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Short Communication

Potential dependent structure of an ionic liquid at ionic liquid/water interface probed by x-ray reflectivity measurements

Naoya Nishi [a],*, Tomoya Uruga [b], Hajime Tanida [b]

[a] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
[b] Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan

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ABSTRACT

The structure at air interface and water (W) interface of a hydrophobic ionic liquid (IL), trioctylmethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($[TOMA^+][TFPB^-]$), has been studied using x-ray reflectometry. Multilayering of ions has been found at the IL/air interface, with the topmost ionic layer having lower density than the IL bulk. For the IL/W interface, x-ray reflectivity data depends on the phase-boundary potential across the IL/W interface. When the phase-boundary potential of W with respect to IL, $\Delta_{IL}^{W}\phi$, is $+0.20$ V, $TFPB^-$ ions are accumulated at the topmost ionic layer on the IL side of the IL/W interface. On the other hand, when $\Delta_{IL}^{W}\phi = -0.27$ V, the accumulation of $TOMA^+$ ions occurs with bilayer thickness, which is probably due to local interaction between $TOMA^+$ ions at the topmost layer and at the second layer through interdigitation of their alkyl chains. To quantitatively analyze the x-ray reflectivity data, we construct a model of the electrical double layer (EDL) at the IL/W interface, by combining the Gouy–Chapman–Stern model on the W side and the Oldham model on the IL side. The constructed model predicts that the EDL on the IL side is within the topmost layer for the phase-boundary potentials in the present study, suggesting that the $TOMA^+$ bilayer found at the negative potential results from the local interaction beyond the framework of the present mean-field theory. Even at the positive potential the surface charge density predicted by the EDL theory is significantly smaller than that estimated from x-ray reflectivity data, which implies that densification of the topmost ionic layer leads us to overestimate the surface charge density.

1. Introduction

Liquid–liquid two-phase system composed of water (W) and hydrophobic ionic liquids (ILs), which are liquid salts composed of hydrophobic cations and anions, has potential applications in the fields of electroanalytical chemistry, such as liquid–liquid extraction of ions [1–9], two-phase electrochemical synthesis [10–12], ion-selective electrodes [13–18], and salt bridge [19,20]. Despite the broad applicability of the IL–W two-phase system for electroanalytical chemistry, only a limited number of studies have been reported to obtain the information on molecular-level structure at the IL/W interface. Pioneering studies on the structure at the IL/W interface are molecular dynamics (MD) simulations performed by Lynden-Bell et al. [21] and by Wipff et al. [22–26], Wipff et al. revealed orientation of IL cations, 1-methyl-3-alkylimidazolium ions ($C_n mim^+$) at the IL/W interface [24,26]. They suggested that C_4mim^+, a cation having short alkyl chain, does not show any preferential orientation at the $[C_4mim^+]PF_6^-$/W interface [24] and $[C_4mim^+][C_1C_1N^-]$/W interface [26] ($C_nC_nN^-$ denotes bis(perfluoroalkanesolfonyl)amide) whereas C_8mim^+ with longer alkyl chain tends to be anisotropically orientated with its octyl chain protruding to the IL phase at the $[C_8mim^+]PF_6^-$/W interface [24]. Their works are followed by subsequent MD simulation studies at the IL/W interface by the same group [27–31], and by others [32–37], focusing on the liquid–liquid extraction [27,30,31], adsorption of large-size solutes such as polyoxometalates [28,29], and nanoparticles [35,36], miscibility of IL with W [32–34], and the interfacial structure [37]. A recent study [37] on the interfacial structure confirmed the orientation of IL cations at the $[C_8mim^+][C_1C_1N^-]$/W interface and $[C_{12}mim^+][C_1C_1N^-]$/W interface similar to that of C_8mim^+ suggested by Wipff et al. [24]. Compared to these extensive simulation studies on the IL/W interface, experimental techniques are limited to a few because not many techniques can probe the structure at the IL/W interface, a buried liquid–liquid interface, at a molecular level. Nishi et al. used second harmonic generation (SHG), a second-order nonlinear optical spectroscopy having interface selectivity, to study the IL/W interface [38,39]. They prepared novel ILs based on cations having both high hyperpolarizability (i.e., SHG activity) and high hydrophobicity, to study the orientation of the IL cations at the IL/W interface. Orientation analysis revealed that dodecyl chain of the IL cations is protruding to the IL phase, similar to that proposed by MD [24,37]. Ouchi et al. successfully performed sum frequency generation (SFG) vibrational spectroscopy,

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* Corresponding author.
E-mail address: nishi.naoya.7e@kyoto-u.ac.jp (N. Nishi).

