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Surface segregation in binary mixtures of imidazolium-based ionic liquids

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ABSTRACT

Surface composition of binary mixtures of room-temperature ionic liquids has been investigated using time-of-flight secondary ion mass spectrometry at room temperature over a wide composition range. The imidazolium cations with longer aliphatic groups tend to segregate to the surface, and a bis(trifluoromethanesulfonyl)imide anion (Tf_2N^-) is enriched at the surface relative to hexafluorophosphate (PF_6^-). The surface of an equimolar mixture of Li[Tf_2N] and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) has a nominal composition of [bmim][Tf_2N] because of surface segregation and ligand exchange. The surface segregation of cations and anions is likely to result from alignment of specific ligand-exchanged molecules at the topmost surface layer to exclude more hydrophobic part of the molecules.

1. Introduction

Room temperature ionic liquids (RTILs) are a new class of chemicals that have recently prompted a significant amount of research. They are composed solely of ions, and destabilization of the ionic lattice by asymmetrically shaped cations and anions is thought to lower the melting point of RTILs relative to that of typical ionic compounds. The unique physicochemical properties of RTILs, including high thermal stability, high ionic conductivity, and negligible vapor pressure, are ideal for a number of applications as a solvent for green chemical synthesis [1–3] and a conductive media for lithium ion batteries [4,5] and fuel cells [6,7]. For these practical applications, the interfacial properties of RTILs are quite important because chemical reactions are first catalyzed by the species at the interface. To date, the structure and composition of liquid-vacuum (air) interface of imidazolium-based RTILs have been studied extensively using a variety of surface sensitive techniques, such as sum frequency generation (SFG) [8–11], direct recoil spectrometry (DRS) [12,13], X-ray photoelectron spectroscopy (XPS) [14–17], time-of-flight secondary ion mass spectrometry (TOF-SIMS) [14,18–20], metastable impact electron spectroscopy (MIES) [21,22], high resolution electron energy loss spectroscopy (HREELS) [21], and high-resolution Rutherford backscattering spectroscopy (HRBS) [23,24]. A consensus has been made that both cations and anions are sharing the surface, but there exist conflicting reports on the orientation of the imidazolium ring [8–13]. Molecular dynamics (MD) simulations showed that cation is aligned with the imidazolium ring being parallel to the surface and that the longer aliphatic chains of the imidazolium cations are likely to protrude outside from the surface [25,26]. The predicted alignment is in good agreement with the experimental results of SFG [8–11], angle-resolved XPS [16,17], and HRBS [23,24]. The surface enrichment of aliphatic carbon was also observed for alkyl chains attached to the anion [17]. The surface composition of a Pt salt additive ([$Pt(NH_3)_4$]Cl_2) in 1-ethyl-3methylimidazolium ethylsulfate ([emim][$EtOSO_3$]) has been analyzed using angle-resolved XPS (AR-XPS) [27]; it was revealed that the [$Pt(NH_3)_4$]$^+$ (Cl^-) ion is enriched (depleted) in the near surface region, suggesting that larger and more polarizable ions tend to segregate to the surface. This phenomenon resembles that observed previously for aqueous solutions of alkali halides and other ionic compounds [28–30]. Minor impurities, such as silicone and hydrocarbons, also tend to segregate to the surface of RTILs [14,31–34]. Thus, the surfaces of pure and slightly contaminated RTILs have been studied extensively, but no systematic studies on the surface structure and composition of RTIL mixtures exist to the best of the author's knowledge. This paper is devoted to the analyses of surface segregation of cations and anions in some binary mixtures of RTIL based on TOF-SIMS. TOF-SIMS is one of the most surface sensitive techniques that probe the topmost surface layer, so that it is expected that the surface enrichment of specific cation and anion moieties, if any, can be investigated straightforwardly based on the sputtered ion intensities as a function of their composition in the bulk. The interactions underlying surface segregation of both cations and anions in concentrated and dilute solutions are discussed, together with a ligand exchange phenomenon. To this end, the cations interactions are investigated specifically using mixtures of 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]) with [emim][PF_6] and [omim] tetrafluoroborate ([omim][BF_4]) with [emim][BF_4], together with the anions interactions in a mixture of 1-butyl-3-methylimidazolium bis(trifluoromethanelsulfonil)imide ([bmim][Tf_2N]) with [bmim][PF_6]. The surface composition of Li[Tf_2N] in [bmim][PF_6] is also investigated to explore the possibility of ligand exchange.

