Investigation of multilayered structures of ionic liquids on graphite and platinum using atomic force microscopy and molecular simulations

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Abstract

The molecular level orientation and structure of ionic liquids (ILs) at liquid-solid interfaces are significantly different than in the bulk. The interfacial ordering influences both IL properties, such as dielectric constants and viscosity, and their efficacy in devices, such as fuel cells and electrical capacitors. Here we report the layered structures of four ILs on unbiased highly ordered pyrolytic graphite (HOPG) and Pt(111) surfaces, as determined by atomic force microscopy (AFM). The ILs investigated are 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]), 1-ethyl-3-methylimidazolium perfluorobutylsulfonate ([emim][C₄F₉SO₃]), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene bis-(trifluoromethylsulfonyl)imide ([MTBD][Tf₂N]), and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene perfluorobutylsulfonate ([MTBD][C₄F₉SO₃]). Molecular dynamics (MD) simulations provide complementary information on the position and orientation of the ions. These ILs form a cation layer at the IL-solid interface, followed by a layer of anions. [Emim]⁺ and [MTBD]⁺ have similar orientation at the surface but [MTBD]⁺ forms a thinner layer compared to [emim]⁺ on both HOPG and Pt(111). In addition, [Tf₂N]⁻ shows stronger interactions with Pt(111) surfaces than [C₄F₉SO₃]⁻.

Keyword

Ionic liquids, interfacial microstructure, atomic force microscopy, molecular dynamics

1. Introduction

Ionic liquids (ILs) are promising candidates for a variety of applications including energy storage and conversion systems,^{1,2} lubrication^{3–5} and gas separations^{6,7}. In most of these applications, IL-solid interfaces are involved and the nanostructures of ionic liquids at the interface play an important role in determining the performance of the system. Characterization of the structure of ionic liquid-solid interfaces is thus critical to developing a fundamental understanding of these important materials at a molecular level.

Previous studies have shown that ionic liquids form layered structures at the liquid-solid interface that can extend up to 10 nm from the surface.⁸ The difference in the structures at the boundary and in the bulk liquid can lead to different properties of ILs, and further influence the behavior of ILs at the interface. The orientational distribution of ILs can go from nearly isotropic in the bulk phase to highly oriented at the surface. IL cations and anions are collectively ordered in these layered structures. The physical properties of ILs, such as dielectric constants, polarizability, and viscosity, can depend on orientations, resulting in changes in the thermodynamics and kinetics at the interface.⁹

Investigating the structures of IL-solid interfaces constitutes a significant experimental challenge, which requires the use of multiple and complementary analytical methods able to probe the interfacial arrangement and dynamical evolution of the ions. Pioneering efforts have used sum frequency generation (SFG),^{9,10} X-ray reflectivity,^{11,12} X-ray photoelectron spectroscopy (XPS),^{13,14} surface force measurement (SFA),^{15–17} scanning probe microscopy (including scanning tunneling microscopy (STM))^{18–20} and atomic force microscopy (AFM)^{21–23} to characterize the surface structure of ionic liquids at solid interfaces. The arrangement of the first layer of ions in contact with the solid is determined by the nature of the solid surface. The distance that the layered structure extends from the surface depends on how well the electric field of the solid is screened by the first layer of ILs.⁹

Conventional models for dilute electrolytes are not applicable to IL systems where the ion charge density is much higher and there is no molecular solvent present.²⁴ Strong ion-surface interactions, which are mainly due to electrostatic attraction and van der Waals interactions, together with cation-anion interactions, can induce significant ion ordering at the liquid-solid interface, resulting in the formation of an innermost (Stern) layer.⁸ As mentioned above, ion ordering can extend for successive layers up to several nanometers in the liquid. Recent studies on the structure and dynamics of ILs near solid surfaces show that ions close to the solid surface display solid-like structure and slower dynamics than are present in the bulk liquid.^{25,26}

Previous AFM studies of layered structures of ionic liquids formed at solid surfaces have focused on highly oriented pyrolytic graphite (HOPG), mica, silica, Si(110) and Au(111). Specifically, Atkin and Warr measured solvation layers of 1-ethyl-3-methylimidazolium acetate ([emim][Ac]) on graphite and suggested that the cation adopted a flat conformation.²² Bovio et al. investigated the nanostructures of 1butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][Tf₂N]) on surfaces including mica, silica, Si(110) and HOPG.²⁷ They reported a structural model with a basic periodicity in the perpendicular direction of about 0.6 nm. The rearrangement of ions near the solid surface results in a solid-like phase and the thickness of the layers is compatible with the ion pair sizes. Measurements by Yokota et al. revealed that $[bmim][Tf_2N]$ and 1-butyl-3-methylimidazolium tetrafluoroborate form layered structures with high stability on HOPG and mica surfaces.²⁸ Several flat layers can be observed when scanning the surface with the AFM tip. Each step height is regulated to be ~ 0.8 nm. Gong et al. found that the monolayer thickness for 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([bmim][FAP]) on an amorphous carbon surface is 0.84 nm and suggested that there is π - π + stacking between [bmim][FAP] and amorphous carbon because of the aromatic imidazolium rings.²⁶ More recent studies by Black et al. investigated the electrical double layer structure of 1-ethyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]) on a HOPG substrate and correlated the positions of ion layers with the predictions from molecular dynamics (MD) simulations.²⁹

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They also looked into the effect of tip properties on the AFM measurements and proved that the layer positions measured are independent of cantilever/tip properties including stiffness, chemistry, geometry, and cleaning procedure.³⁰

