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High-Pressure Study of Solvation Properties of Room-Temperature Ionic Liquids

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Abstract. The solvation properties of some room-temperature ionic liquids consisting of imidazolium cations and various anions were examined by means of the high-pressure spectroscopy with solvatochromic probes. We measured the pressure dependence of Kamlet-Taft solvatochromic parameters ($\pi^*$, $\beta$) and microviscosity ($\eta$). It was found that $\pi^*$ and $\beta$ were not so sensitive to the types of imidazolium cations and polyatomic anions, but the type of monoatomic anions. The pressure dependence of microviscosity was found to obey the empirical power-law equation.

1. Introduction
Room-temperature ionic liquids (ILs) are salts that are liquid at room temperature. In recent years, there have been a large number of papers associated with ILs. Because of their specific properties such as nonvolatility, noncombustibility and high ion conductivity as well as their possibility for synthetic variation with combinations of anions and cations, ILs are expected to not only be alternatives to volatile organic solvents or as safety electrolytes of batteries [1, 2], but outspread their application fields to a wide variety of science [3], for example, recent studies have let them enter in the spotlight as space materials [4]. To support these applications, it is important to know various physical and chemical properties of ILs. For this reason, a number of studies on physical and chemical properties of ILs such as polarity and viscosity have been ongoing [2, 5-11]. Furthermore, in order to put ILs reliably to practical use, it is necessary to know how these properties are affected by pressure or temperature, especially on a molecular scale.

Despite much attention, little is still known about the solvation properties of ILs particularly at high pressure. The control of average intermolecular distance between solvent (anion, cation) and solute (probe molecule) by pressure gives us the opportunities to have the further insight into solvation structures of ILs. Among several approaches based on the linear solvation energy relationships (LSER) that have been proposed to describe the solute-solvent interactions on the molecular scale, one of the most successful methods is the one that Kamlet and Taft have proposed [12-16], which has been widely used for various solvents including ILs [17-20]. The Kamlet-Taft parameters $\pi^*$, $\alpha$ and $\beta$ are related to the polarity/polarizability, hydrogen bond donation ability and hydrogen bond acceptance or electron pair donation ability to form a coordinative bond of the solvent, respectively. In accordance with the Kamlet-Taft expression, these parameters can be given from the wavenumber $\nu_{max}$ of the longest wavelength absorption.
peak of the probe in a solvent as follows [18].

\[ \nu_{\text{max}} = \nu_0 + s\pi^* + a\alpha + b\beta \]  

(1)

where \( \nu_0, s, a, \) and \( b \) are solvent-independent coefficients indicative of its sensitivity to each solvent property.

In this study, we examine the pressure dependence of the parameters \( \pi^* \) and \( \beta \) by means of UV/VIS absorption spectroscopy, in order to find how the solvation properties and structures of ILs are affected by pressure. Moreover, a microviscosity \( \eta \) of ILs is also examined with a fluorescence probe DCVJ which is well-established as an indicator of solvent microviscosity [20-22], in order to discuss the solvation structures of ILs from a different perspective.

2. Material and Methods

The eight ILs used in this study are based on the 1-butyl-3-methylimidazolium cation ([bmim][+]), 1-ethyl-3-methylimidazolium cation ([emim][+]), and 1-hexyl-3-methylimidazolium cation ([hmim][+]) with the anions BF\(_4\), PF\(_6\), Cl\(^-\), Br\(^-\), and I\(^-\), and all of them were received from Tokyo Chemical Industry Co. and used without further purification. The solvatochromic indicators \( N,N\)-diethyl-4-nitroaniline (Oakwood Products), 4-nitroaniline (Aldrich), and the fluorescence probe 9-(dicyanovinyl)-julolidine, DCVJ, (Molecular Probes) were used as received. The concentrations of all solutions for UV/VIS absorption experiments were \( 1 \times 10^{-4} \) mol/L, and for fluorescence experiments were \( 5 \times 10^{-5} \) mol/L, respectively. A sample-filled internal cell made of quartz (the optical path length was 5 mm) which had a section of stretch plastic tube was inserted in a stainless steel (JIS SKD-62) high-pressure cell with four sapphire windows sealed with o-rings and gasket rings, which was connected to a high-pressure pump (Hikari High-pressure Machinery KP-5-B). The internal cell was compressed through the pressure medium of the silicone oil (Shin-Etsu KF-96L-1.5cs). The cell body had a tubelike flow channel, in which the constant-temperature water was circulated to maintain the temperature. For absorption measurements, the high pressure cell unit was inserted directly into the UV/VIS spectrometer chamber (Jasco UV/VIS V-560 Spectrophotometer). For fluorescence measurements, the high pressure cell unit was set up in a dark chamber, and the 435 nm excitation light from a Hg-Xe lamp (Moritex Co. MUV-202U) selected by a monochromator (ISA HR-320) was irradiated to the sample through the optical window of the cell. The fluorescence from the sample was collected by quartz lenses (\( f = 100 \) mm, 40 mm) and analyzed by a Ocean Optics USB2000-FLG Spectrofluorometer.

