

Physicochemical Properties of a Pocket Existing in an Ionic Liquid.

イオン液体中に存在する孔の性質に関する研究

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SYNOPSIS

本研究ではイオン液体中に存在することが示唆されている pocket および水と混合したときのその中の水の性質を巨視的視点および微視的視点の両方で明らかにすることを目的とする。巨視的な視点として屈折率からイオン液体水系の性質を調べるために理想混合則から計算した屈折率と実測の屈折率の差を規格化した。その結果、イオン液体の種類に依存せず、巨視的視点からはイオン液体の個性がほとんど現れないことがわかった。pocket に関する報告が多くなされている 1-butyl-3-methylimidazolium tetrafluoroborate, ([C₄MIM][BF₄])と水および炭素数を系統的に変えたアルコールを混合し、pocket の大きさおよび pocket 中の水の運動性を調べた。その結果、pocket の大きさは少なくとも 100Å³程度はある可能性が高いことが示唆された。また、水や小さなアルコールはイオン液体にあまり動きを制限されず pocket 間を移動しているのに対して大きなアルコールはイオン液体と共に運動していることが示唆された。次にイオン液体のアルキル鎖の炭素数を系統的に変化させイオン液体の疎水性を増やした場合の pocket およびその中の水の運動性に関する知見を得た。その結果、イオン液体のアルキル鎖が長くなるほど中の水の運動性は低下することが明らかとなった。しかし、どのアルキル鎖長においても水はイオン液体にあまり動きを制限されず、pocket 間を移動していることが明らかとなった。一方、水の運動性とイオン液体の運動性の比はアルキル鎖が長いほど増加する結果が得られた。これは、アルキル鎖長を長くすると pocket の表面の疎水性が強くなり、水との相互作用が低下するためだと考えられた。以上のようにイオン液体中に存在する pocket および水と混合したときのその中の水の物性を明らかにした。

Keyword: Alcohol, Chemical shift, Ionic liquids, NMR spectroscopy, Self-diffusion coefficient, Water

1. Introduction

Ionic liquids (ILs) have very unique properties, such as incombustibility, low volatility, high thermal stability and ionic conductivity. ILs which are salts, but they are different from typical salts since they have large organic cations and/or anions and exist as liquid state around room temperature. ILs are called designer solvents because anions or cations can be exchanged easily, and the physicochemical properties can be adjusted according to the intended use. Some ILs have unique nano-heterogeneous structures composed of nanoscale polar and nonpolar domains, and the nonpolar domain becomes thicker as the alkyl chain length increases. In this structure, the existence of a pocket (holes) have also been suggested. The existence of the pocket has been supported by carbon dioxide absorption experiments. Huang *et al.*^[1] reported that 1-butyl-3-methylimidazolium hexafluorophosphate has a smaller volume expansion than that of an organic solvent when dissolving CO₂. Such volume behavior is interpreted to indicate that the IL has a large pocket compared to the molecular solvent, and that CO₂ occupies the pocket. In the case that water is mixed with ILs, water is also confined in the pocket in ILs, and the pocket is called "water pocket"

As described above, since ILs have properties different from those of typical solutions, ILs have been attracted the interest of researchers in a wide range of fields. Especially, the physicochemical property of "pocket" or "water pocket" is a hot topic in solution chemistry. Some of these studies provided experimental

and theoretical evidence for the existence of water pockets in the ILs. In one recent report, Sieffert *et al.*^[2] suggested the presence of a water pocket where water molecules diffuse and rotate in the nano-heterogeneous structure of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide/water mixture based on molecular dynamics simulation. Studying the same IL, Rollet *et al.*^[3] obtained data for the self-diffusion coefficient at 0.3–30 water mol% by using pulsed field gradient spin-echo NMR, and suggested that the water pocket are connected at the local scale. Subsequently, using small-angle neutron scattering (SANS) measurements, Gao *et al.*^[4] investigated the microstructure of mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄MIM][BF₄]) and water at 70–84 water mol% and the water cluster size has a radius of 5.5 Å at 74 water mol% as determined by SANS. Remarkably, Kashin *et al.*^[5] succeeded in obtaining the morphology and formation dynamics of water-containing compartments in [C₄MIM][BF₄] at ~20 water wt% directly by field-emission scanning electron microscopy, and the radius of a water-containing particle was determined to be 330 Å at 10 water vol% by dynamic light scattering measurements. A variety of morphologies were detected and depended on the water concentration. In addition, Abe *et al.*^[6] reported that the radius of the water pocket was about 8 Å at 69.9 water mol% in 1-butyl-3-methylimidazolium nitrate, as determined by SANS. As described above, the size of the water pocket depends on viewpoints. Furthermore, the

physicochemical properties of the water confined in the water pocket and the size of the pocket are not elucidated well. The physicochemical properties of the water confined in ionic liquid having various alkyl chain length is also not clarified.