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2. Experimental

RTIL samples were purchased from Kanto Regents (Tokyo, Japan). They were used as received without further purification. The weighed samples were diluted in methanol at a concentration of 0.2 mmol/ml. The concentrations of [omim][PF_6], [bmim][Tf_2N], and Li[Tf_2N] were further reduced by serial dilutions. The RTIL mixtures (from 1:1 to 1:3000) were prepared by blending these methanol solutions. After complete mixing, aliquots of 20 μL were spin-coated (5000 rpm for 30 s) onto a mirror-finished polycrystalline Ni plate. Prior to spin-coating, the Ni substrate was cleaned with methanol in an ultrasonic bath. The samples were inserted immediately into a load-lock chamber and degassed at room temperature. After degassing the sample to attain the vacuum in 10^{-5} Pa range, it was transferred to an ultrahigh vacuum (UHV) chamber.

The TOF-SIMS measurements were performed in the UHV chamber by excitation of the samples with a He^+ beam (2 keV) that was generated in a differentially-pumped electron-impact-type ion source. The dc primary ion intensity at the sample was 20 nA, and the operation spot size was ca. 5 mm in diameter. The beam was chopped into pulses (40 ns in width and 20 kHz in repetition rate) using electrostatic deflection plates. The normal working pressure during the TOF-SIMS measurement was 1×10^{-8} Pa, but the present experiment was performed in a 10^{-7} Pa range. The sample was biased and a grounded stainless steel mesh was placed close to the sample surface (extraction field of 125 V/mm). The secondary ions were pulse counted using a microchannel plate after traveling through a field-free linear TOF tube; the TOF-SIMS spectrum was created using a multichannel scaler. The measurements were made at room temperature within a beam fluence of less than 10^{11} ions cm^{-2}.

3. Results and discussion

Fig. 1 shows positive TOF-SIMS spectra obtained from spin-coated films of (a) [emim][PF_6], (b) [omim][PF_6], and (c) their equimolar mixture. The $emim^+$ and $omim^+$ cations ($m/z = 111$ and 195) are sputtered together with fragment ions. The $emim^+$ cation is comparable to or greater than the fragment ions in intensity whereas the $omim^+$ intensity is considerably small relative to the fragment ion intensities from the octyl chain (e.g., $C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$, and $C_3H_7^+$). This behavior might be explained as the exposure of the aliphatic chain to the vacuum: The emission of the imidazolium cation tends to be self-blocked by its long side chain protruding to the vacuum side. The spectral features from their mixture resemble those of pure [omim][PF_6]; only a very small amount of the $emim^+$ cation is recognizable. The amount of $emim^+$ in the topmost layer is at most 2–3% of that of $omim^+$ as estimated from the deconvolution of the TOF-SIMS spectrum. The depletion (enrichment) of $emim^+$ ($omim^+$) in the topmost layer is thought to be driven by the exclusion of the longer aliphatic chain of the imidazolium cation from the bulk. The similar phenomenon is observed using equimolar mixture of [bmim][PF_6] and [emim][PF_6] (not shown). In this case, the surface composition of $emim^+$ is estimated to be about 1/3 of that of $bmim^+$. Thus, the cation coverage in the topmost layer of the binary mixtures is found to be dependent on the length of aliphatic chains.