The measurements of absorption and fluorescence spectra were carried out at pressures ranging between 0.1 – 300 MPa at 45 °C. The values of \( \pi^* \) and \( \beta \) were calculated by the equations below [17].

\[ \pi^* = 0.314 \times (27.52 - \nu_{NN}) \]  

(2)

\[ \beta = 0.358 \times (31.10 - \nu_{NA}) - 1.125 \times \pi^* \]  

(3)

where \( \nu_{NN} \) is the wavenumber of the absorption peak of \( N,N\)-diethyl-4-nitroaniline, a nonprotonic indicator (\( a = 0, b = 0 \)), and \( \nu_{NA} \) is that of 4-nitroaniline (\( a = 0 \)) in unit of \( 10^{-3} \) cm\(^{-1}\). The microviscosity \( \eta \) was calculated by [21],

\[ \log \Phi = C + x \log \eta \]  

(4)

where \( \Phi \) is the fluorescence quantum yield, \( C \) and \( x \) are constants (for DCVJ, \( x \) has been reported to be 0.6 [23]). The viscosities at ambient pressure and 45 °C were measured with an Ostwald viscosimeter (Sansyo Co.). Pressure dependence of Kamlet-Taft parameters \( (\pi^*, \beta) \) and microviscosity \( (\eta) \) were thus estimated for eight ILs.
3. Results and Discussion

3.1. $\pi^*$, polarity/polarizability parameter

The pressure dependence of absorption maximum of \(N,N\)-diethyl-4-nitroaniline in [bmim]PF\(_6\) is shown in figure 1 (a). As pressure increases, the absorption peak of \(N,N\)-diethyl-4-nitroaniline shows a redshift and an increase of absorbance. The increase of absorbance is caused by an increase of the concentration as a result of compression of sample solutions. The redshift of the absorption peak plays a key element of discussion to find out how solvents will interact with solutes [12, 17]. The pressure dependence of $\pi^*$ value estimated from this shift for each IL is shown in figure 1 (b). Most of ILs show the values near 1.0 at ambient pressure, which is comparable to that of DMSO among conventional solvents. The ILs having the monoatomic anions (halogen anions), ILs(mono), exhibit larger $\pi^*$ value than ILs(poly) having the polyatomic anions (PF\(_6^-,\) BF\(_4^-,\)) which increase in the order of I\(^-\) > Br\(^-\) > Cl\(^-\). This seems to correspond to the order of the ion radius, indicating that the polarizability of anion would affect the $\pi^*$ value, because the polarizability of ion generally increases as it becomes bigger or heavier. On the other hand, the $\pi^*$ is not so sensitive to the alkyl-chain length of the imidazolium cation or the type of polyatomic anions. With increasing the pressure, the $\pi^*$ value increases for all ILs examined here. This behavior is reasonable because it is known that the polarity/polarizability $\pi^*$ value of the solvent should be proportional to the solvent density at moderate temperatures [18].
3.2. \( \beta \), hydrogen bond acceptance ability parameter
The pressure dependence of absorption spectra of 4-nitroaniline in [bmim]PF\(_6\) is shown in figure 2 (a). The peak shows a redshift and an increase of absorbance as observed for \(N,N\)-diethyl-4-nitroaniline. Figure 2 (b) shows the pressure dependence of \( \beta \) value for each ILs, in which a remarkable difference of \( \beta \) values between ILs(mono) and ILs(poly) is found; the former is about 0.4-0.5 bigger than the latter. This means that relatively strong hydrogen bond is formed between the probe and the monoatomic anions. Additionally, the \( \beta \) value of ILs(mono) increases in the order of \( \text{Cl}^- > \text{Br}^- > \text{I}^- \) at ambient pressure, which agrees with the order of their electronegativities. It is known that hydrogen bond is enhanced as the acceptant is more electrically-negative, so the observed order confirms the discussion that the monoatomic anions of ILs(mono) form stronger hydrogen bond with the solute than polyatomic anions of ILs(poly).

