

Effect of solid substrates on the molecular structure of ionic liquid nanofilms

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KEYWORDS: ionic liquids, nanofilm, layering, interface

ABSTRACT: Fundamental understandings of the interfacial molecular structure of solid-confined ionic liquids (ILs) have significant impacts on the development of many cutting-edge applications. Among the extensive studies on the molecular structure at the IL/solid interface, direct observation of a double-layering quantized growth of $[C_n\text{mim}][\text{FAP}]$ on mica was recently reported. In the current work, the atomic force microscopy (AFM) results directly show that the growths of $[\text{Bmim}][\text{FAP}]$ nanofilms on silica and amorphous carbon are different from the double-layering growth on mica. The growth of $[\text{Bmim}][\text{FAP}]$ nanofilms on silica is dominated by the aggregation of the IL molecules, which can be attributed to the inadequate negative charging of the silica surface resulting in a weak electrostatic interaction between silica and the IL cation. $[\text{Bmim}][\text{FAP}]$ on amorphous carbon shows a fairly smooth film for the thinner nanofilms, which can be attributed to the π - π^+ parallel stacking between the cation imidazolium ring and the randomly distributed sp^2

carbon on the amorphous carbon surface. Our findings highlight the effect of different IL/solid interactions, among the several competing interactions at the interface, on the resulting molecular arrangements of various IL.

1. INTRODUCTION

Ionic liquids (ILs) are molten salts that are in the liquid state at room temperature (RT). They are usually made of organic cations and organic or inorganic anions with bulky and asymmetric conformations. As a result, the electrostatic force and the lattice formation are dampened, leading to the low melting point.¹⁻⁴ Since the successful synthesis of air- and water-stable ILs, ILs have attracted a great deal of academic and industrial research interest due to their exceptional physiochemical properties, and ILs with a variety of chemical structures have been designed, synthesized, and studied.⁵⁻¹² Among all the booming applications of ILs, the IL/solid interface is particularly important to the revolution of many cutting-edge applications, e.g., media lubricants in the data storage industry,¹³⁻¹⁶ additives for engine lubrication,¹⁷⁻¹⁹ gas separation and carbon capture media,²⁰⁻²² green electrocatalysis,²³⁻²⁵ and battery electrolytes.²⁶⁻²⁹ Fundamental understanding of the interfacial molecular structure of ILs is critical to the performance of solid-confined ILs.

Previous surface force apparatus (SFA), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR), and computational studies indicate that solid-confined ILs present as solid-like molecular layers on a variety of solid substrates, including mica, gold, sapphire, silica, amorphous carbon, graphite, etc.^{1, 30-43} Specifically, tapping mode AFM and non-contact mode AFM have been used to characterize the surface morphology of solid-confined ILs because of their negligible disturbance to the films and universality of solid

substrates. However, consistent experimental results and the underlying mechanisms of IL molecular structure when confined on various solid substrates are yet to be achieved. For instance, Gong et al. studied the change of film topography with increasing thickness for DMPIIm on silica.³⁰ They observed a transition from a smooth layered structure to a rough drop-on-layer structure as a result of the competing IL/solid attraction and IL cohesion. Meusel et al. investigated the growth of [Mmim][NTf₂] layers on Au(111) by physical vapor deposition (PVD). Alternating cations and anions in a checkboard arrangement were observed within the first wetting layer due to the attractive interaction between the IL ions and the respective image charges from Au(111).^{36,43} Liu et al. studied the interfacial structure of [Bmim][PF₆] on mica and detected the coexisting liquid-like nanodroplets and solid-like layers.⁴⁴ Later, Bovio et al. extended the work by Liu et al. and studied the interfacial structures of [Bmim][NTf₂] on mica, amorphous silica, oxidized Si(110), and highly oriented pyrolytic graphite (HOPG).⁴⁵ On mica, silica, and oxidized Si(110), they observed solid-like layering structures with the height of the stacking terraces up to 50 nm, while liquid-like nanodroplet domains were observed on HOPG.

