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Liquid- or Solid-Like Behavior of [omim][BF₄] at a Solid Interface?

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ABSTRACT: The objective of this work is to clarify the nature of the lamellar structure reported by several authors for ionic liquids at solid interfaces. The ionic liquid 1-methyl-3-octylimidazolium tetrafluoroborate, [omim][BF₄], has been deposited on a solid aluminum substrate from ethanol solutions and the resulting interfacial structure was investigated using atomic force microscopy imaging. The results have been analyzed using supplementary structural data obtained by molecular dynamics simulations. The main conclusion is that the behavior of the IL films is strongly dependent on time and concentration of the IL in solution. After 100 h of equilibration, the structure of the film changes as the concentration of the film-forming solution increases, reaching a sponge-like structure. At the concentration of 0.5 mg/mL, there is a drastic increase in the film maximum peak height that remains constant as the concentration further increases.

SECTION: Surfaces, Interfaces, Catalysis
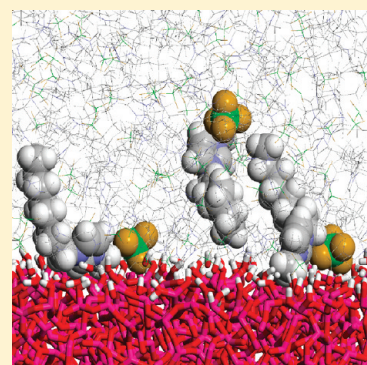
The study of solid/liquid interfaces involving ionic liquids is relevant for those applications where ILs are used as thin films deposited on solid surfaces, such as in lubricancy, micro-electromechanical or microelectronic devices, electrochemistry and heterogeneous catalysis. Despite the need for a correct characterization of those interfaces at a molecular level, the amount of research in this area is still scarce and, sometimes, controversial.

Previous studies are based on sum-frequency vibrational spectroscopy (SFVS),[1] X-ray reflectivity,[2] atomic force microscopy (AFM),[3−6] and molecular simulations.[3,7,8] All authors have found that the presence of a surface in contact with the ionic liquid induces the formation of a lamellar structure parallel to the solid substrate surface, but the nature of these layers is still unclear. Some studies suggest that at room temperature the ionic liquids are present as coexisting liquid and solid phases anchored at the interface.[3,5] Other studies[4] indicate that ILs form a disordered sponge-like structure at the solid/liquid interface, with no evidence of solid-like phases.

Bovio et al.[3] used AFM to image 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([bmim][Tf₂N]) films deposited on silica, mica, and graphite by drop-casting from highly diluted methanol solutions (<1 × 10⁻³ mg/mL) and found layered terrace-like structures on silica and mica. In contrast, the uncharged graphite surface did not yield any type of layering. The flat terraces and sharp steps together with their rigidity over long time suggested that those structures were solid-like. However, molecular dynamics simulations performed by the same authors[9] for a [bmim][Tf₂N] film on silica led to a different conclusion: the density modulation of the simulated samples decayed into an approximately homogeneous and fluid-like density distribution around 2 nm from the solid interface.

Wang et al.[7] studied the behavior of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) and 1-methyl-3-octylimidazolium hexafluorophosphate ([omim][PF₆]) at an uncharged graphite surface using molecular dynamics simulation and found that the density of IL is greatly enhanced near the interface, and the density oscillations (corresponding to three layers) extend to ∼1.5 nm into the bulk liquid. They also demonstrated that the interfacial region has a network structure formed by polar and nonpolar domains.