In the present experiment, some of the spin-coated films are not uniform in thickness as evidenced by that Ni^+ (m/e = 58 and 60) is sputtered from the substrate to some extent (see Fig. 1(a)). The Ni^+ ion is recognizable for the RTIL films except for [omim][PF_6] and [omim][BF_4]. The same occurs when pure RTILs are deposited instead of their methanol solutions. In general, the morphology of a thin liquid film changes inevitably with time because of the surface tension and interaction with the substrate. The morphological change of the spin-coated films can be identified from the disappearance of light interference patterns after the TOF-SIMS measurement. [omim][PF_6] and [omim][BF_4] can avoid the morphological change because of higher viscosity. The secondary ion intensities are likely to undergo the film morphology effect, but the TOF-SIMS spectra from the equimolar mixtures of [omim][PF_6]/[emim][PF_6] and [bmim][PF_6]/[emim][PF_6] can be deconvoluted using those of the pure RTILs. In this study, therefore, the ion intensities from RTIL mixtures are compared directly to each other because they are expected to provide information about how the surface coverage of cations and anions changes as a function of bulk composition.

In Fig. 2 are shown negative TOF-SIMS spectra from the spin-coated films of (a) [bmim][Tf_2N], (b) [bmim][PF_6], and (c) their 1:10 mixture. The spectra are dominated by fragment ions, such as C^-, CH^-, O^-, F^-, C_2^-, C_2H^- and $C_2H_2^-$; intact PF_6^- (m/e = 145) and Tf_2N^- (280)

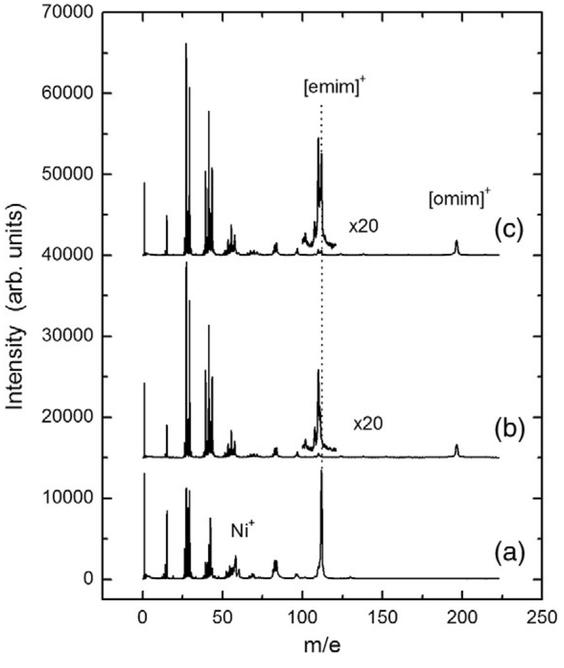

Fig. 1. TOF-SIMS spectra of positive ions sputtered from spin-coated thin films of (a) [emim][PF_6], (b) [omim][PF_6], and (c) their 1:1 mixture.

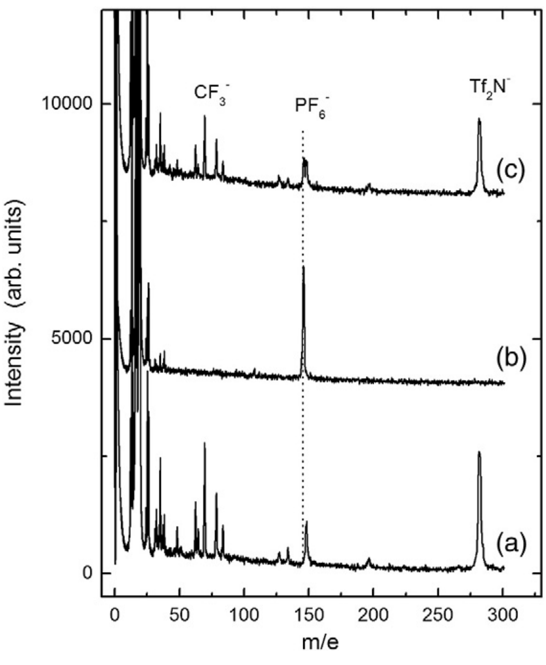

Fig. 2. TOF-SIMS spectra of negative ions sputtered from spin-coated thin films of (a) [bmim][Tf_2N], (b) [bmim][PF_6], and (c) their 1:10 mixture.