Among the extensive studies on the molecular structures at the IL/solid interfaces, Wang et al. recently reported direct observation of a double-layering quantized growth of [C_nmim][FAP] (n = 2, 4, 6) on mica under tapping mode AFM.⁴⁶ At the start of the nanofilm growth process, IL was observed to grow on more mica surface areas at the constant thickness of 2 monolayers (ML). Then at a critical growth stage, the film thickness increased discontinuously by 2 ML. Afterward, the overall film thickness remained constant at 4 ML. Based on the observed minimum building block of 2 ML, Wang et al. proposed a double-layering interfacial molecular structure of IL cations and anions on mica. The unique quantized growth was attributed to the competition of multiple interactions at the interface, including the electrostatic interaction between the IL cation and the

intrinsically negatively charged mica surface, the electrostatic interaction between the IL cation and IL anion, and the solvophobic interaction.

Here, our AFM results directly show no double-layering growths of [Bmim][FAP] nanofilms on silica and amorphous carbon. Instead, the growth of [Bmim][FAP] nanofilms on silica is determined by the aggregation of the IL molecules because of the weak negative charging on silica, and consequently, the weak silica/cation electrostatic interaction. For [Bmim][FAP] confined to amorphous carbon, a fairly smooth film growth has been observed for the thinner nanofilms due to the π - π^+ stacking between the cation imidazolium ring and the randomly distributed sp^2 carbon on amorphous carbon. The results highlight the effect of the IL/solid interactions on the IL interfacial molecular structure.

2. EXPERIMENTAL SECTION

Materials

The IL studied was 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([Bmim][FAP], $\geq 99.0\%$), which contains a cation imidazolium ring and was acquired from Millipore Sigma. [Bmim][FAP] has exceptional hydrophobicity, and it can be readily dissolved in 2,3-dihydrodecafluoropentane (trademark as Vertrel XF by Chemours, purchased from Fisher Scientific, and used as received) to make dilute solutions.¹⁵ The vapor pressure of Vertrel XF is 30.1 kPa (0.297 atm) at 25 °C. The molecular structures of [Bmim][FAP] and Vertrel XF are shown in Figure 1. Muscovite mica substrates (highest grade V1) were purchased from Ted Pella. Fresh and clean mica substrates were made before usage by cleaving from the edge with a sharp-pointed tweezer. Silicon wafers (2" P/B <1-0-0> 1-10 ohm-cm) were purchased from

WaferPro and pretreated by a BioForce Nanosciences UV/Ozone Procleaner for 10 minutes before usage to remove hydrocarbon contaminations. The amorphous carbon substrates used were carbon overcoat (COC) that were acquired from Seagate. The surface is composed of an amorphous carbon film with sp^2 and sp^3 hybridization ($\sim 70\%/30\%$) fabricated by PECVD. Figure S1 shows the AFM images and the corresponding line profiles of the bare surfaces of mica, silica, and amorphous carbon.

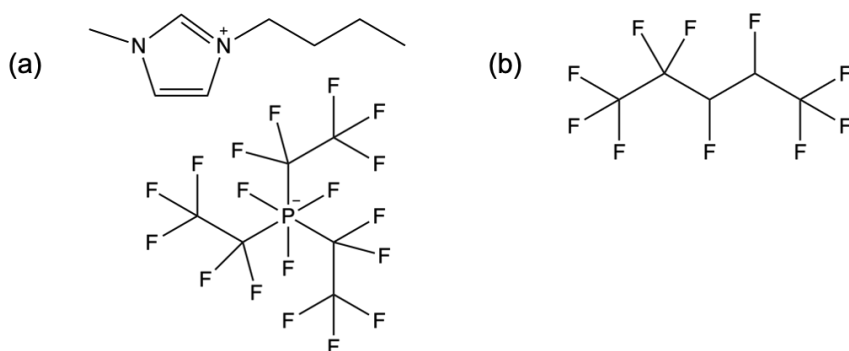


Figure 1. Chemical structures of (a) [Bmim][FAP] and (b) Vertrel XF.