In a study by Atkin et al. in 2009, the force-separation data for [emim][Tf₂N] on a gold substrate (Au(111)) indicated four solvation layers formed within a distance of 3 nm from the solid surface.³¹ The innermost layer was at a separation of 0.65 nm. Hayes et al. conducted measurements for 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][FAP]) on a Au(111) surface at open circuit potential.³² Discrete cation (0.30 nm) and anion (0.50 nm) sublayers nearest to the interface were observed in the force versus separation profile from the AFM measurement and the sum (0.80 nm) is consistent with the ion pair dimension. A study by Li et al. evaluated the effect of alkyl chain length on the nanostructures of imidazolium-based ILs on the Au(111) surface.³³ The results suggested that the first layer away from the IL-solid interface is of mixed composition and slightly enriched in cations. Compared to [bmim][FAP], [emim][FAP] has a more structured interface because the imidazolium rings are oriented more parallel to the solid surface. For 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate ([hmim][FAP]), more layers are formed and higher forces are needed to rupture the layers due to the longer cation alkyl chain length, which results in increasing strength of the solvophobic interactions.

Although AFM is a valuable tool to study the structure of ILs at interfaces, the measured force profiles require interpretation to infer composition and configuration of the layered structures. MD simulations are an excellent tool to probe both cation-anion and ion-solid interactions and help interpret the experimental results. 1,3-Dimethylimidazolium chloride,³⁴ 1-butyl-3-methylimidazolium hexafluorophosphate,^{35–37} and [emim][Tf₂N]²⁹ have been modeled on graphene or graphite surfaces using MD simulations, which showed well-ordered layered structures formed near the uncharged surface. Cations are closest to the surface and the imidazolium rings are preferentially oriented parallel to the surface. There are also some simulations of ionic liquids on metal surfaces. For example, [emim][Tf₂N]

on a Ag(111) electrode was studied recently by Zhang et al. using a combination of AFM and MD simulations.³⁸ Wang et al. recently modeled [emim][Tf₂N] on a Au(111) surface with MD simulations and concluded that the IL molecules have a worm-like arrangement on the solid surface.³⁹ This has been previously observed with experiments on Au(100) surfaces using combined in situ STM and differential capacitance measurements.⁴⁰ Overall, the combination of experimental measurements and molecular simulations provide a detailed understanding of the structure of ion layers at IL-solid interfaces.

The ILs investigated here were chosen based on their use as electrolytes in polymer electrolyte membrane fuel cells to enhance oxygen reduction reaction (ORR) activity of carbon supported platinum catalysts (Pt/C).⁴¹ In particular, protic 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene ([MTBD]⁺) based ILs show better performance compared to commonly studied ILs such as [emim][Tf₂N]. The addition of [MTBD]⁺-based ILs results in improvement of ORR activities in fuel cells due to their hydrophobicity, interactions with Pt, and their protic nature^{41,42}. Among all the ILs we previously investigated, Pt/C catalyst modified with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene perfluorobutylsulfonate $([MTBD][C_4F_9SO_3])$ exhibits the highest specific activity toward the ORR and stabilizes the ORR catalysts.^{41,42} We note that other researchers have also reported interesting findings when they have introduced [MTBD]-based ILs with PtNi or Pt nanoparticles for catalysis and electrochemistry applications.^{43–45} Given this background, we chose four ILs for molecular level investigation of their behavior at IL-solid interfaces. [Emim][Tf₂N] was selected as the reference or "base case" IL since previous AFM studies of its structure on both HOPG²⁹ and Au(111)³¹ can be used for validation of our experimental technique. $[MTBD][C_4F_9SO_3]$ was chosen due to its excellent performance in fuel cell tests.^{41,42} 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene bis(trifluoromethylsulfonyl)imide $([MTBD][Tf_2N])$ and 1-ethyl-3-methylimidazolium perfluorobutylsulfonate ($[emim][C_4F_9SO_3]$) are the two other obvious choices since they contain the components of [MTBD][C₄F₉SO₃] but differ from the reference IL by either the cation or the anion, but not both. HOPG and Pt(111) were chosen as solid

supports as representative of the two components of the carbon supported platinum catalysts used in the fuel cell application.

The layered structures of these four ILs formed near the surface of HOPG and Pt(111) are investigated by measuring force-separation curves with atomic force microscopy (AFM). Molecular dynamics (MD) simulations are performed to aid in the interpretation of the distribution and configuration of ions near the solid surfaces. In particular, we report MD simulations of [emim][Tf₂N] and [emim][C₄F₉SO₃] on HOPG and Pt(111). This study provides additional insights and understanding towards the formation of layered structures of ILs at IL-solid interfaces.

2. Methods

2.1. Materials

IL Synthesis. 1-Ethyl-3-methylimidazolium bromide (97.0%), 1-ethyl-3-methylimidazolium chloride (98%), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (98%), potassium nonafluoro-1-butanesulfonate (98%), bis(trifluoromethane)sulfonimide lithium salt (99.95%), and nitric acid (70%) were purchased from Sigma-Aldrich and used as received. Water was obtained from a 18.2 Ω ·cm laboratory Millipore system.

AFM measurements. The solid substrates used were platinum(111) sputter-coated on silicon (Intlvac Thin Film) with a thickness of 250 nm, and highly ordered pyrolytic graphite (HOPG, Grade 2, Structure Probe, Inc.).

