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# Linear relationship between the $^1$H-chemical shift of water in a highly concentrated aqueous solution of an ionic liquid and the Jones–Dole *B* coefficient

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## ABSTRACT

In this study, we investigated the chemical shift of water in several ionic liquid-water mixtures using NMR spectroscopy. The chemical shift gradually moved to higher magnetic fields with increasing ionic liquid concentration. Remarkably, the present results indicate that the extrapolated value of the chemical shift at 0 mol% water concentration was linearly related to the Jones–Dole *B* coefficient of the cations and anions, as determined by viscosity measurements. Therefore, the trend for the ion–water interaction strength that is exhibited in water-rich regions holds even in the water pockets confined within the nano-domain structure of ionic liquid, where a very small number of water molecules occupy the limited space.

## 1. Introduction

Ionic liquids (ILs) are known as room temperature molten salts, because they can exist in a liquid state at room temperature. Usually, this is accomplished by introducing a bulky cation in the constituent ions [1]. One of the major benefits of using ILs as an alternative to conventional organic solvents lies in the fact that the desirable physical and chemical properties of ILs can be tuned by selecting appropriate combinations of cations and anions [2]. Thus, ILs are sometimes called designer solvents. This is an important advantage, as it allows an IL to be designed for a specific reaction, such as to solubilize an enzyme. Interest in using ILs as a new type of solvent for biomolecules has been rapidly increasing. In fact, ILs can offer excellent enzyme activity, stability, and selectivity [3,4].

In general, liquids can be treated as homogeneous systems. However, a consensus that ILs typically show unique spatial heterogeneity due to their inherent polar/nonpolar nanophase separation (nanostructural organization) [5–7] has been established. Nanostructures are also formed when ILs are mixed with water, but no macroscopic phase separation occurs [8,9]. The presence of a co-solvent such as water reduces the electrostatic attraction between the ions and decreases the overall cohesive energy, resulting, for example, in decreased viscosity. Specifically, water affects both the translational and rotational dynamics of the IL, thereby enhancing its relaxation rate [10–12]. Water is believed to be situated in the polar domains and closely associated with anions. At low water content, the ions are selectively coordinated by individual water molecules. At higher water concentrations, the nano-domain structure holds somewhat, although the ionic network is nonspecifically disrupted or swollen to some extent by the water clusters [11]. In addition to the intensive studies of the nano-domain structure of ILs, interest in the nature and properties of water in the local structure of ILs has also been increased. Recently, Abe et al. [13] succeeded in providing direct evidence of “confined water,” or water pockets, by small-angle X-ray scattering (SAXS) and neutron scattering (SANS) analyses. Subsequently, we found that the NMR peaks for water ($H_2O/D_2O$ mixture) in ILs are clearly split, indicating the presence of two discrete states of confined water: $H_2O$ and HOD [14]. The proton and/or deuterium exchange rates among the water molecules were slowed significantly in water pockets confined within the nano-domain structure of several ILs. Therefore, these findings demonstrate a completely new type of confinement of liquid water in soft matter.

On the other hand, the interactions between water and ions in aqueous “ordinary salt” solutions have already been clarified by many methods. For example, *B* coefficients can be calculated from the Jones–Dole empirical equation (Eq. (1)) for the relative viscosity of an electrolyte solution as a function of salt concentration $c$ [15,16].

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc + Dc^2 \qquad (1)$$

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where $\eta$ is the viscosity of the solution, $\eta_0$ is the viscosity of the solvent (water in this case), and $c$ is the molar concentration. The $A$ coefficient, known as the Falkenhagen coefficient, represents solute–solute or electrostatic interactions, and can be calculated theoretically [17–19]. The $A$ values, however, are usually small, and are therefore often omitted in calculations of the $B$ coefficient [18]. The $B$ coefficient represents solute–solvent interactions, whereas the $D$ coefficients primarily reflect solute–solute and solute–solvent interactions. For most salts at low concentrations ($c < 0.5$), the $D$ coefficients can be neglected, but they are necessary at higher concentrations [16].

Strongly hydrated ions have strong interactions with water molecules and increase the structuring of water, resulting in lower fluidity (higher viscosity) of the solution than that of pure water. Therefore, these ions are named structure makers or kosmotropes. On the other hand, some ions are weakly hydrated in aqueous solutions. These have weak interactions with water and reduce the structuring of water, causing a higher fluidity of the solution. For this reason, this effect is known as negative hydration, and these ions are often referred to a structure breakers or chaotropes [19,20]. Interestingly, it is possible to estimate NMR $B'$ coefficients from the spin–lattice relaxation time of $^1$H of water [19,21]. The NMR $B'$ coefficient reflects the microscopic properties of the hydrated ions, whereas the Jones–Dole $B$ coefficient considers the bulk macroscopic properties resulting from the viscosity. Intriguingly, there is a direct relationship between the results for the two types of $B$ coefficients [19]. Here, the important point is that the $B$ coefficients generally represent the strength of the ion–water interactions in a dilute aqueous solution. However, because of the unique features of ILs, which can maintain the liquid state even at room temperature, it may be possible to obtain information on the opposite situation, *i.e.*, a small amount of water in a concentrated IL solution.

In this study, to obtain more information on the physical properties of water confined in ILs (in water pockets), *i.e.*, the connection between the microscopic and macroscopic physicochemical properties for aqueous ILs, we investigated the chemical shift of water in IL-water mixtures using NMR spectroscopy. We believe that the results will be useful for the actual application of ILs in various fields.

