Spreading of Nanodroplets of Ionic Liquids on the Mica Surface

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ABSTRACT: Previously, the molecular structure of ionic liquids (ILs) next to a solid surface has been extensively studied because the IL–solid interfaces are critical to many important applications. What is largely unknown is the mobility of ILs confined to a solid surface. The solid-like stable structure of ILs on the solid surfaces has been reported in previous research, which indicates that the mobility of ILs next to a solid surface is quite low and the structure of ILs will not change with time. However, here, we show that the nanodroplets of ILs flow on the mica surface, which suggest that, at a small scale, the solid-like stable structure of ILs on the solid surfaces indeed changes with time. Interestingly, although the IL nanodroplets show a layered structure, no terrace-like flow of the droplet has been observed, which has been attributed to the weak mica–IL interaction at low humidity.

INTRODUCTION

Ionic liquids (ILs) have garnered a lot of interest because of their outstanding physicochemical properties.1–3 The IL–solid interfacial behavior is especially critical to many important applications, such as lubrication4–6 and catalysis.7 To date, many experimental and computational studies on the molecular structure of ILs on the solid surface have been reported.8 Liu et al. demonstrated the coexistence of drop-on-layer structure and solid-like ordered layers of ILs on the mica surface.9 Bovio et al. reported that ILs formed the solid-like layering structure on mica and silica surfaces.10 On the basis of experimental and computational studies, Bovio et al. also showed the remarkable stability of the layering structure of ILs on the silica; for example, the layering is stable for a few months, revealing that ILs on the silica are solid-like and have very low mobility.11 Yokota et al. showed the layered structure at IL–solid interfaces is solid-like rather than liquid-like using frequency-modulation atomic force microscopy (AFM) and also concluded that the solid-like layering structure is highly stable.12 Using surface force apparatus (SFA), Buo-Malham et al. showed that ILs on the mica surface exhibit a solid-like response.13 Dragoni et al. provided evidence for the solid-like behavior of ILs on the mica, which might explain the remarkable stability of ionogels made of inorganic nanoparticles and ILs.14 Solid-state nuclear magnetic resonance (NMR) experiments showed that the IL at the IL–solid (laponite clay) interface forms a thin solid layer.15 Atkin et al. investigated the structure of ILs on the Au(111) surfaces and reported that an interfaceal layer of ILs was strongly bound to the solid surface, which could not be ruptured by the colloid probe.16 They also reported that ILs self-assemble at the solid surface via hydrogen bonding.17 On the basis of SFA results, Perkin et al. also reported the ordered self-assembly structure of ILs on the mica surface.18,19 Using molecular dynamics (MD) simulation, Sha et al. demonstrated that the IL layer possesses the highest density next to the solid surface, which is believed to be in a solid-like or solid state because of strong interactions at the graphite–IL interface.20

In all of the abovementioned studies, the solid-like low mobility of ILs was reported. Interestingly, the liquid-like flow of ILs on solid surfaces was also reported. Wang et al.21 found that macroscopic IL droplets spread on the mica surface gradually and there is a precursor film ahead of the spreading front. Beattie et al.22 found that molecular-thin precursor films emerge from the macroscopic droplet of ILs on the mica surface. Clearly, further research is required to fully understand the mobility of ILs on a solid surface.23 The study on the spreading of a droplet, especially at a small scale, provides insight into the mobility of the liquid at the liquid–solid interface.24 It has been reported that the microdroplets of poly(dimethylsiloxane) (PDMS) spread slowly on a silicon wafer and a series of distinct molecular layers were observed at the spreading front, which is defined as “terrace-like” flow.24 However, to date, only macroscopic spreading of ILs on mica has been studied, and there has been no report on the spreading of IL nanodroplets.25 Here, we report the first experimental results on the spreading of the IL nanodroplets on the mica surface. AFM results revealed a very slow spreading process, for example, up to ~30 h, in which the nanoscale IL undergoes the transition from a droplet to a “pancake”. Interestingly, although IL nanodroplets show a
random layering structure, no terrace-like flow has been observed.