The research objectives of the doctoral thesis are following:

- (1) Revealing the macroscopic properties of ILs/water mixtures based on the refractive index.
- (2) Estimating the size of a pocket formed in a typical IL and elucidating the physicochemical properties water confined in a pocket formed in an IL based on chemical shift, self-diffusion coefficient density and viscosity.
- (3) Elucidating how the physicochemical properties of a pocket and water confined in the pocket change depending on the alkyl chain length of the ILs based on chemical shift, self-diffusion coefficient, density and viscosity.

2. Material and method

The following ILs and alcohols were purchased from the Kanto Chemical Co., Inc. or Sigma Aldrich Co. or Fujifilm Wako : 1-ethyl-3-methylimidazolium diethylphosphate ([C₂MIM][DEP]), 1-butyl-3-methylimidazolium acetate, ([C₄MIM][OAc]), 1-butyl-3-methylimidazolium iodide, ([C₄MIM][I]), 1-methyl-3-octylimidazolium bromide, ([C₈MIM][Br]), N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate ([DEME][BF₄]), ethylammonium nitrate (EAN), and propylammonium nitrate (PAN), 1-ethyl-3-methylimidazolium tetrafluoroborate ([C₂MIM][BF₄]), 1-butyl-3-methylimidazolium tetrafluoroborate, ([C₄MIM][BF₄]), 1-hexyl-3-methylimidazolium tetrafluoroborate, ([C₆MIM][BF₄]), 1-methyl-3-octylimidazolium tetrafluoroborate, ([C₈MIM][BF₄]), and 1-decyl-3-methylimidazolium tetrafluoroborate, ([C₁₀MIM][BF₄]), methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. The ultrapure water used in experimental work was supplied by a Synergy UV system (Millipore Inc.)

The refractive index was determined using a refractometer (Reichert ABBE MARK III, Reichert). The ¹H and ¹⁹F Chemical shift and self-diffusion coefficient measurement were carried out using an AVANCE III HD instrument (Bruker, 600 MHz).

3. Result and Discussion

3.1 Macroscopic properties of ionic liquid/water systems^[7]

The refractive index of ILs, which are combinations of various cations and anions, and water mixture were investigated. The nine ILs used in this study can be mixed with water in the whole concentration region. The refractive index of pure IL varied depending on a combination of anion and cation. On the other hand, the refractive index (*n_D*) loosely decrease with increasing water concentration until around 75 water mol%. Above 75 mol% refractive index rapidly decreased with

increase water concentration in all cases. The concentration dependence was clearly different from the linear concentration dependence predicted according to ideal mixing law.

Subsequently, we calculated the difference (Δn_D) between the refractive index predicted from ideal mixing law and that of experimentally observed. The maximum value of Δn_D ($\Delta n_D(max)$) varied greatly depending on the IL species, and decreased in the following order: [C₂MIM][BF₄] < [DEME][BF₄] < [C₄MIM][BF₄] \cong EAN < PAN < [C₂MIM][DEP] < [C₄MIM][OAc] < [C₈MIM][Br] < [BMIM][I]. This order almost good agreement with the pure IL refractive index. In spite of the ILs having different combinations of cations and anions, Δn_D had the same concentration dependence for all ILs in this study. Moreover, the water concentration of $\Delta n_D(max)$ showed around 25 mol% regardless of IL species. Finally, Δn_D normalized to unity at the water concentration corresponding to the maximum Δn_D is plotted for each IL (this study and literature). Interestingly, plots of the IL concentration dependence of the normalized Δn_D (Δn_D (minimum)=0 and Δn_D (maximum)=1) for all ILs in this study overlapped completely. The plots were fitted by the following Eq. (1) :

$$\text{Normalized } \Delta n_D = \frac{-1.4962}{e^{0.1064(100-x)}} - 0.015147(100 - x) + 1.5198 \quad (1)$$

$(R^2 = 0.99662)$

where *x* is the water concentration. There already has been reported that IL/water systems have unique physicochemical properties such as nano-heterogeneous structure, but at least for the normalized Δn_D , the specificity of each IL doesn't almost appear in a macroscopic view.