## 2. Experimental

Six typical ILs: 1-butyl-3-methylimidazolium tetrafluoroborate (usually abbreviated as [BMIM][$BF_4$]), [BMIM][Cl], [BMIM][Br], [BMIM][I], 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][$BF_4$]), and *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate ([DEME][$BF_4$]) were purchased from Kanto Chemical Co., Inc. and used as-received without further purification. The molecular structures of the respective cations are shown in Fig. 1. An $H_2O/D_2O$ mixture prepared with a 1:1 volume ratio was used as water, in a similar manner to that previously reported [14]. The $H_2O$ was supplied by a Synergy UV system (Millipore Inc.), and $D_2O$ (99% D) was obtained from Kanto Chemical Co., Inc. We altered the mixing ratio $x$ of IL to water over a wide range, from 5 to 90 mol% IL. The solubilities of [BMIM][Cl] and [BMIM][Br] in water were limited to $x < {\sim}50$.

All $^1$H NMR spectra were obtained using an ECA-500 (JEOL) with a 500.1 MHz proton resonance frequency. In the NMR measurements, an $H_2O/D_2O$ mixture was used as water to minimize the proton dumping effect in the water-rich region. This phenomenon is commonly observed with a high magnetic field NMR apparatus. Furthermore, a double NMR sample tube was used to separate the lock solvent and the sample solution, and also to avoid the proton dumping effect. The inner tube (3 or 4 mm O.D., depending on $x$) with the lock solvent, $CDCl_3$ with 1 vol% tetramethylsilane (TMS), was inserted into the outer tube (5 mm O.D.) along with the sample. The TMS peak was used as a reference chemical shift of 0 ppm. $^1$H NMR was measured under the following conditions: 15 ppm spectrum width, 65,536 data points, 0.114 Hz (=0.00023 ppm) digital resolution, 4 scans, and 23 ± 0.1 °C.

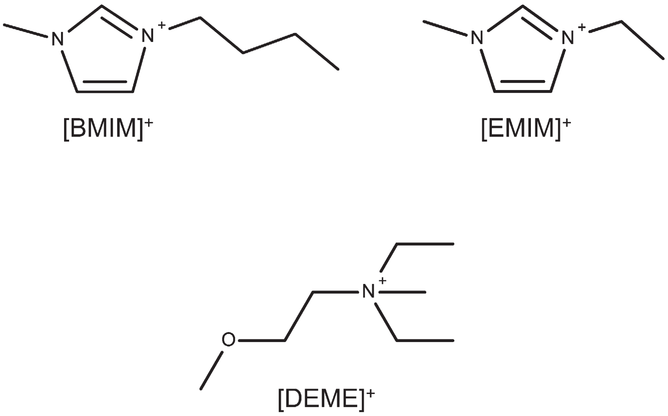

**Fig. 1.** Molecular structures of the cations used in this study: 1-butyl-3-methylimidazolium ([BMIM]$^+$), 1-ethyl-3-methylimidazolium ([EMIM]$^+$), and *N*-*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium ([DEME]$^+$).

## 3. Results and discussion

An NMR chemical shift provides important information concerning individual atoms, and reflects inter- and intra-molecular interactions such as the electrostatic interactions of hydrogen bonding and van der Waals forces. Typical $^1$H NMR spectra obtained for the IL-water mixtures are shown in Fig. 2. Note that the water peak was split into two, which is in accordance with the previous results [14]. Here, the shielded and de-shielded water peaks correspond to HOD and $H_2O$, respectively [14]. We revealed that this phenomenon was due to a very slow proton exchange rate between the two types of water molecules, *i.e.* $H_2O$ and HOD. Fig. 3 shows the chemical shift $\delta$ of $^1$H for water in various ILs containing common cations or anions as a function of IL concentration ($x$). Overall, the chemical shift moved to higher magnetic fields (shielded) with increasing $x$, finally converging to a certain value (hereinafter called the "converging chemical shift"). This is associated with reduced hydrogen bonding in the three-dimensional hydrogen bonded network structure of water [22].

Interestingly, no significant changes were observed in the chemical shifts obtained from the $BF_4^-$-based ILs with changes in the cation ([DEME]$^+$, [BMIM]$^+$, and [EMIM]$^+$), but the chemical shifts varied greatly depending on the type of anion, as shown in Fig. 3. The converging chemical shift decreased in the order of [BMIM][$BF_4$] > [BMIM][I] > [BMIM][Br] > [BMIM][Cl], implying a dependence on the ionic radius of the anions. The chemical shift of the water was strongly influenced by the anions, in accordance with the previous study [14], likely due to the strong interaction between the water molecules and the anions. Furthermore, simulation studies suggested that the anion–water interaction is much stronger than the cation–water interaction in the IL-water mixtures [23,24].

Then, we estimated the values of $\delta_{100\ \mathrm{mol\%\ IL}}$ in various ILs by extrapolating $\delta$ to $x = 100$. The relationships with the Jones–Dole $B$ coefficients of the anion determined by the viscosity (○) [19] and NMR relaxation measurements (◇) [25] are shown in Fig. 4. The NMR $B'$ coefficient of $I^-$ was determined by linear approximation, assuming a linear correlation between the Jones–Dole $B$ and NMR $B'$ coefficients for $BF_4^-$, $Cl^-$, and $Br^-$. This linear correlation was previously reported by Marcus and coworkers [19]. Remarkably, the values of $\delta_{100\ \mathrm{mol\%\ IL}}$ at 0 mol% water concentration were well correlated with both the Jones–Dole $B$ and NMR $B'$ coefficients, although the slopes were slightly different. The important point is that the trend for the ion–water interaction strength in water-rich regions holds even in water-poor regions (in other words, in the water pockets of the nano-domain IL structure). These results concerning the properties of small amounts of water in a restricted space in a concentrated IL solution provide important new information that may be useful for finding novel applications of ILs-water mixed solutions.