Methods

IL nanofilms on solid substrates were fabricated by dipcoating using a KSV Instruments dipcoater. During the thin film fabrication processes, solid substrates were vertically dipped into and withdrawn from the dilute IL solutions at the speed of 1 mm/second.⁴⁷⁻⁴⁸ As a common solvent in the hard disk drive industry, Vertrel XF evaporates instantly and completely after dipcoating. As the nanofilm thickness trends with the concentration of the [dipcoating solution](#), various stages of the nanofilm growth were realized by fabricating the IL nanofilms

independently using solutions with a sequential increase in concentration.^{13, 15-16} The thicknesses of IL nanofilms on silica and amorphous carbon were measured by ellipsometry using a J.A. Woollam alpha SE spectroscopic ellipsometer at the incident angle of 70°. Before dipcoating, native oxide thicknesses were first determined for bare silicon wafers, and the optical constants of the bare amorphous carbon surfaces were first determined using the B-Spline model. The thicknesses of the IL nanofilms on the solid substrates after dipcoating were determined using the Cauchy dispersion model.⁴⁸ Tapping mode AFM was used to characterize the surface topography of the IL nanofilms on the solid substrates. The scans were conducted using a Veeco Dimension V Scanning Probe Microscope at the scan size of 10 μm by 10 μm and the pixel density of 256 by 256, and the AFM probe used was a MikroMasch NSC14/AL BS probe (160 kHz resonance frequency, 5.0 N/m force constant, 8 nm tip radius). All experiments were performed at RT.

3. RESULTS AND DISCUSSION

Nanofilm growth on silica and amorphous carbon

Double-layering quantized growth of the mica-confined $[\text{C}_n\text{mim}][\text{FAP}]$ ($n=2, 4$, and 6) nanofilms, which results from the competition among several interactions at the interface between ILs and mica, has been recently reported.⁴⁶ As the nanofilm grows, the film thickness remains constant at 2 ML as the film covers more mica surface for nanofilms fabricated from the concentration lower than 0.75 g/L by dipcoating. Then for the transition from 0.75 g/L to 1 g/L, the thickness increases discontinuously by 2 ML. However, similar double-layering interfacial molecular structure of ILs is not observed for $[\text{Bmim}][\text{FAP}]$ on silica and amorphous carbon.

The film topography (and the corresponding line profiles) from AFM and the average film thickness from ellipsometry for [Bmim][FAP] nanofilms on silica at various film growth stages are shown in Figure 2a and Figure 2b, respectively. The three-dimensional (3D) AFM images of [Bmim][FAP] nanofilms on silica in Figure S2 also illustrate the topography evolution at various stages of film growth with the 3D projections of the surface topography. Table S1 also lists the conversion of mass concentrations to molar concentrations for IL dipcoating solutions at various film growth stages. The average film thickness increases linearly with the IL concentration from 0.5 g/L to 2 g/L, whereas distinct film topographies are observed at various film growth stages. At the initial stage of IL film growth on silica, fairly smooth nanofilm with no distinct layering feature has been observed for the nanofilm fabricated from the 0.5 g/L solution at the scan size of 10 μm by 10 μm and the vertical scale of 10 nm, while the average film thickness is measured as 0.44 nm by ellipsometry. By reducing the scan size to 2 μm by 2 μm , which increases the lateral resolution by 5 times, and by reducing the vertical scale to 2 nm, tiny and discrete IL spikes with the height oscillating at 0-1 nm are revealed. Assuming [Bmim][FAP] molecules are cubic, the edge length can be calculated with the bulk density ρ of 1.63 g/cm³ at RT, the molar weight M of 584.23 g/mol, and the Avogadro constant N_A by $\sqrt[3]{\frac{M/N_A}{\rho}}$. The monolayer thickness of the [Bmim][FAP] nanofilms roughly equals the 0.841 nm edge length, so the heights of the observed IL spikes randomly oscillate below 1 ML. This nanofilm topography of tiny spikes on silica is very different from the nanofilm topography on mica with the double-layering building block at the same stage of film growth. While the first double-layering quantized growth of [C_nmim][FAP] on mica occurs at the concentration increase from 0.75 g/L to 1 g/L, the first dramatic topography change for [Bmim][FAP] on silica occurs at an earlier film growth stage. As the concentration increases from 0.5 g/L to 0.75 g/L and the average thickness increases to