2.2. Synthesis of ionic liquids

The procedure for IL synthesis can be found in the Supporting Information, along with ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra for all four ILs (Figures S1-S12 in Supporting Information). The full name, abbreviation and purity of the ILs used in this work are shown in Table 1. The chemical structures of the cations and anions are shown in Table 2.

Table 1. Full Name, Abbreviation and Purity of Ionic Liquids.

Full Name	Abbreviation	Purity
1-ethyl-3-methylimidazolium bis- (trifluoromethylsulfonyl)imide	[emim][Tf ₂ N]	98%
1-ethyl-3-methylimidazolium perfluorobutylsulfonate	[emim][C ₄ F ₉ SO ₃]	98%
7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene bis- (trifluoromethylsulfonyl)imide	[MTBD][Tf ₂ N]	98%
7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene perfluorobutylsulfonate	[MTBD][C ₄ F ₉ SO ₃]	98%

Table 2. Chemical Structures of Cations and Anions.

Structure	Name	Abbreviation
	1-ethyl-3-methylimidazolium	[emim]+
N N H+	7-methyl-1,5,7- triazabicyclo[4.4.0]dec-5-ene	[MTBD]+
F ₃ CO ₂ S ^{-N-} SO ₂ CF ₃	bis(trifluoromethylsulfonyl)imide	[Tf ₂ N] ⁻

$ \begin{array}{c c} F_2 & & \\ F_3C \\ C \\ F_2 \\ F_2 \\ F_2 \end{array} \begin{array}{c} P_2 \\ P_2 \end{array} \end{array} perfluorobutylsulfonate \qquad \begin{bmatrix} C_4F_9SO_3 \end{bmatrix}^2 \end{array} $
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Water byproduct was removed from the ionic liquids by further drying the samples at 323.15 K under vacuum for 24 h. Prior to characterization and measurement, the water content of each IL was determined by a Metrohm 917 Karl Fischer coulometer and was less than 0.05% by weight (or 500 ppm) for all the ILs. The structures and purities of the ILs were verified by ¹H, ¹³C and ¹⁹F NMR (Bruker AVANCE III 500) spectroscopy with the dried IL dissolved in deuterated dimethyl sulfoxide (DMSO-d6, 99.9 atom % D, Sigma-Aldrich) containing 1% v/v tetramethylsilane. Any residual halide in the aqueous phase in contact with the ILs was not detectable by adding an AgNO₃ aqueous solution, consistent with halide content less than 0.2 wt%.

2.3. Preparation of the solid substrates

Atomically smooth graphite surfaces were freshly cleaved from HOPG sheets shortly before the experiment. The platinum substrate was washed sequentially with 2-propanol and the Millipore water in an ultrasonic bath for 30 minutes each and then dried with dry nitrogen before the AFM measurements.

2.4. AFM measurements

The experiments were performed with a commercial atomic force microscope (MFP-3D Origin+ AFM, Oxford Instruments, Asylum Research, USA) using silicon tips (HQ-13-Au, Oxford Instruments, Asylum Research, USA). AFM tips were cleaned by a UV/Ozone cleaner (UV/ozone ProCleaner Plus, BioForce Nanosciences, USA) for 10 min prior to use. The nominal spring constant of the cantilever is about 0.2 N/m. The thermal tune method was used to determine the spring constant for each tip. Forcedistance curves were collected in a droplet of ILs on HOPG and platinum surfaces under ambient conditions. We estimate that this exposure to the atmosphere could result in an increase in the water content at the solid surface to several thousand ppm over the course of the experiment (see SI for more details). For the measurement of [MTBD][C₄F₉SO₃], which has a melting point of 316.15 K,⁴⁶ a heated fluid cell (BioHeater, Oxford Instruments, Asylum Research, USA) was used to maintain the temperature at 318.15 K so that [MTBD][C₄F₉SO₃] remained liquid during the measurement. The force-distance curves were measured by recording the normal deflection of the cantilever while approaching the cantilever to the solid surface. After the cantilever contacts the surface, the deflection continuously increased until a given set point is reached. At least 50 curves were collected for each IL on a solid surface at a rate between 0.01 to 0.05 Hz with a scan distance between 40 and 50 nm. For the HOPG surface area investigated, there is no obvious defects such as terraces.

2.5. Data process and interpretation

The collected force-distance curves were converted to force-separation curves in order to quantitatively determine the thickness of the layered structures directly. The force-separation curves were aligned along the x-axis by the hard walls, which is defined as separation = 0. To describe it statistically, histograms along the x-axis were constructed with a bin size of 200 over 30-40 force curves for each experiment. The peaks shown in the histograms were fit with Gaussian functions to determine the peak positions. The fitting parameters for the peaks can be found in Tables S1 and S2 in the Supporting Information. Examples of force separation curves for each experiment can be found in Figure S13 to S20 in the Supporting Information.