3.2 Physicochemical properties of water confined in the pocket formed in a typical ionic liquid [C₄MIm][BF₄] and the size of the pocket. ^[8]

In order to investigate the size of the pocket, water and alcohols having various alkyl chain length was mixed with [C₄MIm][BF₄]. As a result, volume expansivity calculated using density of [C₄MIm]BF₄/alcohol and [C₄MIm]BF₄/water systems were clearly smaller than that of IL/CO₂ systems^[1] and organic solvent/CO₂ systems and were less than 4 % up to 20 mol%. Therefore, adding water or alcohols into [C₄MIm]BF₄ didn't increase solution volume significantly, indicating that the water and alcohols may enter into the pocket formed in the IL at less than 20 mol%. In other words, the pocket size is more than 1-hexanol size (100 Å³) at least.

Moreover, the concentration dependence of the *D* and the ¹H chemical shift of the IL were shown in Fig. 1. Almost no differences in ¹H (Fig. 1 (a)) and ¹⁹F chemical shifts of the IL were observed up to 20 water or alcohol mol% despite the addition of water to 1-hexanol. This result indicates that the addition of water

or alcohols hardly affects the structure of the pure IL. The ^1H chemical shifts for the hydroxyl groups of alcohols and water were in good agreement with each other in Fig. 1 (b). This suggests that water and alcohols may exist in almost the same environment, although characteristics such as the molecular size, hydrophobicity, and shape, are also different. In the same region, the D of IL was also not affected by mixing of water or the alcohols, and was in good agreement with each other comparing the same water or alcohol concentration (Fig. 1 (c)).

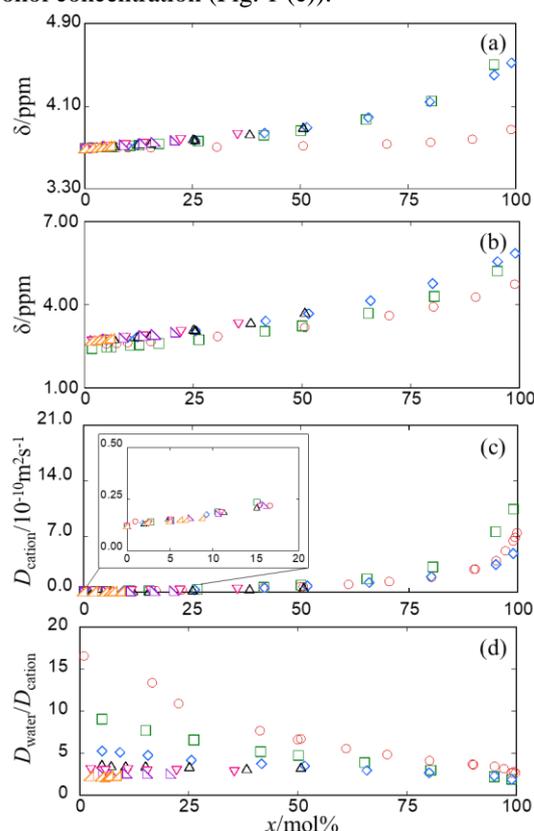


Figure 1. ^1H chemical shift and D for the IL/water and IL/alcohol systems and D ratios of the water to cations at 298 K. (a) ^1H chemical shift of methyl group of cation, (b) ^1H chemical shift of the hydroxyl group of alcohols and water, (c) D of cation, (d) $D_{\text{water}}/D_{\text{cation}}$. Legend: water (○), methanol (□), ethanol (◇), 1-propanol (△), 1-butanol (▽), 1-pentanol (⊠), and 1-hexanol (⊡).

