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Air–liquid interface of ionic liquid + H_2O binary system studied by surface tension measurement and sum-frequency generation spectroscopy

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Abstract

Surface of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) + water mixture is investigated using surface tension measurement and sum-frequency generation spectroscopy. The liquid surface is mostly covered by the $[BMIM]^+$ cations at very low bulk concentration. An unusual increase in surface tension from mole fraction $c \approx 0.016$ up to ≈ 0.05 suggested that the BF_4^- anions start to appear at the surface from $c \approx 0.016$ until the anions and cations are equally populated at $c \approx 0.05$ or higher. From the analysis of the spectra, the terminal methyl group of the butyl chain in the cation is polar-oriented with its symmetry axis aligning rather vertical to the surface for the whole range of concentration.

1. Introduction

Room-temperature ionic liquid (RIL) is a salt consisting of certain organic cation and anion, and is in liquid phase at room temperature [1,2]. Because these ionic liquids are nonvolatile, nonflammable, and are good solvent for many chemicals, they are gaining interest as environment-friendly solvents for a range of chemical processes [3–5] or as possible constituents in electrochemical applications [6,7]. Since interfacial properties, such as structure and chemical composition are important for these applications, a few studies regarding RIL surfaces were performed using direct recoil spectroscopy (DRS) [8], surface tension measurement [9], neutron scattering [9,10], metastable atom electron spectroscopy [11], and sum-frequency vibrational spectroscopy [12,13]. These studies as well as several theoretical calculations suggested that both cations and anions are populated at the surface with a specific orientation, and thus the surface of pure RIL has been understood to a certain extent. On the other hand, many RILs are known to be miscible with water. As the mixture of RIL with water is expected to have interesting properties, several experimental studies about the bulk properties of the mixture were performed [14–16]. As far as the above RIL + water mixture is concerned, the surface of the mixture is also crucial for the practical applications of RILs [17], and many fundamental issues related to this surface need to be investigated [18]. Recently, the anomalous behavior of surface tension from several RILs mixed with water was observed,

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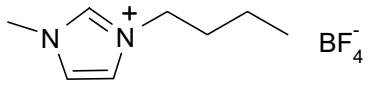

Fig. 1. Chemical structure of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4).

and possible relation to their bulk properties such as molecular aggregate formation was inferred from neutron scattering measurement [9]. However, information at the molecular level, such as surface chemical composition and molecular conformation responsible for this surface tension behavior has not been available as yet.

In this Letter, we investigated the surface molecular structure of RIL + water mixture using surface tension measurement and surface sum-frequency generation (SFG) vibrational spectroscopy. We chose 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) shown in Fig. 1, because it is one of the most popular ionic liquids and is miscible with water in the entire range of bulk mole fraction. Results from our study indicated that the liquid surface was mostly covered by the cations even at very low bulk concentrations of the mixture, and anions would appear at the surface as the concentration of RIL increased in the mixture.

2. Theoretical background

Surface tension of the mixture system can be used to yield the surface chemical composition of the binary mixture system using Gibbs adsorption equation [19]

$$\Gamma = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln a}, \tag{1}$$

where Γ, a, γ, R, and T are the surface excess, the activity of the solute–solvent system, the surface tension of the mixture, ideal gas constant, and the temperature, respectively. To calculate the surface excess from the above equation, one needs to convert the solute concentration of the bulk mixture into activity a. However, in many cases the activity of the specific solute–solvent system is not well known, and the quantitative determination of the surface excess is challenging.

The theory regarding the surface SFG has been described in detail elsewhere [20,21]. It is based on the SFG process in which an infrared beam at frequency ω_{IR} and a visible beam at frequency ω_{VIS} overlap at the surface and generate a sum-frequency signal at frequency $\omega_{\mathrm{SF}} = \omega_{\mathrm{IR}} + \omega_{\mathrm{VIS}}$. For an interface between two centrosymmetric bounding media, SFG is often dominated by the nonlinearity at the interface. The sum-frequency signal strength is given by

$$I(\omega_{\mathrm{SF}}) \propto \left|\chi_{\mathrm{NR}} + \sum_q \frac{A_q}{\omega_{\mathrm{IR}} - \omega_q + \mathrm{i}\Gamma_q}\right|^2, \tag{2}$$

where χ_{NR} is the nonresonant contribution to the susceptibility, and A_q, ω_q, and Γ_q are the strength, frequency, and the damping constant of the qth vibrational mode, respectively. The strength of the specific vibrational mode obtained by fitting the spectra using Eq. (2) allows one to deduce the information about the surface structure from the following equation:

$$A_{q,ijk} = N_{\mathrm{s}} \sum_{\xi\eta\zeta} a_{q,\xi\eta\zeta} \left\langle \left(\hat{i}\cdot\hat{\xi}\right)\left(\hat{j}\cdot\hat{\eta}\right)\left(\hat{k}\cdot\hat{\zeta}\right)\right\rangle, \tag{3}$$

where N_{s} is the surface number density of molecules, $a_{q,\,\xi\eta\varsigma}$ is the molecular hyperpolarizability of the qth vibrational mode in the ($\xi\eta\zeta$) direction in the molecular frame, (ijk) is the set of unit vectors in the laboratory coordinates, and the angle bracket denotes an ensemble average over the orientation of surface molecules.

3. Experimental

3.1. Sample preparation

Tetrafluoroborate salt of 1-butyl-3-methyl imidazolium ([BMIM]BF_4, purity better than 99 wt%, water content <350 ppm, chloride content <20 ppm) was purchased from C-TRI in Korea, and used without further purification.

3.2. Surface tension

Equilibrium measurements of the surface tension were performed using a DuNuoy Tensiometer (Surface Tensionmat, Fisher) with a platinum ring with a mean circumference of 6 cm, and a ring/wire radius ratio of 53.8. We calibrated the surface tension on the basis of pure water (72 mN/m), methyl alcohol (22.0 mN/m), xylene (29.7 mN/m), and triethylene glycol (45.1 mN/m) at room temperature (25 °C) [22].

3.3. SFG

The laser system for SFG experiment employed a mode-locked picosecond Nd:YAG laser (Continuum PY91, 45 ps, 10 Hz) with an optical parametric generator/amplifier (OPG/OPA) to generate the tunable IR pulse. The second harmonic of the Nd:YAG laser output generated from KTP crystal was used as the input visible beam. Typical input energies were ≈1.4 mJ/pulse and ≈200 μJ/pulse, beam sizes were 1 mm and 200 μm, and incident angles were 49° and 57° for the visible and IR beams, respectively. The IR frequency was calibrated with the absorption lines of polystyrene, and all spectra were normalized to the SFG spectra from a z-cut quartz surface. Refractive indices, $n(\lambda)$, of [BMIM]BF_4 used in quantitative analysis were n(532 nm) = 1.41 and n(3.0 μm) = 1.37 at 25 °C [13].