2.6. Gaussian

Gaussian calculations were performed to estimate anion size using an isolated cation or anion in the gas phase. We use the BVP86 density functional theory (DFT) functional and the tzvp basis set, as implemented in the Gaussian 16 program.⁴⁷ After geometry optimization is achieved, the 3D dimensions of the ions are calculated by VMD software.⁴⁸ The .xyz files with optimized structures are imported into VMD and the "minmax" option is used in the measure command to obtain the box size of the ions. The

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charge intensity and distribution on the ions are further determined by using COSMOtherm software⁴⁹ with BP_TZVP_C30_1701 as the COSMO-RS parameter set.⁵⁰

2.7. Molecular dynamics simulation

Molecular dynamic (MD) simulations were conducted to investigate the electric double layer (EDL) structures for both $[\text{emim}][\text{Tf}_2\text{N}]$ and $[\text{emim}][C_4\text{F}_9\text{SO}_3]$ on HOPG and Pt(111). The one-electrode model was used in constant potential MD simulations at a potential of 0V. This allows for fluctuations in charge for atoms on the surface while maintaining an overall potential of 0V. We utilize a singleelectrode set up within the MD simulation cell. Compared with a two-electrode model, the one-electrode model we have used can generate the same EDL structure more efficiently by avoiding the need to tune the number of ion pairs to produce a bulk-like region in the two-electrode model⁵¹. The electrodes were modeled by three layers of solid atom sheets with an area of $5.50 \times 5.50 \text{ nm}^2$ and a gap of 0.341 nm and 0.226 nm between each two layers for HOPG and Pt(111), respectively. All-atom models were used to model [emim][Tf₂N]⁵² and [emim][C₄F₉SO₃]⁵³, and the interactions between carbon atom in HOPG⁵⁴/Pt atom in Pt(111)⁵⁵ and the ionic liquids were described by a Lennard-Jones potential plus electrostatic interactions between induced charges in the electrode and partial charges on the atoms of the ionic liquid ions. The MD simulations were performed with the GROMACS software package⁵⁶ with a time step of 2 fs. All chemical bonds, including those involving H atoms, were constrained by the LINCS algorithm⁵⁷. Temperature was maintained at room temperature (298 K) by V-rescale thermostat⁵⁸. The particle mesh Ewald method⁵⁹ with a 0.12 nm grid spacing in reciprocal space was used to control the electrostatic interactions. The cut-offs for both electrostatic interactions in real space and nonbonded van der Waals interactions were set to 1.2 nm. To remove the interactions between periodic images, the slab correction was used in the MD simulations⁶⁰. Each simulation was first equilibrated in the NVT ensemble for 20 ns, and then sampled in the NVT ensemble for 30 ns to get trajectories for analyzing ion number density and orientation profiles.

3. Results and Discussion

The layered structures of $[\text{emim}][\text{Tf}_2\text{N}]$ at the IL-HOPG interface have been studied previously.²⁹ Here, we repeated these measurements to validate our methodology. The results are shown in Figure 1. Figure 1(a) shows the histogram of the force-separation data for $[\text{emim}][\text{Tf}_2\text{N}]$ on HOPG. The peak at zero nm separation corresponds to the HOPG solid surface. The other peaks in the histogram are fit with five Gaussian functions, resulting in peak positions at 0.32, 0.46, 0.55, 0.80, and 0.91 nm (see Table S1 for the full width at half maximum (FWHM) of these peaks). In the work of Black et al.,²⁹ they showed that the first cation layer formed by $[\text{emim}][\text{Tf}_2\text{N}]$ on the HOPG surface is 0.34 nm away from the solid surface and the first anion layer is 0.54 nm away from the solid surface.



Figure 1. (a) Histograms of force-separation data for $[emim][Tf_2N]$ on a HOPG surface with multiple Gaussian fittings. (b) Ion density distribution from MD as a function of distance from a graphite surface for $[emim][Tf_2N]$ at 298 K. Red line indicates cation, blue line indicates anion and purple line is the sum.

(c) Orientation of $[\text{emim}]^+$ in the first cation layer on graphite at 298 K from MD simulations. (d) Orientation of $[\text{Tf}_2\text{N}]^-$ in the first anion layer on graphite at 298 K from MD simulations.

Figure 1(b) shows the ion density distribution as a function of distance from the graphite surface for [emim][Tf₂N] calculated by MD simulations. The simulations indicate that the first layer is the cation at around 0.34 nm from the solid surface and the second ion layer (which has double peaks) at around 0.48 nm and 0.56 nm is an anion layer. There is also a small cation peak at 0.62 nm, which is hard to distinguish in the total number density from the much larger portion of the anion double peak at 0.56 nm. Beyond that, there are cation and anion peaks at 0.90 and 0.93 nm, respectively, followed by alternating anion and cation peaks at longer distances. This indication of alternating charge cation-anion pairs has been observed in previous studies.^{29,61,62}

From the MD simulations, we identify the experimental peak at 0.32 nm as the first cation layer. The peaks from the AFM measurements at 0.46 nm and 0.55 nm likely correspond to the first anion layer that has a double peak in the MD simulation around 0.5 nm. The two small peaks in the experimental measurements at 0.80 nm and 0.91 likely correspond to the next cation and anion layers, respectively. The ion density is highest near the solid surface and gradually decreases when it is further away from the solid surface. The dominant range for ion layering is within 1 or 1.5 nm from the surface, which is also true for the other ILs studied in this work. Generally, the ion density peaks predicted by the MD simulations show good agreement with the experimental results fitted with Gaussian functions.