**RESULTS AND DISCUSSION**

1-Butyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate (BMIM-FAP) was applied on the mica via dip-coating at a relative humidity (RH) of ~20% at room temperature. The topography of the sample was characterized by AFM as a function of time, and the results are shown in Figure 1. Initially, many IL droplets, with a height of ~40 nm and a diameter of ~800 nm, were observed, which is consistent with previous reports. Recently, on the basis of the experimental results of both AFM and attenuated total reflectance Fourier transform infrared spectroscopy, Gong et al. proposed that the water adsorption on the mica promotes the extended layering of ILs on the solid surface, whereas dewetting of ILs, that is, droplets, occurs when the water is removed from the mica surface. They proposed a “water-enabled surface charging” mechanism to explain the finding. Because ILs have low dielectric constants, they do not dissolve and mobilize K⁺ ions on the mica surface effectively. As a result, ILs cannot induce the charging on the dry mica surface. However, when water, which has a high dielectric constant, is adsorbed on the mica surface, K⁺ ions will be dissolved and then leave the mica surface. Therefore, the wet mica surface will be negatively charged. Afterward, the cations of the IL take the “empty” site left by K⁺, initiating the alternative layering of cations/anions of the IL. As a result, on mica, the IL forms a layered structure at high humidity and shows droplets at low humidity. The finding here that BMIM-FAP showing nanodroplets at 20% RH is consistent with the proposed mechanism. Zhang et al. investigated the effect of water on the molecular structure of ILs on the mica surfaces with two different charge densities by MD simulations. They demonstrated that water changes the layering structure of IL ions next to the mica surface, as well as the lateral and orientation ordering. Cheng et al. performed AFM force–distance experiments and reported the bilayer formation of ILs at the charged mica surface in the presence of water. Meanwhile, they showed that the ILs are disordered at the low-charged surface in dry environments.

Interestingly, the nanodroplets gradually spread on the mica surface with time. As shown in Figure 1, the IL nanodroplets initially spread isotropically. However, once getting closer to each other, the droplets spread anisotropically. It should be noted that the tapping-mode AFM tip did not disturb the liquid molecular layers because we repeated the scanning of the morphology and did not observe any difference, which agrees well with Beattie’s and Liu’s reports. The central height profiles of one nanodroplet (droplet 1 as labeled in Figure 1), as a function of evolution time, are shown in Figure 2. It clearly showed that the droplet becomes a pancake after ~30 h. However, no terrace-like flow was observed. In a terrace-like flow, a monolayer will develop and flow on the substrate while the rest of the droplet stays still. After a certain time, the second monolayer will develop on top of the first one and flow while the rest of the droplet on top of the two monolayers stays still. With the evolution of the flow, a terrace-like structure will be formed. As shown in Figure 2, the BMIM-FAP nanodroplet flows like a bulk liquid, and there is no sign of terrace-like flow.

A typical AFM topography image during the spreading is shown in Figure 3. Interestingly, from the corresponding line profile of the nanodroplet, during the spreading, the IL showed a clear sign of layering structure as evidenced by the step-like feature with a thickness of either 1 or 2 nm, which corresponds to either a monolayer or a double-layer structure. In other words, although no terrace-like flow was observed, the IL nanodroplet does have a layered structure.

The layered structure of the BMIM-FAP nanodroplet is further demonstrated by the AFM image in the late stage, for example, after 40 and 49 h, of spreading as shown in Figure 4. Although, in most cases, the layering is not clearly visible (Figure 4d), the layering structure was still observed in some locations (as shown in the red arrows of Figure 4c) when these nanodroplets merge and form “uniform” (but porous) films.
The results indicate that the nanodroplets are composed of layers of IL molecules. Interestingly, many "holes" are observed as shown in Figure 4, which could be attributed to airborne hydrocarbon contamination and the resulting lower surface tension in the local area.