Hayes et al.[4] used AFM force plots to study the structure of pure ILs near solid surfaces. The stepwise force profiles indicated a lamellar structure whose step widths are in excellent agreement with the predicted ion pair diameters (0.53 to 0.79) nm. In particular, the interfacial ordering of [bmim][PF₆] on mica is particularly pronounced, and six solvation layers were observed. These authors have claimed that the sponge-like structure of the bulk ionic liquid, where the ions form a network of polar and nonpolar domains due to electrostatic and solvophobic clustering of similar molecular groups, transforms at the interface into a lamellar phase that eventually decays into the bulk sponge-like structure. No evidence of an IL solid-like phase at the IL/substrate interface has been found by these authors. Liu et al.[5] observed liquid drops on top of fluid layers when depositing [bmim][PF6] films on mica from 8 × 10⁻² mg/mL solutions, but, when the concentration was reduced, the layer underneath became ordered in some areas showing solid-like features, which indicates the coexistence of liquid and solid phases.
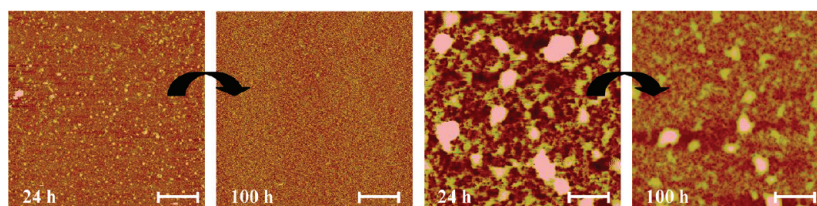
Figure 1. AFM topographic images of [omim][BF4] films on an Al-sputtered silicon wafer recorded at 24 and 100 h after film deposition. The films were obtained by spin-coating deposition of 0.125 (left figures) and 2.5 mg/mL (right figures) IL solutions. Scale bars: 5 μm.
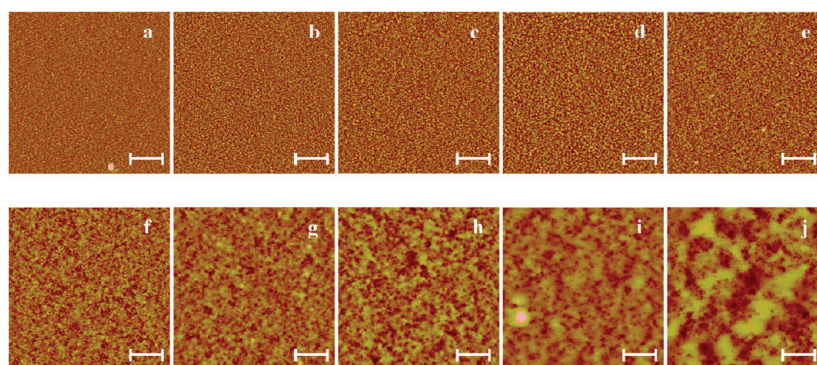

Figure 2. AFM topographic images of [omim][BF4] films on Al-sputtered silicon wafers recorded 100 h after spin-coating deposition of different IL/ethanol solutions with increasing concentration: 0 (a), 0.062 (b), 0.125 (c), 0.25 (d), 0.5 (e), 1.0 (f), 1.25 (g), 1.5 (h) 2.0 (i), and 2.5 mg/mL (j). Scale bars: 1 μm.

Yokota et al.[6] applied frequency-modulation AFM to the interfaces of [bmim][Tf$_2$N] and [bmim][BF$_4$] with two substrates of highly oriented pyrolytic graphite (HOPG) and mica and observed that step-terrace structures were formed at the interfaces. The mean values of step heights depended on the substrate, and for the IL/HOPG interfaces they were in good agreement with the ion pair diameters. In contrast with Hayes, these authors claimed that the nature of the layered structures was solid-like, taking into account their high stability.

In the present work, we characterize wetting films of 1-methyl-3-octylimidazolium tetrafluoroborate ([omim][BF4]), a room-temperature ionic liquid with surfactant properties due to the length of the side chain of the imidazolium ring. The wetting films were obtained by spin coating from ethanol solutions. Several substrates were attempted, namely, silicon, boro-silicate glass, and aluminum, but only the latter was wetted by the IL. The IL films deposited on Al-coated silicon wafers were studied using AFM. The main goal of our study is to investigate the influence of the concentration of the IL solution on the interfacial structure trying to explain the apparent contradiction between the results obtained with IL films deposited from highly diluted solutions and those relative to pure ILs.

First, we investigated the time dependence of the film structure by imaging the films at 24 and 100 h after being produced. They were kept at room temperature inside a desiccator containing silica gel. Figure 1 shows images of those films deposited with solutions of concentrations 0.125 and 2.5 mg/mL. After 24 h, liquid droplets are observed on top of a layer for the films obtained with both concentrations. At the end of 100 h, drops are reduced in number and decreased in size for the higher concentration and spread completely for the lower concentration.

Figure 2a–j shows a collection of representative AFM images of IL films obtained from solutions of increasing IL concentration

after 100 h of film deposition. The drop-on-the-layer behavior observed for the films obtained with the more concentrated solutions (Figure 1) is not visible in these images because they were obtained in areas free of drops. These drop-free areas, calculated from image analysis, represent ca. 94 and 92% of the total surface area, respectively, for the concentration of 2 and 2.5 mg/mL.

The films obtained with much diluted IL solutions (concentrations <0.5 mg/mL) are almost indistinguishable from the columnar structure of the bare Al-substrate (Figure 2a). These images clearly demonstrate the absence of any reaction at the Al/ionic liquid interface.