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which is also one of the interface-selective second-order nonlinear optical spectroscopy, at the [C_4mim$^+$][$C_1C_1N^-$]/W interface and [C_8mim$^+$][$C_1C_1N^-$]/W interface [40]. They revealed that $C_1C_1N^-$ is orientated with the SO_2 moiety pointing toward the W phase at both the interfaces and that more $C_1C_1N^-$ ions tend to be in the C1 (*cis*) conformation when increasing the alkyl chain of the IL cations from C_4mim$^+$ to C_8mim$^+$. They also noted that CH stretching vibrational modes were not observed at the IL/W interface even for [C_8mim$^+$][$C_1C_1N^-$], the IL of the cation with a long alkyl chain, in contrast to the CH modes pronouncedly appeared at the air interface of the ILs. The disappearance of the CH modes at the IL/W interface seems to be due to the counter orientation of the topmost-layer cations and the second-layer cations, causing the cancellation of the SFG signals for the CH modes.

Since ILs are composed of ions and may be regarded as dense electrolyte solutions, electrochemical point of view is important to consider the structure of the IL/W interface. There exists phase-boundary potential across the IL/W interface and electrical double layers (EDLs) are formed on both IL and W sides of the interface [41–43]. Local ion concentrations in EDLs are generally different from those in bulk. Electrocapillarity (dependence of surface tension on the phase-boundary potential) studies [44–49] at the IL/W interface confirmed fundamental features of the EDL such as surface excess and specific and non-specific adsorption of IL ions at the IL/W interface. These studies suggested that the EDL at the IL/W interface is not far from the view of the Gouy–Chapman–Stern model [50–52] that has long been the theoretical basis for EDL at the electrochemical interfaces such as electrode/electrolyte solution interface.

The EDL in IL is known to have several unique structures such as layering of ions [53–61] and transition of the ionic layer to solid-like phase [58,62–64]. Such unique structures seem to be the cause for ultraslow dynamics of the interfacial structure at the IL/W interface [65–68] and the IL/electrode interface [69–73]. Charging properties are also unique; “lattice saturation” and “overscreening” are theoretically proposed [74] and experimentally confirmed [54,75]. The former results from the excluded volume effect between ions in the EDL, not that between ions and electrode that the Gouy–Chapman–Stern model takes into account [52]. The latter is the formation of alternately charged ionic multilayers due to coulombic interaction between neighboring ions. Because of these interesting phenomena that ILs have presented, it should be worth to investigate the EDL at the IL/W interface by a technique having interfacial selectivity at a molecular level. X-ray reflectometry (XR) is a suitable technique for the purpose. Extensive XR studies by Schlossman et al. have already been performed for the EDL at the electrochemical oil–water interface, where the two liquid phases contain electrolyte ions and the phase-boundary potential can be controlled [76–81]. They revealed that the conventional EDL theory, which includes only coulombic interaction between ions via averaged electric potential, is insufficient to elucidate their XR data and that ion-solvent potential of mean force and ion-ion correlation potential play a crucial role in the ion distribution especially in the EDL in oil. In this paper, we introduce a XR study at air and water interface of a hydrophobic IL, trioctylmethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ([TOMA$^+$][TFPB$^-$]). We will show that XR can probe the phase-boundary-potential dependent structure in the EDL on the IL side of the IL/W interface.

2. Experimental and theoretical

2.1. Preparation of ionic liquid

[TOMA$^+$][TFPB$^-$] was prepared from [TOMA$^+$]Cl$^-$ (TCl) and Na$^+$[TFPB$^-$] [7,82], and purified using the same method for [TOMA$^+$][$C_4C_4N^-$] described elsewhere [57]. Na$^+$[TFPB$^-$] was synthesized using a procedure similar to that previously reported by Nishida et al. [83] from 3,5-bis(trifluoromethyl)bromobenzene and sodium tetrafluoroborate.