0.58 nm, IL aggregates into thicker and bigger islands on silica. The local thickness of the nanofilm is not uniform, and the maximum local thickness is ~ 3.5 -4 nm, equivalent to the thickness of ~ 4 ML. As the concentration continues to increase to 1 g/L and then 1.25 g/L, the IL nanofilms connect into bigger and thicker islands. The nanofilms are not uniform either, and the maximum local thickness increases slightly to ~ 4 -4.5 nm, equivalent to the thickness of ~ 5 ML. As IL covers more silica surface at the concentration of 1.5 g/L, the nanofilm further develops into a more uniform film, which looks like a thin sponge, with slightly reduced local thickness. All the aforementioned nanofilms were fabricated under relative humidity (RH) $> 24\%$. Eventually, for the IL nanofilm fabricated from the 2g/L solution under 44% RH, a sponge-like film with the local thickness of ~ 5 ML can be observed. However, nanodroplets with irregular geometries are observed instead for the 2 g/L IL nanofilm fabricated under 18% RH (Figure 2c). As labeled by the dashed lines at the specific cross-section of the enlarged $2\ \mu\text{m}$ by $2\ \mu\text{m}$ scan, a ~ 5 ML-tall nanodroplet layer rests on top of another ~ 5 ML-thick bottom layer.