Black et al.²⁹ showed that the first cation layer formed by $[\text{emim}][\text{Tf}_2\text{N}]$ on the HOPG surface is 0.34 nm away from the solid surface and the first anion layer is 0.54 nm away from the solid surface. This is in good agreement with our AFM results of 0.32 nm and two anion peaks at 0.46 nm and 0.55 nm. However, they did not observe experimentally the small peaks we identified at 0.80 and 0.91 nm. Black et al.²⁹ also ran MD simulations of $[\text{emim}][\text{Tf}_2\text{N}]$ on HOPG and calculated the ion orientations. The results presented here are similar to those published previously. Both indicate a prominent cation peak around 0.3 nm and double anion peak around 0.5 nm. However, we note that the two components of that anion peak are more distinct in the previous publication.²⁹ Both MD simulations have the next cation peak around 0.6 nm. Here this is followed by both cation and anion peaks around 0.9 nm. In the previous publication²⁹ this region was dominated by the cation peak, with the second anion peak being very small and positioned closer to the surface than 0.9 nm. These small differences in the ion density distributions can be attributed to some differences in the two simulations. For instance, Black et al. ²⁹ used a 1.1 nm cut-off, while a 1.2 nm value is used here. Moreover, the thermostat employed in the previous work was Berendsen, while a v-rescale technique is used here. Finally, the sizes of the electrode are also different. Nonetheless, our results are in generally good agreement with the previous report.

To put the distance of the anions and cations from the surface into perspective, we calculated the ion dimensions of $[\text{emim}]^+$ and $[\text{Tf}_2\text{N}]^-$ as the size of the boxes to enclose the ions and found them to be $0.75 \times 0.41 \times 0.29 \text{ nm}^3$ and $0.73 \times 0.32 \times 0.30 \text{ nm}^3$, respectively. Previously reported ion dimensions calculated from the van der Waals radii for $[\text{emim}]^+$ and $[\text{Tf}_2\text{N}]^-$ are $0.85 \times 0.55 \times 0.28 \text{ nm}^3$ and $1.09 \times 0.51 \times 0.47 \text{ nm}^3$, respectively.⁶³ Cheng et al. reported the dimensions of $[\text{emim}]^+$ and $[\text{Tf}_2\text{N}]^-$ to be $0.76 \times 0.38 \times 0.22 \text{ nm}^3$ and $0.75 \times 0.66 \times 0.42 \text{ nm}^3$, respectively.⁶⁴ A study by Perkin et al. claimed the size of $[\text{emim}]^+$ to be $(0.76 \pm 0.03) \times (0.36 \pm 0.08) \times (0.22 \pm 0.04) \text{ nm}^3$.⁶⁵ Our calculations for the sizes of the ions compare favorably with the previously published estimates.

The orientations of $[\text{emim}]^+$ and $[\text{Tf}_2\text{N}]^-$ were obtained from MD simulations for the first cation and anion peaks, as shown in Figures 1(c) and 1(d). The imidazolium rings on the $[\text{emim}]^+$ cation are primarily near 0° and 180° orientations, indicating that the plane of the imidazolium ring is parallel to the graphite surface. For the $[\text{Tf}_2\text{N}]^-$ anion, the MD simulations show two sub peaks for the first anion layer near 0.5 nm and two different orientations exist for the two sub peaks. The first sub peak is oriented at 90° (formed by the vector between the two carbon atoms and the normal vector of the solid surface), which means the anion is parallel to the graphite surface. The second sub peak has the vector between the two carbon atoms at either 45° or 135° to the normal vector of the solid surface, which means the anion is tilted at 45° to the solid surface. The dimensions of the cation and the experimental thickness of the first cation layer (Figure 1(a)), is completely consistent with the imidazolium rings of the cations being parallel to the solid surface. The thickness of the anion layer is smaller than the calculated dimensions of the anion, which is likely due to the attractions between the cations and anions.

Overall, there is good agreement between the current study and that presented by Black et al.²⁹ for both the experimental results and the MD simulations for $[\text{emim}][\text{Tf}_2\text{N}]$ on HOPG. Moreover, the experimental and simulation results are consistent. Therefore, we consider both our experimental technique and MD simulations adequately validated.

In this and subsequent paragraphs we present new results for the ordering of $[\text{emim}][C_4F_9SO_3]$, [MTBD][Tf₂N] and [MTBD][C₄F₉SO₃] on HOPG. In Figure 2, we show the experimental and computational results for $[\text{emim}][C_4F_9SO_3]$ on HOPG. In Figure 2(a), based on the distribution of the data points and the ion densities calculated from MD simulations (Figure 2(b)), we fit five peaks with Gaussian functions. The peak positions are 0.29, 0.43, 0.63, 0.78, and 0.91 nm (see Table S1 for the FWHM of these peaks). Clearly, the first peak at 0.29 nm consists of [emim]⁺ cations and the first anion peak is located at 0.43 nm. After that, there are several layers, with the region between 0.6 and 1.0 nm attributed primarily to various orientations of the cations, according to the MD simulations. The orientations of $[\text{emim}]^+$ and $[C_4F_9SO_3]^-$ for the first cation and anion peaks were calculated from the MD simulations and are plotted in Figures 2(c) and 2(d). For the [emim]⁺ cation close to the graphite surface, the plane of the imidazolium ring shows orientations near 0° and 180°, which is similar to what we observed for [emim][Tf₂N]. The imidazolium rings are parallel to the graphite surface and the peak location of 0.29 nm is consistent with the dimension of the cation. For the $[C_4F_9SO_3]^-$ anion, the results show that the angle formed by the vector between the sulfate and terminal carbon and the normal vector of the solid surface is either 80° or 100°. This means the vector between the sulfate and terminal carbon is primarily parallel to the solid surface. The dimensions for $[C_4F_9SO_3]^-$ are $0.77 \times 0.31 \times 0.30$ nm³, which is similar to the size of $[Tf_2N]^-$. From the charge distributions we calculated from COSMOtherm (Figure S20 in supporting information), the charge on $[Tf_2N]^{-1}$ is more delocalized while, for $[C_4F_9SO_3]^{-1}$, the

negative charge is mainly located on the $-SO_3$ group. Overall, on the HOPG surface, [emim][Tf₂N] and [emim][C₄F₉SO₃] have peak locations that are similar to one other, with cations being the closest and parallel to the solid surface, followed by a layer of anions, as shown in Scheme 1.



