similar to that for [bmim][TFSI] solutions. These results clearly show that the absorption peak

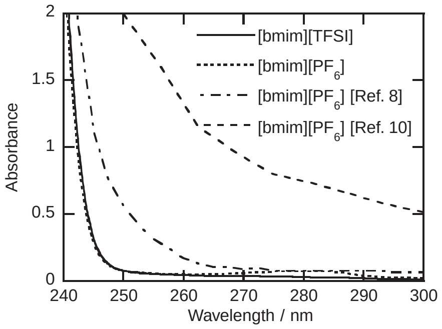

Figure 1. Absorption spectra of the ionic liquids in an 1-cm quartz cell. The results reported previously are also shown.

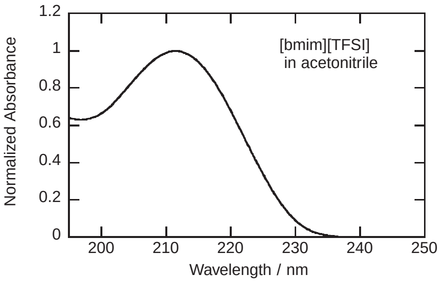

Figure 2. Absorption spectrum of [bmim][TFSI] in acetonitrile recorded in a 1-cm cell.

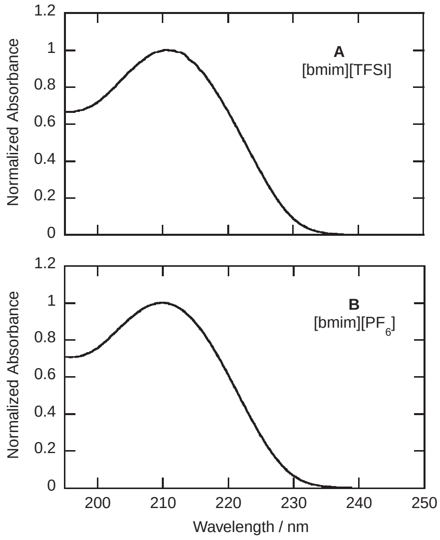

Figure 3. Absorption spectra of [bmim][TFSI] (A) and [bmim][PF6] (B) in the liquid phase in a thin optical cell.

is due to an isolated imidazolium cation free from any strong intermolecular interactions.

Figures 3a and 3b show absorption spectrum of ionic liquids, [bmim][TFSI] and [bmim][PF_6], respectively, recorded in the thin optical cell. The absorption peaks for [bmim][TFSI] and [bmim][PF_6] were at 210.5 and 210 nm, respectively. The actual absorbance observed was about 2 and therefore the thickness of the cell was estimated to be about 1 μm using the value of molar concentration $M = 3.42\,\mathrm{mol\,dm^{-3}}$ for [bmim]-[TFSI] and assuming that the absorption coefficient is the same as that in solution.

The shapes of the [bmim][TFSI] and [bmim][PF_6] spectra are similar to that of the imidazolium cation in solution, indicating that the electronic structure is not strongly affected by intermolecular interactions. This means that electronic structure of the liquid can be considered as the simple sum of those of isolated cation and anion, whereas the strong Madelung potential shifts the energy level of the cation and anion. There are two possible intermolecular interactions affecting the electronic structure in the system: One is the electronic coupling between imidazolium cations and the other is the charge-transfer (CT) interaction between the cation and anion. Small electronic coupling between imidazolium cations may be explained that imidazolium cations are well separated by an anion between them. Small CT interaction between a cation and an anion would be due to high ionization potential of fluorinated compounds, for example the ionization potential of PF_6^- has been evaluated using computational techniques to be 8.7 eV.[14] Accordingly, in an ionic liquid the imidazolium cation is electronically isolated from the surroundings.

Ultraviolet photoelectron spectroscopy (UPS) is a powerful tool for exploring the electronic structure of molecules and frequently electronic intermolecular interactions can be discussed by comparison of the spectrum of an isolated molecule with the spectrum of a molecule in the condensed phase. The UPS technique has already been applied to the study of electronic structure of imidazolium ionic liquids.[15,16] Accordingly, the UPS spectra of imidazolium ionic liquids can be roughly reproduced by the sum of the calculated spectra for the cations and anions. A recent UPS study of isolated ion pairs of ionic liquids in the gas phase shows that their UPS spectrum is similar to that in the liquid phase.[17] These UPS studies imply that a weak electronic interaction in ionic liquids, which is consistent with the present results: absorption spectra of ionic liquids are similar to those in solutions.

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