It is unclear why the IL nanodroplet has a layered structure but does not show terrace-like flow. One possible reason is that IL−mica attraction is too weak to initiate the flow of the bottom layer. Previously, Gong et al. showed that moisture is critical to the surface charging of the mica and the resulting mica−IL attraction. Only when the RH is high, for example, above ~50–60%, K⁺ on the mica will be dissolved and mobilized so that it will leave the surface of mica. As a result, the cation of the IL will occupy the empty site and initiate the layering of the IL. In the current study, RH is only 20%, and the water-enabled surface charging of mica will not occur. As a result, the IL−mica attraction is not strong enough for the flow of the monolayer to occur. However, the bulk-like liquid flow is still possible as evidenced by the results shown in Figure 2. Further research at various RH is required to uncover the governing mechanism.

Macroseale spreading of BMIM-FAP on the mica surface was also investigated by characterizing the time-dependent contact angles of BMIM-FAP on the mica. As shown in Figure 5, the contact angle is initially ~22°, decreases slightly within the first 5 min, and then stabilizes at around 17°. There was no significant change of the contact angle for up to 8 h afterward. Clearly, our AFM (Figures 1 and 2) and contact angle results indicate that the spreading kinetics of IL droplets at the macroscale and nanoscale is very different. The spreading is much slower, that is, two to three orders of magnitude, at the nanoscale. A possible mechanism is as follows. The solid-like layered structure of ILs at the IL−mica interface only extends to a few to tens of nanometers from the mica surface. Within this region, the mobility of the solid-like ILs is expected to be significantly lower than that of bulk ILs. The nanoscale droplets are within this region and therefore spread very slowly. For the contact angle tests of macroscale droplets, this nanoscale effect cannot be detected at all because of the resolution limit of the contact angle tester. Instead, the faster
spreading of macroscale droplets, which have the mobility of bulk ILs, is captured.

**CONCLUSIONS**

In conclusion, we characterized the spreading of IL nanodroplets at the IL–mica interface by AFM. Our results showed that a nanodroplet of IL spreads on the mica surface very slowly and eventually becomes a pancake. The result suggests that ILs confined to a solid surface have much lower mobility than the bulk phase; however, they are still mobile. As a result, the topography of the nanocapped IL is strongly dependent on time. Interestingly, although the IL nanodroplet shows a layered structure, no terrace-like flow of the droplet has been observed. This has been attributed to the weak mica–IL interaction at low humidity.

**EXPERIMENTAL SECTION**

**Materials.** A high purity grade (>99%) IL, BMIM-FAP (viscosity: 93 cP; mp: 3 °C), was purchased from EMD Millipore Corp. The BMIM-FAP was used as received. A good solvent for BMIM-FAP, 2,3-dihydrodecafluoropentane that is commercially known as Vertrel XF, was purchased from Miller-Stephenson Chemical Co. and utilized without further purification. Muscovite mica of grade V1 with a thickness of ∼1.5 × 2 cm. In each experiment, a razor blade was inserted into a mica sheet from the edge, and thus, two pieces of mica were produced.

**Sample Fabrication.** BMIM-FAP was dissolved in the Vertrel solvent at 1 g/L and then dip-coated on the mica according to a previously established procedure in our lab, with a KSV-DCX2 dip-coater staying on top of a Kinetic Systems vibration-free platform. The withdrawal rate of the mica was 60 mm/min.

**Characterizations.** Tapping-mode AFM images were obtained with a Veeco Dimension V system. The sample was imaged in soft tapping mode with an Olympus AC200TS silicon AFM probe (nominal spring constant: 9.7 N/m; resonance frequency: 115 kHz). The experiments were performed and characterized in a clean room to avoid humid air contamination from the ambient atmosphere. The static contact angle of BMIM-FAP on the mica surface was measured using a VCA Optima XE contact angle tester at room temperature and an RH of ∼20%.

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**Notes**
The authors declare no competing financial interest.

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