Figure 2. (a) Histograms of force-separation data for $[\text{emim}][C_4F_9SO_3]$ on HOPG surface with multiple Gaussian fittings. (b) Ion density distribution from MD as a function of distance from graphite surface for $[\text{emim}][C_4F_9SO_3]$ at 298 K. Red line indicates cation, blue line indicates anion and purple line is the sum. (c) Orientation of $[\text{emim}]^+$ in the first cation layer on graphite at 298 K from MD simulations. (d) Orientation of $[C_4F_9SO_3]^-$ in the first anion layer on graphite at 298 K from MD simulations.



Scheme 1. The ordering and orientations of cations and anions at IL-solid interface, using $[emim][Tf_2N]$ on HOPG surface as an example. The red objects are cations and the blue objects are anions.

The histograms of the force-separation data for [MTBD][Tf₂N] and [MTBD][C₄F₉SO₃] on HOPG from the AFM experiments are plotted in Figure 3(a) and 3(b). Gaussian calculations indicate that the two six-membered rings of [MTBD]⁺ are co-planar so that the entire cation is flat, with dimensions of $0.71 \times 0.59 \times 0.27$ nm³. The histogram for [MTBD][Tf₂N] does not exhibit much structure past 0.6 nm. Based on what we learned from our results for [emim][Tf₂N] on HOPG in this distance region, we fit three Gaussian peaks, resulting in peaks centered at 0.23, 0.38, and 0.55 nm (see Table S1 for the FWHM of these peaks). The first peak at 0.23 nm is undoubtedly a cation layer and the distance from the surface is consistent with the smallest dimension of [MTBD]⁺, indicating that the planar bicyclic ring of the cation is parallel to the HOPG surface. This is similar to what we observe for [emim][Tf₂N] on HOPG. Beyond the first cation layer, there is a layer of anions. From the locations of the peaks used to fit the histogram, it suggests that the [Tf₂N]⁻ anion has different orientations and thus forms two sub peaks at 0.38 and 0.55 nm. Based on the simulations for [emim][Tf₂N] on HOPG, the [Tf₂N]⁻ anion in [MTBD][Tf₂N] has an orientation near 90° (formed by the vector between the two carbon atoms and the normal vector of the solid surface) in the first sub peak. The orientation of anion in the second sub peak is similar to what is shown in Figure 1(d).

In Figure 3(b) the histogram of separation values for [MTBD][C₄F₉SO₃] is shown. Like [MTBD][Tf₂N], there is an absence of clear structural components at distances greater than 0.6 nm. We managed to fit four peaks to the data, which are centered at 0.20, 0.32, 0.45, and 0.58 nm (see Table S1 for the FWHM of these peaks). Consistent with the other three ILs on HOPG, the first layer closest to the solid surface for [MTBD][C₄F₉SO₃] undoubtedly consists of cations. The plane of the bicyclic ring of the cation should be essentially parallel to the HOPG surface, as indicated by the peak location of 0.20 nm. We note that the [MTBD]⁺ cations for both [MTBD][Tf₂N] and [MTBD][C₄F₉SO₃] are actually closer to the HOPG surface than the [emim]⁺ cations, despite being of similar size. Beyond the first cation layer, there is an anion layer with [C₄F₉SO₃]⁻ anions forming two sub peaks at 0.32 and 0.45 nm. After that, another layer of cations forms at 0.58 nm. Unlike [emim]-based ILs, which still have a few layers formed beyond 0.6 nm, there is no obvious layering structure formed for [MTBD]-based ILs. This suggests that even though [MTBD]⁺ is closely packed next to the HOPG, its interactions may be screened beyond a certain distance. However, further investigation with MD simulations is needed to explore this speculation.



Figure 3. Histograms of force-separation data for [MTBD]-based ILs on HOPG surface with multiple Gaussian fittings: (a) [MTBD][Tf₂N]; (b) [MTBD][C₄F₉SO₃].

We then investigated the layered structures of the four ILs on a Pt(111) surface. In Figure 4, the results for [emim][Tf₂N] on Pt(111) surface are shown, with Figure 4(a) showing the histogram of the force-separation data. MD simulations were performed to analyze the ion density distribution as a function of distance from the solid surface for [emim][Tf₂N] on Pt(111) and these results are shown in Figure 4(b). Based on the two sets of information, we fit four Gaussian peaks to the AFM data and the centers of those peaks are at 0.24, 0.47, 0.72, and 0.80 nm (see Table S2 for the FWHM of these peaks). In the MD simulation results, it shows that there is a cation layer closest to the Pt surface at around 0.30 nm. A layer of anions follows this at 0.43 nm. These two peaks correspond well with the fits to the experimental AFM data in Figure 4(a) (cation layer at 0.24 nm and anion layer centered at 0.47 nm). Compared to the layer thickness of [emim][Tf₂N] on HOPG, the thickness of the first (cation) ion layer on platinum is less, indicating that the cation layer is more compressed on the platinum surface. The ion number densities calculated from MD simulations for the first cation and anion layers are also larger than those for [emim][Tf₂N] on HOPG, which implies stronger interactions between Pt and both the cations and anions. The experimental peaks at 0.72 nm and 0.80 nm appear to correspond to an anion peak and a combined anion + cation peak in the MD simulations. Figures 4(c) and 4(d) show the orientations of