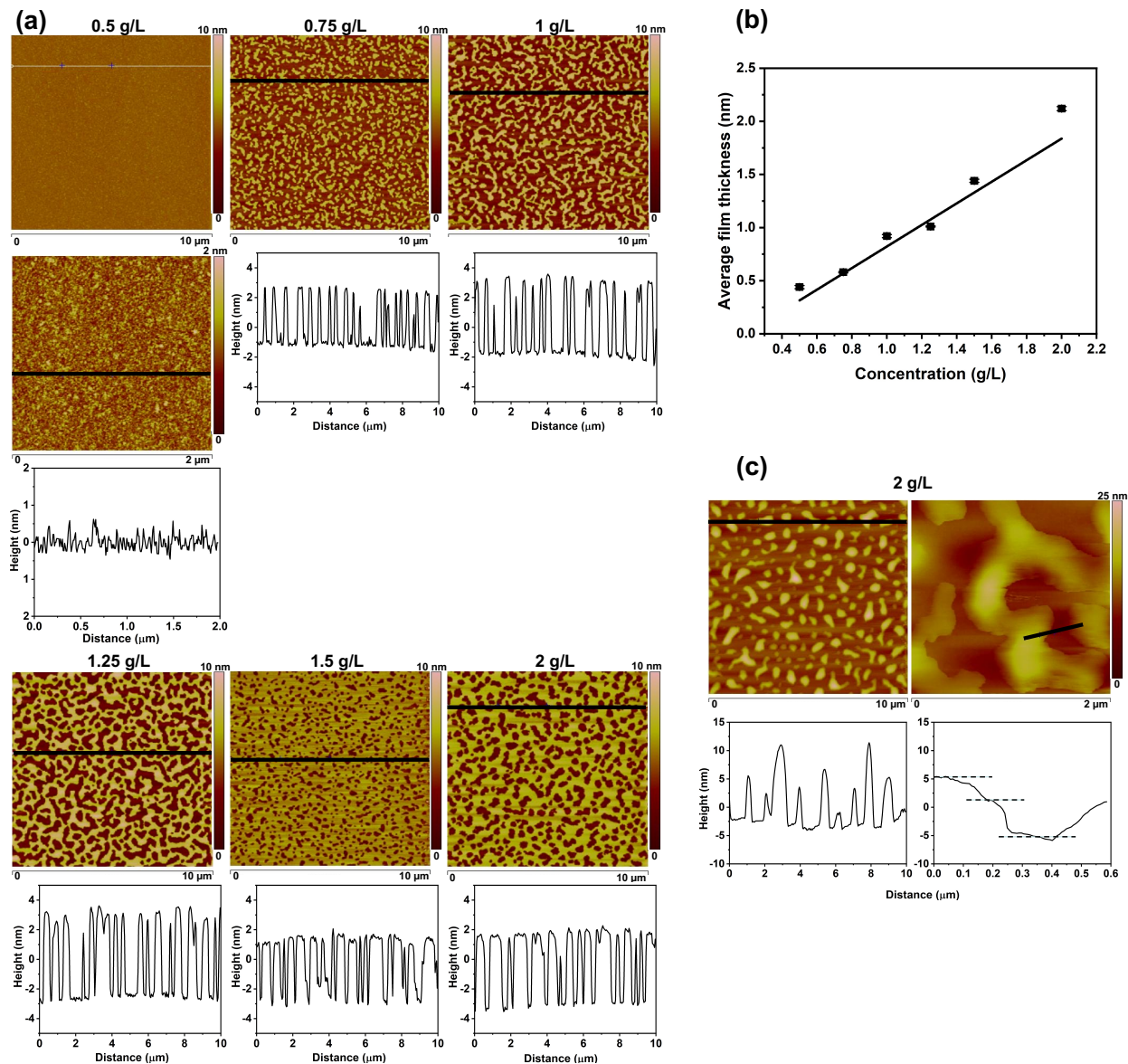


Figure 2. (a) AFM images and their corresponding line profiles of [Bmim][FAP] nanofilms on silica at various growth stages. The x-axis and y-axis in the line profiles are the distance (μm) along the cut and the height (nm) across the cut, respectively. (b) Average film thickness of [Bmim][FAP] nanofilms on silica at various film growth stages from ellipsometry. (c) AFM images and line profiles of the [Bmim][FAP] nanofilm on silica fabricated from the 2g/L solution at low RH (18%).

The nanofilm growth behavior of [Bmim][FAP] on amorphous carbon is different from those on both silica and mica, which are in the modes of aggregation and double-layering growth, respectively. As shown in Figure 3, the nanofilm remains featureless with low surface roughness at the initial stages of film growth, i.e., nanofilms fabricated from the concentrations of 0.25 g/L to 1 g/L. The thickness results from ellipsometry¹⁵ (Figure 3) indicate the presence of the ultrathin IL films. Then for the 1.5 g/L and 2 g/L nanofilms, although they remain smooth, some tiny pores start to appear in the nanofilms. It is worth noting that the average film thickness measured by ellipsometry keeps increasing as the film grows, even when the nanofilm is smooth. Eventually, when fabricated from the 2.5 g/L solution, the nanofilm develops into a sponge-like film with the maximum local thicknesses of ~4-5 ML.