In the present study, D_{cation} and D_{anion} were almost the same value in all systems. Thus the alcohols and water hardly affect the structure of the IL as well as chemical shift data. On the other hand, the D of the alcohol decreases as the alkyl chain length increases. In order to compare the movement of the IL and the alcohols in more detail, the D ratios of the alcohols or water to anion or cation were calculated as shown in Fig. 1 (d). The magnitude of concentration dependence was following order: water > methanol > ethanol > 1-propanol, and no significant differences were observed for the alcohols above 1-propanol. The water moved fastest in the IL, and the alcohol movement decreased as the alkyl chain

length of the alcohol increases. As for 1-propanol to 1-hexanol, the D s of alcohols were close to that of the IL which indicates that the movement of the alcohols are restricted in the pocket.

The following dynamic model could be obtained for the water and alcohols in the IL as shown in Fig. 2. The structure of the pure IL hardly change from the view of the dynamic (self-diffusion coefficient) and static (chemical shift) properties, even though 1-hexanol was added up to 20 mol%. Considering no limiting effect was observed in all the systems in this study, this suggests that the movement of water in the IL isn't restricted in the pocket and that of the alcohols having longer alkyl chain length is restricted.

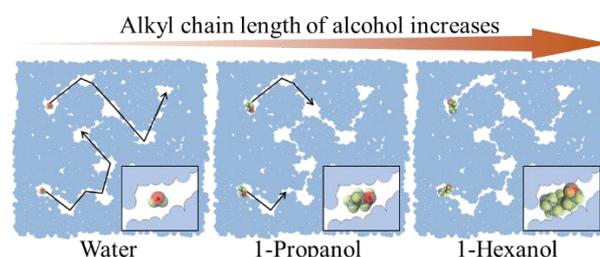


Figure 2. Dynamic model of a pocket in water/IL and alcohol/IL systems with the least amount of water or alcohol. Arrows show the distance travelled

3.3 The influence of the alkyl chain length of ionic liquid $[\text{C}_n\text{MIm}][\text{BF}_4]$ to physicochemical properties of the pocket formed in the IL and water confined in the pocket.^[9]

In order to investigate the properties of water in the pocket in ILs with various hydrophobicity, water was mixed with ILs having various alkyl chain length $[\text{C}_n\text{MIm}][\text{BF}_4]$ ($n=2, 4, 6, 8, 10$). As a result, volume expansivity of $[\text{C}_n\text{MIm}][\text{BF}_4]/\text{water}$ systems were very small and that of $[\text{C}_{10}\text{MIm}][\text{BF}_4]/\text{water}$ system was less than 1 % at 50 mol%, suggesting that the water enters into the pocket at low water concentration.

Moreover, the D and the ^1H chemical shift of IL were shown in Fig. 3. There was not significant change in the ^1H and ^{19}F chemical shift of IL compared to that of pure IL up to ca. 50 water mol% in Fig. 3 (a). This result indicates that the addition of water hardly affect the structure of the ILs in IL-rich region. The ^1H chemical shift of water showed almost the same concentration dependence over the whole concentration region regardless alkyl chain length of the IL (Fig. 3 (b)). There has been reported that water interacts stronger with anions than cations. Therefore, it suggests the interaction between the anion and the water doesn't change significantly regardless of alkyl chain length of cation.

Subsequently, the D s of IL and water didn't change significantly as increasing water concentration in IL-rich region (Fig. 3 (c)). This result indicates that the addition of water hardly affect the structure of the IL regardless of the alkyl chain length of ILs similar to the

chemical shift data. The D of water was clearly larger than that of the IL.

As well as section 3.2, we calculated the D ratio of the water to the anion or cation (Fig. 3 (d)). In the IL-rich region, the D ratios clearly increased with longer alkyl chain. It means that in the system having longer alkyl chain length of IL, the water move faster than IL relatively.

