



Characterizing solid/ionic liquid interfaces in the presence of water and nonionic surfactants



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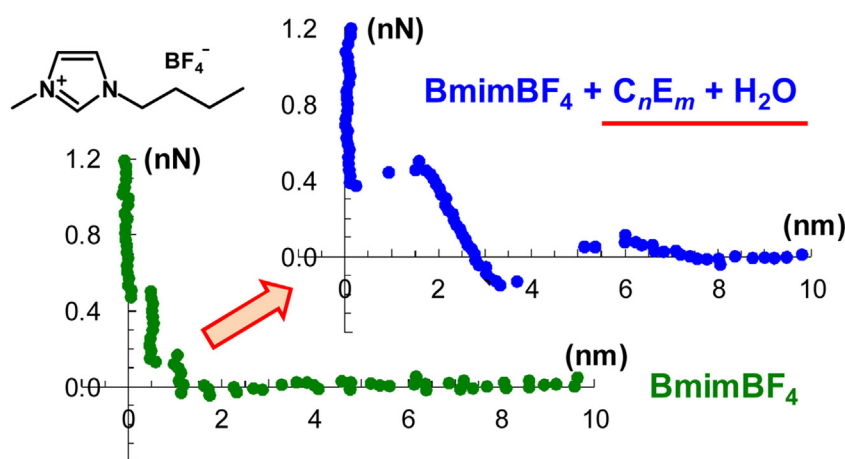
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HIGHLIGHTS

- We focus on the adsorption of C_nE_m on silica/mica from $BmimBF_4$ + water mixtures.
- The C_nE_m surfactants can be adsorbed on silica even in the presence of water.
- The C_nE_m surfactant aggregates grow on silica as a function of its concentration.
- Multi-step repulsions were observed in solvophobic C_nE_m systems with water.
- The C_nE_m surfactant adsorption was significantly inhibited on mica.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of nonionic surfactants on hydrophilic solid surfaces has been characterized using mixtures of an aprotic room-temperature ionic liquid (RT-IL) with water. The surfactants employed in this study were a series of polyoxyethylene alkyl ethers (C_nE_m , n is the hydrocarbon chain length, and m is the number of oxyethylene units, $C_{10}E_6$, $C_{12}E_6$, $C_{14}E_6$, $C_{12}E_4$, and $C_{12}E_8$), and the RT-IL used was 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$). This RT-IL is completely miscible with water over a whole range of concentrations. Force curve measurements by atomic force microscopy (AFM) demonstrated that the adsorption of the nonionic surfactants occurred at a silica/solution interface even in the presence of added water. The surfactant aggregates formed at the interface grew as a function of the surfactant concentration; an attractive interaction observed below the critical micelle concentration (cmc) changed into a repulsive interaction above the cmc. Interestingly, multi-step repulsive interactions were observed in a few relatively solvophobic surfactant systems (i.e., the surfactants having longer hydrocarbon chain and/or shorter oxyethylene chain) in the presence of added water. It seems likely that these repulsive interactions arise from the repeated structure of the surfactant assemblies formed between the

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cantilever tip and the silica surface. In contrast, the surfactant adsorption was significantly inhibited on mica because of the absence of hydrogen bonding sites and/or the presence of well-structured IL solvation layers on the mica surface.

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1. Introduction

The adsorption characteristics of surfactants at solid/solution interfaces have been of great interest not only in academia but also in industry. A major target in this research field has been aqueous surfactant systems; however, the industrial importance also requires systematic studies focusing on the surfactant adsorption that occurs in non-aqueous media. Room-temperature ionic liquids (RT-ILs) are classified as non-aqueous solvents. Similar to aqueous systems, surfactants can self-assemble in RT-ILs and form micellar aggregates at certain concentrations and temperatures, and this nature is strongly dependent on the combination of the two components [1–3].

It has been reported that RT-ILs generally form their structured solvation layers on hydrophilic solid surfaces (such as silica or mica) in the absence of surfactants [4,5]. These solvation layers sometimes prevent surfactant adsorption. For example, force curve measurements by atomic force microscopy (AFM) have demonstrated that the adsorption of a nonionic surfactant (hexaoxyethylene hexadecyl ether, $C_{16}E_6$) is not observed on silica from a protic RT-IL (ethylammonium nitrate, EAN) [6], and instead, the silica surface is only covered with non-adsorbing $C_{16}E_6$ micelles [7]. Interestingly, the adsorption of Pluronics (polyethylene oxide (PEO) – polypropylene oxide (PPO) – PEO triblock copolymers) has been suggested to occur at the silica/EAN interface [7]. We have also characterized the adsorption of nonionic surfactants (phytosterol ethoxylates) on silica from an aprotic RT-IL (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, EmimTFSI) and found a concentration-dependent growth of the surfactant aggregates adsorbed on the silica surface [8].