2.2. X-ray reflectivity measurement

XR measurements were performed at the beamline BL37XU of SPring-8 using a liquid interface reflectometer [84]. The details of the XR measurements are described elsewhere [57,59]. Briefly, x-ray of 25 keV from the undulator was irradiated to the air or water interfaces of [TOMA$^+$][TFPB$^-$]. The PTFE coated aluminum trough was set on an aluminum block in which temperature-controlled water was flowed. The lower part of the trough was filled with [TOMA$^+$][TFPB$^-$]. The upper part was filled with an aqueous solution for the measurements for the IL/W interface. Temperature was controlled to be 330 K, which is well above the melting point of [TOMA$^+$][TFPB$^-$] (313 K), with an accuracy of 1 K.

The intrinsic surface structure factor, ϕ, as a function of the surface-normal component of the scattering vector, q, was evaluated from the experimentally obtained x-ray reflectivity, R, using the following equation [57,85],

$$|\phi|^2 = \frac{R}{R_F} \exp\left[\sigma_{CWT}^2 q^2\right] \tag{1}$$

where R_F is the Fresnel reflectivity and σ_{CWT} is surface roughness due to thermal capillary waves derived from the capillary wave theory. R_F and σ_{CWT} were calculated using the procedure described elsewhere [57,59].

The q dependence of ϕ was fitted with model functions using the following equation assuming the kinematic approximation [85],

$$\phi = \frac{1}{\Delta\rho}\int_{-\infty}^{\infty} \frac{d\rho}{dz} \exp[iqz]dz, \tag{2}$$

where z is a displacement along the surface normal with $z = 0$ for the interfaces and $z > 0$ for the IL phase, and ρ is the intrinsic electron density averaged in the xy direction (along the surface plane) as a function of z. The electron density difference between two phases, $\Delta\rho$, is ρ_{IL} for IL/air interface and $\rho_{IL} - \rho_W$ for IL/W interface. $\rho_{IL} = 0.373$ e Å^{-3} and $\rho_W = 0.334$ e Å^{-3} were estimated with molecular weights, densities, and number of electrons for IL and W. The ρ_{IL} value is the average of those for TOMA$^+$ and TFPB$^-$ in the IL, $\rho_C = 0.247$ e Å^{-3} and $\rho_A = 0.499$ e Å^{-3}; $\rho_{IL} = (\rho_C + \rho_A)/2$. The difference between ρ_C and ρ_A enables us to detect the EDL in IL by XR; local concentration change for the IL cation and anion leads to electron density in the EDL different from that in the IL bulk.

2.3. EDL calculation

We performed a model calculation for the electrical double layer (EDL) at the IL/W interface. The basic idea of the model is the same as the modified version [86] of the Verwey–Niessen model [87] for oil/water interface. The modified Verwey–Niessen model consists of two EDLs of the Gouy–Chapman–Stern type on the oil and water sides of the oil/water interface. The modification means that the modified Verwey–Niessen model [86] incorporates ion-free “inner layer” at the both side of the interface in which ions cannot enter, similarly to the Stern layer at the electrode|electrolyte solution interface. The thickness of the inner layer on the W side is the radius of solvated ions in W usually set to 0.3 nm. On the oil side, the inner layer is thicker than that for W, because generally hydrophobic electrolyte ions in oil are big and have symmetric shape, and the charged part is located inside the ions. The incorporation of the inner layers succeeded in the explanation of the EDL behavior at the oil/water interface [88]. In the present study for the IL/W interface, we adopted the EDL model proposed by Oldham [89] for the IL side of the interface, instead of the Gouy–Chapman–Stern model used for the EDL on the oil side of the oil–water interface, to incorporate the excluded volume effect between IL ions.

Suppose that the IL/W interface is located at $z = 0$, and the IL and W sides of the interface are $z > 0$ and $z < 0$, respectively. We neglect specific