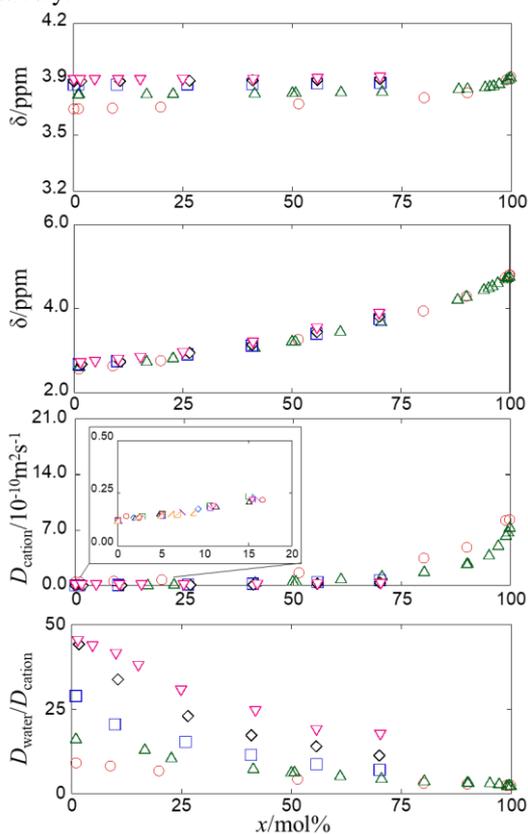


Figure 3. ^1H chemical shift and D for the IL/water systems and D ratios of the water to cations at 298 K.: (a) ^1H chemical shift of methyl group of cation, (b) ^1H chemical shift of the hydroxyl group of water, (c) D of cation, (d) $D_{\text{water}}/D_{\text{cation}}$, Legend: (○), $[\text{C}_2\text{MIM}][\text{BF}_4]$; (△), $[\text{C}_4\text{MIM}][\text{BF}_4]$; (□) $[\text{C}_6\text{MIM}][\text{BF}_4]$; (◇) $[\text{C}_8\text{MIM}][\text{BF}_4]$; (▽) $[\text{C}_{10}\text{MIM}][\text{BF}_4]$.

The surface of the pocket existing in the IL contains both a nonpolar and polar site, and the ratio of polar surface to nonpolar surface decreases as the alkyl chain length of the IL increases. Consequently, the electrostatic interactions between the surface of the pocket and the water molecules decrease and the water molecules in the pocket move more independent of the IL. In addition, since it was reported that the free-hole volume^[10] have a trend to increase with increasing molecular weight, the pocket size may increase with longer alkyl chain to some extent.

It is worth mentioning at this point that the distance travelled of the water in the IL calculated from D decreased as alkyl chain length of IL increase. As IL viscosity increases with longer alkyl chain length of IL, the decreasing of distance travelled of the water is

related in the bulk solution viscosity.

Based on these consideration, I proposed a model (Fig. 4) for water pocket when the alkyl chain length (nonpolar site) of IL changes.

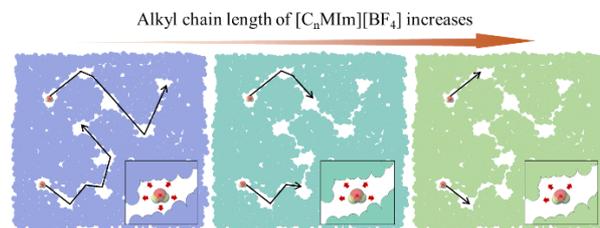


Figure 4. Dynamic model of a pocket in water/IL systems with the least amount of water. Blue shows the polar region, green shows the nonpolar region, red arrows show electrostatic interactions and black arrows show distance travelled.

4. Conclusion

Firstly, from the result of refractive index, it was elucidated that the specificity of each IL doesn't almost appear in a macroscopic view, as the normalized Δn_D had the same concentration dependence regardless of combination of anions and cations.

Secondly, from the results of chemical shifts and D s of $[\text{C}_4\text{MIM}][\text{BF}_4]$ /alcohol and $[\text{C}_4\text{MIM}][\text{BF}_4]$ /water systems, the following model about the pocket and the dynamics of water in confined in the pocket was obtained. The structure of the pure IL is almost maintained in IL-rich region. In the same region where the IL structure mainain, the size of the pocket was at least 100 \AA^3 from a dyna. Moreover, the movement of water is not restricted in the pocket and moves between the pockets.

Thirdly, the physicochemical properties of water pocket and water in the pocket when the alkyl chain length (nonpolar site) of IL changes was elucidated. In the IL having longer alkyl chain length, water moved faster than IL relatively, as reflecting the increasing hydrophobicity of the pocket surface. On the other hand, the distance travelled of the water in the IL decreased as the alkyl chain length of IL decreases. The decreasing of distance travelled of the water is related with increasing the bulk solution viscosity.

The physical property of pocket existing in the ILs and that of the water in the pocket of ILs when water mixed with ILs were elucidated.

5. Reference

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