The \( \beta \) value is not so sensitive to other factors, that is similar to the behavior of the \( \alpha^* \) value. With increasing the pressure, \( \beta \) values of all ILs except [bmim]I decrease. In other words, the hydrogen bond between the probe (hydrogen bond donor) and the anions of ILs is weakened with pressure. This is probably due to the enhancement of the hydrogen bonds between anions and cations in the IL itself, which leads to the destruction of probe–anion hydrogen bonds in reverse. Consequently, the present observation indicates that the hydrogen bond between anion–cation takes priority over that between probe–anion with increase in pressure. On the other hand, it is found that [bmim]I shows an opposite behavior. Although the unique behavior of the \( \beta \) for [bmim]I is attractive, further investigations will be required to understand it properly.

3.3. \( \eta \), microviscosity
‘Microviscosity’ is a local solvent property in the vicinity of the solute. Although it can be distinguished from the bulk viscosity by considering some heterogeneity on a molecular scale, it is equivalent to the bulk viscosity when they are negligible. The fluorescent probe DCVJ is a reliable tool to investigate a microviscosity of solvent under special conditions such as high pressure, which has been confirmed by the comparative experiments with conventional viscous solvents, for instance, the comparison between the pressure dependence of the microviscosity we measured and the literature-based bulk viscosity for glycerol as shown in figure 3. The pressure dependence of the microviscosity for each IL is shown in figure 4. As can be seen from this figure, all of ILs except [bmim]I obey the empirical equation \( \eta = A \exp(Bp) \), where \( A \) and \( B \) are constant and \( p \) is pressure, which is generally accepted as the expression of pressure dependence.

![Figure 3](image3.png)
**Figure 3.** Comparison of the viscosity of glycerol measured by DCVJ with literature-based data.

![Figure 4](image4.png)
**Figure 4.** Pressure-\( \eta \) plot of eight ILs. Solid lines represent the results of least-square fitting with \( \eta = A \exp(Bp) \).
of viscosity for conventional solvents. Only [bmim]I shows the different behavior, the decrease of microviscosity with pressure. We tentatively attribute this result to the contribution of the solvent light absorption. The [bmim]I shows a yellow color and has the absorption maximum at about 365 nm, tailing beyond the fluorescent maximum of DCVJ in the range of 490–530 nm. This may cause the absorption of the excitation light by [bmim]I and furthermore, the reabsorption of fluorescence, resulting in a misestimation of fluorescence quantum yield and hence the microviscosity. Such consideration is supported by the fact that the fluorescence intensity for [bmim]I is by a factor of about one-tenth weaker than for others.

4. Summary
The pressure dependence of polarity/polarizability parameter ($\pi^*$), hydrogen bond acceptance ability parameter ($\beta$) and microviscosity ($\eta$) of some imidazolium-based ILs have been measured by means of the spectroscopic measurements of solvatochromic probes. Although both $\pi^*$ and $\beta$ are not so sensitive to the alkyl-chain length of the imidazolium cation or the type of polyatomic anions, they seems to be rather sensitive to the type of monoatomic anions. For all ILs examined here except [bmim]I, the pressure dependence of the solvation properties shows the similar behavior as for conventional solvents. It appears that the pressure dependence of microviscosity for all ILs except [bmim]I obeys the empirical power-law equation. Because of the interesting behavior of the pressure dependence, more multifaceted studies are needed for [bmim]I.

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