 $[\text{emim}]^+$ and $[\text{Tf}_2\text{N}]^-$ on Pt(111) surface for the first cation and anion peaks by MD simulations. Similar to our results for this IL on the HOPG surface, the orientation of the imidazolium rings on $[\text{emim}]^+$ are mostly near 0° and 180°. This indicates that the imidazolium ring is parallel to the platinum surface. Meanwhile, the $[\text{Tf}_2\text{N}]^-$ anion primarily exists with a 90 ° orientation.



Figure 4. (a) Histograms of force-separation data for $[\text{emim}][\text{Tf}_2\text{N}]$ on Pt(111) surface with multiple Gaussian fittings. (b) Ion density distribution from MD as a function of distance from Pt(111) surface for $[\text{emim}][\text{Tf}_2\text{N}]$ at 298 K. Red line indicates cation, blue line indicates anion and purple line is the sum. (c) Orientation of $[\text{emim}]^+$ in the first cation layer on Pt(111) at 298 K from MD simulations. (d) Orientation of $[\text{Tf}_2\text{N}]^-$ in the first anion layer on Pt(111) at 298 K from MD simulations.

There are no previous studies investigating the layered structures formed by ILs on Pt(111) surfaces. However, some previous work has investigated the nanostructures of $[\text{emim}][\text{Tf}_2\text{N}]$ on metal surfaces such as Au(111). Cheng et al. found that, for $[\text{emim}][\text{Tf}_2\text{N}]$ on a Au(111) surface with negative

potential applied, the cations dominate the 2-3 Å region, followed by the anions at around 4.5-6 Å.⁶⁴ In our case, for the same IL on Pt(111), which has a similar lattice size as Au(111), the first ion layer away from the platinum surface is a cation layer at around 0.24 nm and the second ion layer at around 0.5 nm corresponds to an anion layer. This is consistent with what Cheng et al.⁶⁴ reported in their study for [emim][Tf₂N] on Au(111).

In Figure 5, the experimental and computational results for $[\text{emim}][C_4F_9SO_3]$ on Pt(111) are shown. Based on the ion density distribution calculated from MD simulations in Figure 5(b), four peaks are fit to the data for $[\text{emim}][C_4F_9SO_3]$ and the locations of the peaks are at 0.23, 0.43, 0.55, and 0.71 nm, as shown in Figure 5(a). In Figure 5(b), the cations form a strong layer at around 0.28 nm and there are two small peaks of anions at 0.40 and 0.54 nm. Like $[\text{emim}][\text{Tf}_2\text{N}]$, this suggests that $[\text{emim}]^+$ cations have stronger interactions with the Pt(111) surface than the anions, whether they be $[Tf_2N]^-$ or $[C_4F_9SO_3]^-$. Comparing Figure 4(b) and Figure 5(b), one observes that the number densities of $[Tf_2N]^-$ are much higher than those of $[C_4F_9SO_3]^2$ near the platinum surface, suggesting that the interactions between platinum and $[Tf_2N]^-$ are stronger than between Pt(111) and $[C_4F_9SO_3]^-$. There is also evidence from electrochemistry that $[Tf_2N]^-$ ions have stronger interactions with the Pt surface than $[C_4F_9SO_3]^{-,41,42,66}$ Based on the MD simulations, the peak at 0.71 nm is likely a combination of both anions and cations. The ion orientation of $[\text{emim}]^+$ that are close to the solid surface is near 0° and 180° in Figure 5(c), suggesting that the imidazolium rings are parallel to the surface. For $[C_4F_9SO_3]^-$ in Figure 5(d), they have different orientations in the two sub peaks. The angle formed by the vector between the sulfate and terminal carbon and the normal vector of the solid surface in the first sub peak is primarily 90° , which corresponds to the orientation shown in schematic in Figure 5(d). In the second sub peak, which is further away from the solid surface, the angle becomes 35° or 145°, which corresponds to the vector between the sulfate and the terminal carbon either pointing a bit towards or away from the surface.

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Figure 5. (a) Histograms of force-separation data for $[\text{emim}][C_4F_9SO_3]$ on Pt(111) surface with multiple Gaussian fittings. (b) Ion density distribution from MD as a function of distance from Pt(111) surface for $[\text{emim}][C_4F_9SO_3]$ at 298 K. Red line indicates cation, blue line indicates anion and purple line is the sum. (c) Orientation of $[\text{emim}]^+$ in the first cation layer on Pt(111) at 298 K from MD simulations. (d) Orientation of $[C_4F_9SO_3]^-$ in the first anion layer on Pt(111) at 298 K from MD simulations.

The experimental data collected from force-separation data from AFM for [MTBD][Tf₂N] and $[MTBD][C_4F_9SO_3]$ on Pt(111) are shown in Figure 6. For [MTBD][Tf₂N] (Figure 6(a)) we fit four peaks, based on results for other ILs on Pt(111) and the results for [MTBD][Tf₂N] on HOPG. The peaks are centered at 0.22, 0.39, 0.53, and 0.62 nm (see Table S2 for the FWHM of these peaks). Compared with the dimensions of [MTBD]⁺ and [Tf₂N]⁻, we anticipate that the cations form the first layer next to the solid surface (0.22 nm), followed by a layer of anion with double peaks (0.39 nm and 0.53 nm) and another layer of cations (0.62 nm). The plane of the bicyclic rings of the cation are parallel to the

platinum surface and very tightly packed. The $[Tf_2N]^-$ anions in the first sub peak in the first anion layer have an orientation of approximately 90° based on our simulation results for ILs with $[Tf_2N]^-$.