For IL concentrations $\geq$0.5 mg/mL, films present a sponge-like structure, which changes continuously with increasing concentration. The same pattern seems to be repeated on larger scales to produce irregular shapes as the concentration of the film-forming solution increases. A fractal-type structure characterized by three characteristic heights (corresponding to the dark brown, light brown, and green areas) may be identified in Figure 2f–j. The total height difference between the lowest (dark brown) and highest levels (green) was found to vary between 6 and 8 nm and seems to be independent of the concentration of the film-forming solution. (For concentrations <0.5 mg/mL, the small size of the heterogeneities does not allow any quantification.) The thickness of the innermost step (between 3 and 4 nm) corresponds to four to five layers of 0.75 nm (ionic pair diameter) each. This diameter was calculated by taking the cube root of the molecular volume, which assumes a cubic packing geometry, as described by Horn et al.[10]

The films were further characterized through the determination of the roughness parameters R_q (root-mean-square roughness) and R_{max} (maximum peak height) in 2 $\times$ 2 μm^2 sections of 25 $\times$ 25 μm^2 AFM scans performed 24 and 100 h after the film formation. (See Figure 3.)
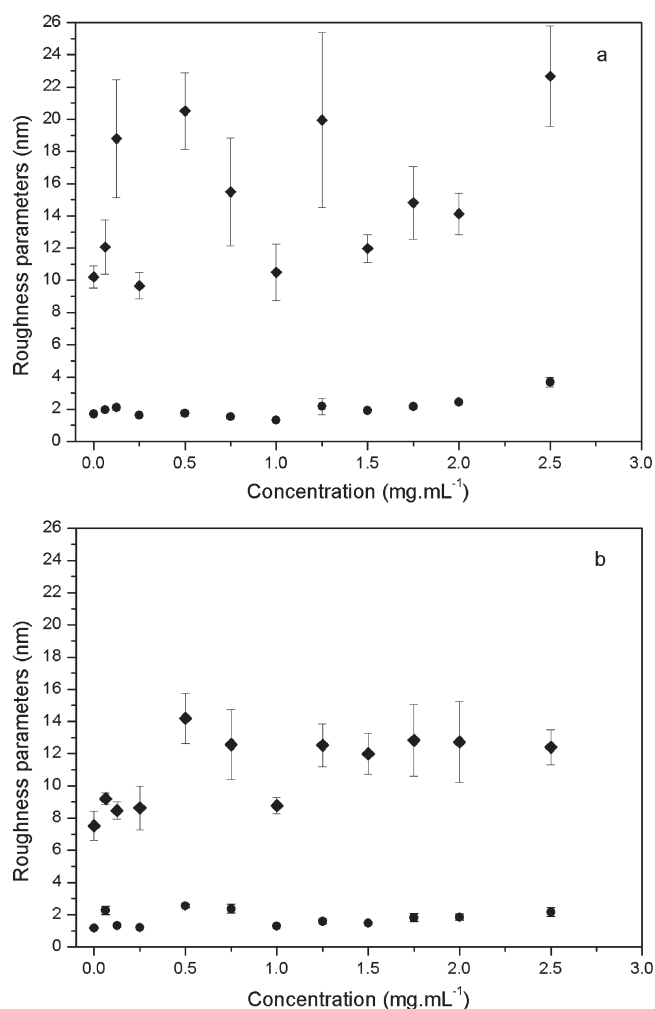
Figure 3. R_q (●) and R_{max} (◆) of the films as a function of the concentration of the film-forming IL/ethanol solutions. The data were obtained 24 (a) and 100 h (b) after film formation in $2 \times 2\ \mu m^2$ sections of the $25 \times 25\ \mu m^2$ total area of the AFM scans.

Figure 3a shows a random distribution for the R_{max} values obtained 24 h after film formation with large error bars, evidencing the presence of heterogeneous films far from equilibrium. R_{max} is higher for these films than for those equilibrated during 100 h (Figure 3b) at all concentrations, which is consistent with the spreading the liquid droplets initially present. In Figure 3b, two regimes may be identified for R_{max} if we neglect the point at 1 mg/mL: for film-forming solution concentrations lower than 0.5 mg/mL, the surface roughness is similar to that of the bare Al substrate; around 0.5 mg/mL, a sharp increase of R_{max} occurs and a plateau is reached for higher concentrations. This trend is in agreement with our previous observation that the total height difference between the lowest and the highest levels on the images for IL concentrations larger than 0.5 mg/mL does not change with concentration of the spin coated solutions.