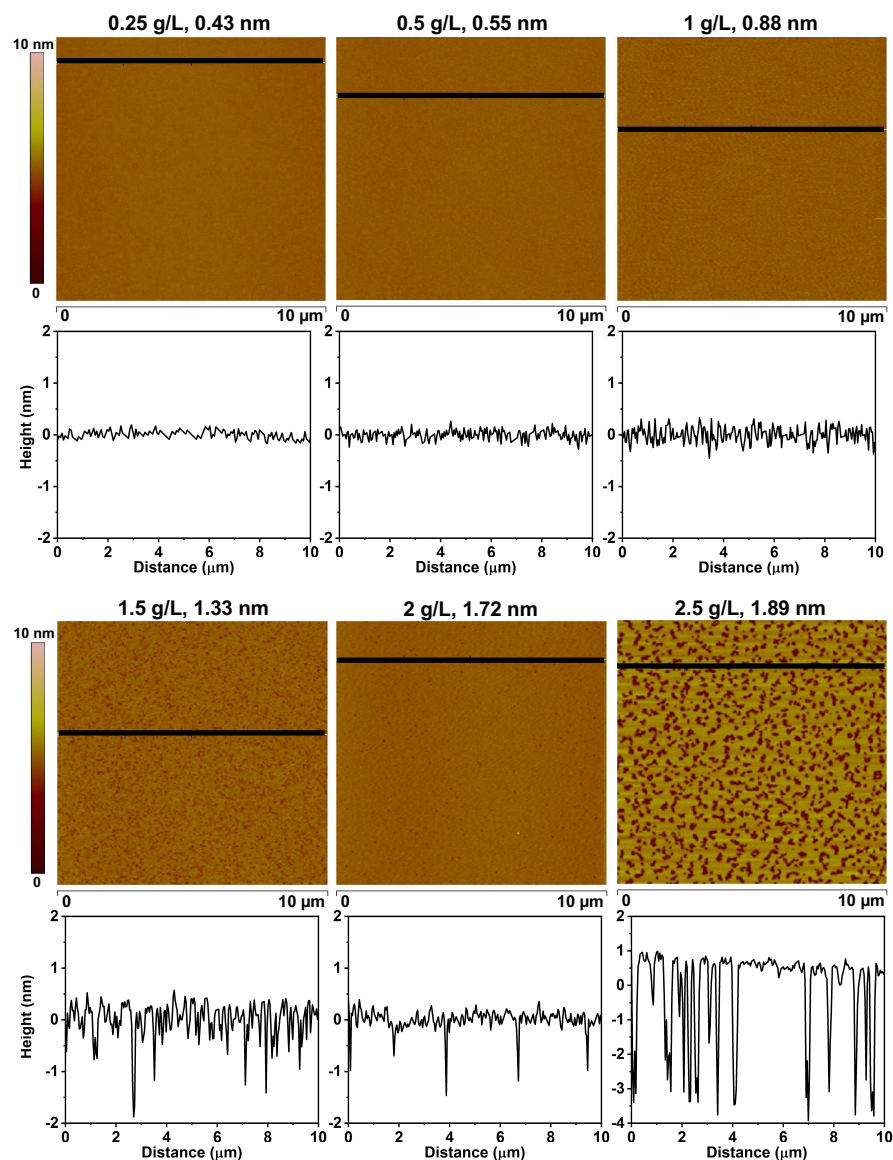


Figure 3. AFM images and their corresponding line profiles of [Bmim][FAP] nanofilms on amorphous carbon at various growth stages. The x-axis and y-axis in the line profiles are the distance (μm) along the cut and the height (nm) across the cut, respectively. The thickness values in the subtitles are the average nanofilm thicknesses at various film growth stages from ellipsometry.

Discussions

The nanofilm morphology results from several competing interactions at the IL/solid interface, including interactions between solid and IL cation, electrostatic interactions between IL cation and anion, cohesive interactions between alkyl chains, etc. The only variable in the system of solid-confined [Bmim][FAP] nanofilms studied herein and previously⁴⁶ is the different solid substrates, i.e., silica, amorphous carbon, and mica as control.