Characterizing the interfacial properties of binary mixtures of RT-IL and water is also an interesting research topic [9–14]. In our recent paper [14], we demonstrated that an interfacial water phase was spontaneously formed on silica in a hydrophilic RT-IL (1-butyl-3-methylimidazolium tetrafluoroborate, BmimBF₄), whereas the formation was not observed on mica in the same RT-IL [14]. However, in the hydrophobic RT-IL, EmimTFSI, the interfacial water phase is formed on the two solid surfaces. This indicates that the adsorption of water molecules onto the solid surfaces is primarily driven by hydrogen bonding, but the hydrophobicity (or hydrophilicity) of the RT-ILs is also a key factor in forming the interfacial water phase. The formation of the interfacial water phase results in lower stability of the colloidal suspensions dispersed in RT-ILs, as reported in the silica [11,14] and gold [15] particle systems.

Here, we focus on the adsorption of a series of polyoxyethylene alkyl ether-type nonionic surfactants (C_nE_m , n is the hydrocarbon chain length, and m is the number of oxyethylene units) on the two hydrophilic solid surfaces (silica and mica) from the mixtures of BmimBF₄ and water. Again, similar to aqueous systems, solvophobic interactions drive the spontaneous micellization of these surfactants even in the mixed solvents [16]. Hence, the critical micelle concentration (cmc) is strongly dependent on the solution composition; an increased water concentration in BmimBF₄ lowers the cmc [16]. Ternary mixtures of surfactant, RT-IL, and water can also form liquid crystals at certain compositions [17–20]. These earlier studies highlight the self-assembly of surfactants that occurs

in bulk solutions of RT-IL with water. However, to the best of our knowledge, the effects of the coexistence of surfactant and water on the structural solvation layers formed at the solid/IL interfaces have not yet been reported.

2. Experimental

2.1. Materials

The imidazolium-type RT-IL, BmimBF₄, was purchased from Aldrich. The purity of this sample is more than 97% based on the information provided by the supplier. Before use, this sample was dried in a vacuum oven set at 80 °C for 8 h under reduced pressure. The concentration of water remaining on the dried sample was measured using a Karl Fischer moisture titrator (Kyoto Electronics Manufacturing, MKC-610) and found to be ca. 0.03 wt%.

All of the polyoxyethylene alkyl ether-type nonionic surfactants, $C_{10}E_6$, $C_{12}E_6$, $C_{14}E_6$, $C_{12}E_4$, and $C_{12}E_8$, were obtained from Nikko Chemicals and used as received without further purification. The cmc of each surfactant from binary mixtures of BmimBF₄ and water was measured through static surface tensiometry [16]. The resultant cmc data are summarized in the Supplementary data, **Table S1**.

Chemically oxidized silicon wafers were used in this study as the silica substrate. The silicon wafers (Nilaco) were immersed in a mixed solution of H₂O:NH₃:H₂O₂ = 5:1:1 (in volume) for 15 min at 80 °C, followed by copious rinsing with deionized water to give a hydroxylated silica surface. Before each measurement, these substrates were cleaned in a UV/O₃ cleaner for 10 min. Muscovite mica substrates were purchased from Nilaco and freshly cleaved before each experiment.

The water used in this study was deionized with a Barnstead NANO Pure Diamond UV system and filtered with a Millipore membrane filter (pore size 0.22 μm).

2.2. Measurements

In situ force curve measurements were performed using a Seiko (Hitachi High-Tech Science) SPI3800 AFM. V-shaped cantilevers with silicon nitride tips (Olympus OMCL-TR800PSA, nominal spring constant = 0.15 N m⁻¹) were used for all AFM experiments. These cantilevers were immersed in ethanol to remove organic contaminant and then cleaned in the UV/O₃ cleaner for 10 min. The solid substrate (mica or silica) was assembled in the AFM instrument, and the AFM fluid cell was immersed in the sample solutions. After equilibration, force curve measurements were performed at room temperature.

3. Results and discussion

3.1. Surfactant concentration

Fig. 1 shows the force curves measured in the binary solutions of $C_{12}E_6$ with BmimBF₄. The surfactant concentrations were set at 0, 0.5, 2, and 4 cmc in BmimBF₄, and the solid substrate used here was silica. In these experiments, water was not added to the system. As mentioned in the Experimental section, the IL sample was

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