To complement the experimental determinations, we have performed molecular dynamics simulations using [omim][BF$_4$] over alumina. Details concerning IL/solid substrate modeling and the implementation of explicit-surface simulations can be found elsewhere.[11] The choice of alumina (aluminum oxide) instead of pure aluminum metal to model the solid substrate in

contact with [omim][BF$_4$] was based on the fact that the sputtered aluminum atoms at the silicon wafer surface will promptly undergo a passivation process forming an alumina layer. Alumina surfaces are generally hydrophilic because of the presence of surface hydroxyl groups.

Molecular dynamics modeling of silica or alumina explicit surfaces have shown[12] that, whereas the net charge is generally negative, charge is not evenly distributed at the surface, causing the existence of positively and negatively charged domains (Figure 4b bottom). It must be stressed that most surfaces based on amorphous materials (like an alumina layer forming at a sputtered aluminum surface) will typically exhibit nonuniform distributions of atoms at the surface, a fact that originates the above-mentioned charge fluctuations (domains) throughout the surface.

Simulation of the ionic liquid over the amorphous substrates has also shown that the first layer of ionic liquid has a nonuniform ion distribution that is a mirror image of the solid surface: the head groups of the ionic liquid cations preferentially adsorb near the negative domains of the substrate and the ionic liquid anions preferentially adsorb near the positive domains (Figure 4b, top). Such reorganization of the ionic liquid at the substrate surface demonstrates the importance of the electrostatic interactions for the adsorption process: the charged domains of the substrate are used as a template for the arrangement of the ionic liquid ions. The net charge of this first ionic liquid layer should have a sign opposite to the surface net charge. In other words, the ion distribution in this first ionic layer will be such that the intensities and distances of the first peaks in the cation and anion density profiles normal to the surface will be only slightly different (Figure 4d). Right above this first ionic layer there will be a region containing the (interdigitated) nonpolar side-chains of the cations (Figure 4e). These results seem to be consistent with the SFVS data on the structure and orientation of [omim][BF$_4$] at the silica interface, which indicated that both the imidazolium ring and the alkyl chain are slightly tilted from the perpendicular to the surface, with the ring near the surface and the alkyl chain further away from it (Figure 6 of ref 1).

This structural layering of the ionic liquid induced by the substrate surface will be repeated because the distance to the solid increases and the distance between layers (that can be inferred from the distance between the density peaks of the anion, cf. circles in Figure 4d) is ∼0.75 nm, in agreement with the previously reported value for the ionic diameter. However, our results show that in the present case the number of layers is very small and that after the first well-defined strongly adsorbed layer the structure/composition of the ionic liquid "decays" very rapidly to that of the bulk ionic liquid. (The density profile of the anion seems to support the presence of around four to five ill-defined layers.) The simulation data are compatible with the AFM images, which do not show evidence of strong layering at the solid interface.

The effect of the IL concentration may be summarized as follows. When the concentration of the IL solution is very low, the films are so thin that they cannot be differentiated from the underlying Al-substrate. The fact that we did not observe solid-like terraces with sharp edges on these films may result from the roughness of the Al substrate that, although small, is certainly higher than that of atomic smooth mica. When the concentration increases, the liquid-like behavior becomes very clear.

In conclusion, our results relating to IL films obtained with a large range of concentrations (0.06 to 2.5) mg/mL filled the gap
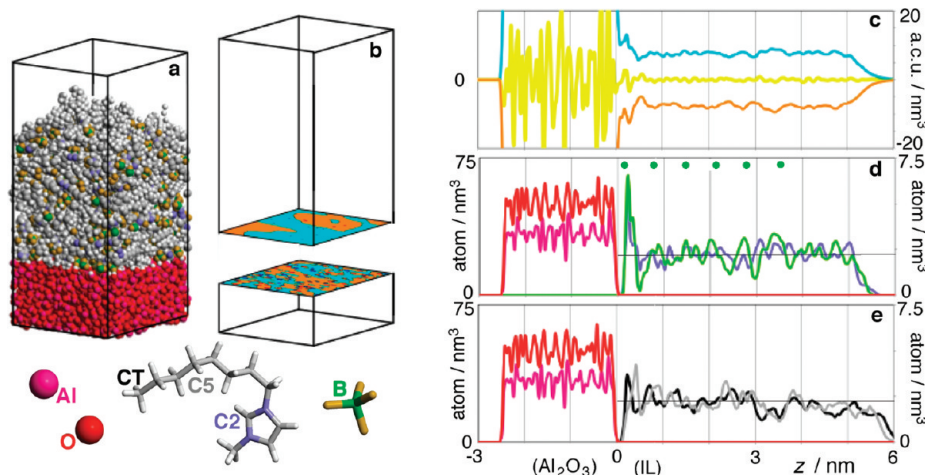
Figure 4. Schematic representation of the molecular dynamics simulation results of [omim][BF$_4$] over alumina. (a) Snapshot of the simulation box and (b) electric field (cyan, positive; orange, negative) at the silica—IL interface produced by the glass (bottom) and by the ionic liquid (top). The ionic liquid ions generate an electrical field that is an approximate mirror image of the charged domains present at the alumina surface. (c—e) Charge— and atom—density profiles along the direction normal to the surface (z). In part c, the total charge—density fluctuations (yellow) are much larger in the glass and induce the organization of the ions of the ionic liquid at the interface. Ionic liquid layering can be rationalized in terms of the density fluctuations of selected atoms of the system (d and e) (aluminum, pink; oxygen, red; boron, green; imidazolium C2 carbon, purple; octyl terminal CT carbon, black; octyl intermediate carbon (C5 from the ring), gray). The green circles in part d highlight the position of the peaks corresponding to the [BF$_4$]$^-$ anion.