In Figure 6(b), for the fitting of the histogram for [MTBD][$C_4F_9SO_3$] on Pt(111), there are two obvious peaks at 0.21 and 0.35 nm. No other peaks could be clearly identified, suggesting weak interactions between [$C_4F_9SO_3$]⁻ and platinum. [MTBD]⁺ and [$C_4F_9SO_3$]⁻ form a cation and an anion layer at the IL-Pt interface. Clearly, the plane of the bicyclic ring plane of [MTBD]⁺ is parallel to the solid surface, while [$C_4F_9SO_3$]⁻ is around 90°, based on the MD simulations results for other [$C_4F_9SO_3$]-based ILs. For [MTBD]-based ILs on Pt(111), the thickness of the first ion layer next to the platinum surface (the cation) is similar to that on HOPG, implying that the cation structure could not be further compressed on the platinum surface. By contrast, the [emim]⁺ layer is more compressed on the platinum surface than on HOPG.



Figure 6. Histograms of force-separation data for [MTBD]-based ILs on platinum surface with multiple Gaussian fittings: (a) [MTBD][Tf₂N]; (b) [MTBD][C₄F₉SO₃].

As mentioned earlier, [MTBD]⁺-based ILs have been found to have very good performance as electrolytes in polymer electrolyte membrane fuel cells.^{41,42} This is partly due to the protic nature of the cation. Moreover, from our results above, it is clear that [MTBD]⁺ is well ordered on both the HOPG and Pt surfaces and forms a layer that is thinner than [emim]⁺, which is beneficial to the proton transfer

between the electrolyte and the electrode. For the anions, it has been shown that anion adsorption on Pt reduces the ORR activity because of the occupation of active sites of the catalyst.⁶⁷ Compared to $[Tf_2N]^-$, $[C_4F_9SO_3]^-$ has weaker interactions with the solid surface due to it being more hydrophobic and thus has a smaller impact on reducing the ORR activity of fuel cells. On the other hand, the compact parallel layer formed by $[MTBD]^+$ next to the solid surface (i.e., the strong interaction between $[MTBD]^+$ and the solid surface) also reduces the adsorption of anions on the surface. With all these factors, $[MTBD][C_4F_9SO_3]$ is found to have better performance in fuel cell applications compared to other ILs such as imidazolium-based ILs. This further suggests that cations with bicyclic planar structures that can form compact and well-ordered cation layers are good candidates for investigation for fuel cell applications. As for the anions, chemical structures that are more hydrophobic and have weaker interactions with HOPG and Pt may be good choices to study.

4. Conclusions

In this work, we measured the layered structures of four ILs ([emim][Tf₂N], [emim][C₄F₉SO₃], [MTBD][Tf₂N], and [MTBD][C₄F₉SO₃]) at the IL-solid interface of both highly ordered pyrolytic graphite (HOPG) and Pt by atomic force microscopy (AFM). Molecular dynamics (MD) simulations for [emim][Tf₂N] and [emim][C₄F₉SO₃] on both HOPG and Pt assisted with the interpretation of the experimental results. Histograms of force-separation data from the AFM measurements for all four ILs on HOPG and platinum surfaces clearly show the existence of ion ordering at the interface. In all cases, the first layer is identified as the cation, which is positioned with the aromatic ring parallel to the surface. This is followed by an anion layer, which usually exists in two configurations, resulting in two distinct subpeaks. In most cases the next layer (a cation) is obvious, with subsequent layers less distinct. The [emim]⁺ cations are slightly closer to Pt than HOPG, suggesting stronger interactions of the cation with Pt than with HOPG. Despite having similar dimensions according to DFT calculations, the [MTBD]⁺ cations are packed closer to the solid surfaces than [emim]⁺. Since the [MTBD]⁺ cations are already extremely close to HOPG, it is not possible for them to be even closer to Pt, even if the interactions between the cation and Pt are stronger than with HOPG. Finally, the structuring is significantly less distinct at distances > 0.6 nm for the [MTBD]⁺ ILs than the corresponding [emim]⁺ ILs, suggesting that [MTBD]⁺ is much more effective in charge screening than [emim]⁺. In fact, for [MTBD][C₄F₉SO₃], we were not able to identify any peaks beyond the initial cation and anion layers. This dramatic difference in the ion layer for [MTBD][C₄F₉SO₃] on Pt compared to [emim][Tf₂N] on Pt may well be related to its better catalytic performance (i.e., higher specific activity toward the ORR and stabilization of the ORR catalyst) in fuel cell applications. Applications using ILs on Pt and carbon will involve electrified surfaces; the investigation of the layered structures of these ILs on Pt and HOPG with applied potentials on the electrode surfaces is underway.

Supporting information

The supporting information is available free of charge at https://pubs.acs.org.

Details of IL synthesis; ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra of IL samples; Estimate of IL Water Content; Location and full width at half maximum of the peaks fit to the experimental data; Charge distribution of anions; Chemical structure of [MTBD]⁺.

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