The surface of freshly cleaved muscovite mica crystal is negatively charged with a charge density of one charge site within the average area of $\sim 0.47 \text{ nm}^2$.⁴⁹⁻⁵¹ It originates from the absorbed ambient water on the mica surface, which dissociates the surface K^+ due to the high dielectric constant of water and initiates the layering process of ILs.^{31, 52} The strong electrostatic force between the IL cation and the negatively charged mica surface, together with the electrostatic force between the IL cation and anion and the solvophobic force, lead to the double-layering quantized growth of [Bmim][FAP] on mica. Under lower RH, instead of layering nanofilms, IL nanodroplets have been observed on mica right after dipcoating, which is attributed to less absorbed water on mica and hindered dissociation of K^+ , and hence weaker solid templating.^{31, 46} For silica, the hydrogen bond formation between the ambient water molecules and the surface silanol groups drives water to absorb on the silica surface, and the intrinsic negative surface charging originates from the dissociation of silanol groups when in contact with water.⁵³⁻⁵⁶ Although the silica surface is also negatively charged, the charge density under neutral pH condition is only one charge site within the area of $\sim 20 \text{ nm}^2$, significantly lower than the mica surface charge.^{35, 53} The growth of [Bmim][FAP] nanofilms on silica is very different from the double-layering growing model of [Bmim][FAP] on mica with the thinnest nanofilm of 2 ML and the quantized film growth of 2 ML.⁴⁶ For the thinnest nanofilm on silica,

instead of the 2 ML-thick sponge-like nanofilm observed on mica,⁴⁶ tiny and discrete IL spikes with the heights randomly oscillating below 1 ML are observed. As the IL film continues to grow on silica, instead of the quantized increase in the film thickness by 2 ML and the following constant total thickness at 4 ML observed on mica,⁴⁶ IL directly aggregates into thicker islands with the maximum local thicknesses of ~4-5 ML. The islands then connect to rough sponge-like films at the constant maximum local thicknesses as the IL film further grows. This aggregation-dominating growing mode of [Bmim][FAP] on silica can be explained by the relatively weak negative charging of the silica surface. Unlike traditional molecular liquids, IL molecules in the bulk phase and in molecular solvents present heterogeneous local nanostructures with segregations of polar and nonpolar domains.¹⁻² The electrostatic force between the cation imidazolium ring and the anion drives the formation of polar groups, and the solvophobic force drives the self-assembly of the alkyl chains into nonpolar clusters.^{35, 51, 57} Since the negative charge density on silica is too low, the electrostatic interaction between the silica surface and the IL cations is too weak to induce a strong templating effect on the IL ions. The molecular structure of silica-confined [Bmim][FAP] behaves similarly to the bulk structure of [Bmim][FAP] molecules due to the preferable self-aggregation. Therefore, the IL nanofilms on silica that are fabricated from higher concentrations retain the island- and sponge-like aggregation structures at the maximum local thicknesses of ~4-5 ML (Figure 2a). Since [Bmim][FAP] is superhydrophobic due to its highly fluorinated anion,³¹ water is unlikely to play a role within the IL nanofilms [except for providing negative charging on the silica surface](#). The trace amount of absorbed water molecules on the silica surface remains within the vacancy between IL cations and silica. For mica-confined IL, on the other hand, the organizing effect of the solid template on the IL nanofilm structure dominates due to the strong electrostatic

interaction at the cation/mica interface, which induces the double-layering structure of IL cations and anion.⁴⁶ It is worth noting that the 2 g/L nanofilm on silica fabricated at low RH appears as nanodroplets with irregular geometries at the maximum height of ~10-15 ML (Figure 2c), similar to the nanodroplet structures for [Bmim][FAP] nanofilms on mica under low RH.^{31, 46} Less absorbed water on silica at low RH hinders the surface hydrolysis reaction, which results in less negative charging and weaker solid templating effect. Therefore, the overwhelming cohesion interactions within the IL molecules lead to the observed nanodroplet structures to reduce the total surface free energy. Similarly, it was previously reported that the friction of IL nanofilms is higher at lower RH presumably because of less water-rendered surface charging and more disordered cation/anion layering.¹⁴