between those obtained with IL films deposited from highly diluted solutions[3,5] and those relative to pure ILs confined between an AFM tip and the surface.[12] Solid-like behavior or solid—liquid coexistence was found in the former case, whereas liquid-like lamellar structures were observed in the latter. Only the results of Yokota,[6] who found solid-like behavior at the bulk IL—solid interface, are in contradiction with the reported data.

It now seems clear that on the same surface liquid-like structures, coexisting liquid and solid phases, and solid-like structures may be formed depending on the concentration of the IL solution used to form the film, the time passed after the film formation, and, obviously, the nature of the substrate and of the ionic liquid components.

EXPERIMENTAL SECTION

The [omim][BF$_4$] ionic liquid was purchased from Solchemar with purity >98%. The purity of the ionic liquid was checked by NMR after the synthesis. The water content, checked by Karl Fischer, was ∼344 ppm, and chlorine content, determined with a selective Cl-electrode, was <50 ppm. The ionic liquid is manipulated in a dry nitrogen atmosphere.

Silicon wafers, 0.8 mm thick, (Siltronic) and boro-silicate BK7 glass disks, 12.5 mm in diameter and 3 mm thick (Melles Griot), were used as substrates. The Al surfaces were obtained by coating 1 × 1 cm^2 pieces cut from Si wafers. The silicon wafers were cleaned using a basic RCA procedure:[13] NH$_4$OH/H$_2$O$_2$/H$_2$O (1:1:5) at 70 °C for 10 min. Then, after 30 min of rinsing in ultrapure water, they were stored in water. For coating, the wafers were dried with nitrogen and mounted in the vacuum chamber (pressure of 10^{-6} bar) of the deposition device (Edwards). After 5 min of evaporation and 30 min for equilibration, the samples were ready. The thickness of the Al coating was determined with an internal quartz crystal microbalance (QCM) to be 30 nm. The Al substrates were kept inside a laminar flow chamber and used within ca. 1 to 2 h after preparation. The glass disks were washed

in a detergent solution, rinsed successively with water, ethanol, and distilled and deionized water and dried according to the procedure described for the silicon wafers. Immediately before use, the glass substrates were submitted to 5 min of argon plasma cleaning.

The "static" contact angles were measured at room temperature by the sessile drop method with a Ramé—Hart goniometer, and the image analysis was done using the axisymmetric drop shape analysis software (ADSA). The contact angles of [omim][BF$_4$] on glass, silicon wafers, and Al substrates are 19, 23, and 4°, respectively.

Films of [omim][BF$_4$] were deposited by spin-coating at 3000 rpm during 60 s from ethanol (99.5% purity grade) solutions with concentrations that varied between 0.06 and 2.5 mg/mL. After deposition, the samples were transferred to a desiccator containing silica gel where they were kept until being imaged. Deposition of IL films was attempted on glass and silicon wafers, but macroscopic droplets spontaneously form upon evaporation of ethanol, which is consistent with the higher contact angles measured on these surfaces. We decided then to restrict our investigation to Al substrates.

The AFM Nanoscope Multimode (Veeco) was operated in tapping mode inside a room with temperature and humidity control. Monolithic silicon tips Nanoworld, type Arrow NCR-W, with a resonance frequency of ca. 285 kHz and a spring constant of 42 N/m were used. The tip height ranges from 10 to 15 μm, and the tip curvature is <10 nm. The roughness parameter, R_a, of the Al substrates determined in 2 × 2 μm^2 sections of 25 × 25 μm^2 AFM scans is ca. 0.9 nm.

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