While both the silica and the mica surfaces are negatively charged, the amorphous carbon surface is charge-neutral. It contains ~70% sp² carbon that is randomly distributed without long-range crystalline order. Besides, the surface hydrophobicity determined by the contact angle results in Figure S3 excludes the effect of absorbed water at the interface. Unlike on negatively charged mica and silica, neither aggregation nor double-layering quantized growth has been observed during the film growth processes on amorphous carbon, indicating a fairly smooth increase in the local film thicknesses. At the interface between IL and amorphous carbon, π - π^+ stacking interaction occurs between the delocalized π^+ electrons from the cation imidazolium ring and the localized π electrons from the sp² carbon on the amorphous carbon surface.^{15, 32} The random distribution of the sp² carbon in the amorphous carbon provides high conformational flexibility for the respective IL cations to arrange themselves and fill in vacant solid surface areas. The IL anions subsequently pack on the cation layer as a result of the electrostatic interaction between the IL ions to maintain electroneutrality.³² Therefore, [Bmim][FAP] forms

the lamella-like smooth parallel layering structure on amorphous carbon. The effective parallel packing and the randomly distributed sp^2 carbon contribute to the smooth growth of the thinner [Bmim][FAP] nanofilms on amorphous carbon. In contrast, it has been previously reported that ethyl-dimethyl-2-methoxyethyl tris(pentafluoroethyl)trifluorophosphate ([MOEDEA][FAP]), which has an aliphatic ammonium cation, forms nanodroplet structures on amorphous carbon instead due to the lack of effective π - π^+ stacking interaction between the nonconjugated cation and substrate.³²

The findings highlight the effect of the different IL/solid interfacial interactions, i.e., strong and weak electrostatic interactions and π - π^+ stacking interaction, between [Bmim] cations and various solid substrates on the IL molecular structures during nanofilm growth. One should note that alternative interfacial molecular structures could also be observed in other systems, such as aliphatic ILs and applied potentials on the solid surface. Our results here further support that the molecular structures of solid-confined [Bmim][FAP] and other ILs in general are determined by the competitions among several interactions at the IL/solid interfaces.

4. CONCLUSIONS

In summary, we report AFM results on the nanofilm growths of [Bmim][FAP] confined to silica and amorphous carbon, which are very different from the recent observation of the double-layering quantized growth of $[C_n\text{mim}][\text{FAP}]$ nanofilms on mica.⁴⁶ For [Bmim][FAP] on silica, tiny and discrete IL spikes with heights below 1 ML are observed at the initial stage of nanofilm growth. As the nanofilm continues to grow, IL directly aggregates into thicker islands and then connects to a rough sponge-like film with the maximum local thicknesses of ~ 4 -5 ML. This aggregation-dominating growing of [Bmim][FAP] on silica is attributed to the weak negative surface charging

of silica, which leads to the weak electrostatic interaction between silica and the IL cation. For the nanofilm growth of [Bmim][FAP] on amorphous carbon, the nanofilms remain smooth and featureless until the last stage, i.e., the nanofilm fabricated from the 2.5 g/L solution. The fairly smooth film growth is attributed to the π - π^+ interaction between the cation imidazolium ring and the randomly distributed sp^2 carbon on the amorphous carbon surface, which results in the smooth parallel packing of IL ions. Our findings suggest that the IL/solid interactions could stand out from the competition of the several interfacial interactions and have significant impacts on the interfacial molecular structure of ILs.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Schematic of the chemical structures of [Bmim][FAP] and Vertrel XF, AFM images and the corresponding line profiles of bare mica, silica, and amorphous carbon, three-dimensional AFM images of [Bmim][FAP] nanofilms on silica, and water and hexadecane contact angle results on bare amorphous carbon (PDF)

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All authors have given approval to the final version of the manuscript.

Acknowledgements

The authors thank the financial support from the National Science Foundation (CBET 1904486), the American Chemical Society Petroleum Research Fund (ACS PRF 54840-DNI5), and the Advanced Storage Research Consortium (ASRC). We also thank Dr. Huan Tang from Seagate Technology LLC for providing the COC samples and valuable discussions.

Notes

The authors declare no competing financial interest.

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