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Effect of alkyl chain length on interfacial structure of imidazolium-based tetrafluoroborate ionic liquids on Au(100) electrodes

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Abstract

The molecular dynamics simulations are employed to investigate the electric double layer structure of three different ionic liquids on single crystalline Au(100) electrodes. We used the same anion BF$_4^-$ and three different cations, 1-C$_n$(n = 2,4,6)-3-methylimidazolium, respectively. We earn to find out how the alkyl chain length of the cation affects their interfacial structure. All ionic liquids have a significant layered structure within the distance 16 Å from the electrode surface, and the results are similar to those of the other research groups. The imidazole ring of cations tends to be distributed parallel to the surface of the neutral electrode due, as the chain length increases, this trend becomes more apparent, due to the increasing of steric hindrance of cations. The same trend has been found in the system of charged Au electrodes.

1. Introduction

Room-temperature ionic liquids (ILs) have various physico-chemical properties, for instance, low melting point, low vapor pressure, high thermal and chemical stability, good electrical conductivity, wide electrochemical window, recyclable, designable and so on [1–8]. These characteristics make ILs become a promising electrolyte of batteries, electrodeposition, electrochemical synthesis, and super capacitors [9]. Nevertheless, interfacial processes are involved in such applications, and the properties of interfacial processes are the most important for the function of such devices. Electrochemical reactions take place at the electrode-electrolyte interface, so the structure of the interface will affect the electrochemical properties. Therefore, it is essential to understand the interfacial behavior of ionic liquids on the surface of electrodes, and it has also attracted extensive attention from lots of experimental and theoretical scientists [10–24].

Gold electrodes are superior to other metal electrodes mainly due to the higher surface atom density and stronger van der Waals interaction of the Au surface than other metal surfaces [10]. Oll et al [11] and others measured the electrochemical window of ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF$_4$]) on the surface of different metals and carbon electrodes, and found that the widest electrochemical window was obtained in the Au/ILs system. Mao et al [12] revealed the interaction between 1-ethyl-3-methylimidazolium bis(tri-fluoromethylsulfonylimide ([EMIM][TFSI]) and Au surface is much stronger than the interaction between 1-ethyl-2,3dimethylimidazolium bis(trifluoromethylsulfonylimide ([EMIM][TFSI]). When the potential is $-0.1$ V–$0.5$ V, the Au/[EMIM][TFSI] interface presents a three-layer structure. The layers will disappear when the potential is greater than $0.5$ V. Zhong et al [13] used cyclic voltammetry (CV) and atomic force microscope (AFM) to study the interface behavior of 1-butyl-3-methylimidazolium bis(tri-fluoromethylsulfonylimide ([BMIM][TFSI]) with a small amount of water on the surface of the Au electrode. Three to five layered structures were observed at the interface, including two charged layers (first and second layers of the system) and three neutral layers (three to five layers of the system). Mao et al [14] found that when the potential is $-0.65$ V, there is no anion and cation adsorption on the gold surface, and shifting the electricity to $-0.7$ V will result in the formation of a loose layer of [BMIM]$^+$ cations that are disorderly adsorbed. It indicates that the surface potential of the electrode will affect the adsorption of the ionic...
liquid on the electrode surface and change the structure of the ionic liquid electric double layer. Drüschler et al [15] used electrochemical impedance spectroscopy (EIS) to study 1-ethyl-3-methylimidazolium tris (pentfluoroethyl)-trifluorophosphate ([EMIM]PF6) and observed the same phenomenon on the surface of Au. It was found that an electric double layer structure was formed near the electrode interface of the system, but the double layer rearrangement is very slow. Unfortunately, the important experiment results of these studies lack reasonable understanding at the molecular scale. Due to the limitations of the experimental methods, it is difficult to interpret the layer structure of the ionic liquids on the surface of the electrode at the molecular level, and also hard to clarify the distribution of anions and cations in the double layer structure and the effect of the charged electrodes on the distribution of anions and cations in the double layer. It is difficult to fully explain the observed stratification of ionic liquids, the different stratification structures that appear on the surface of charged electrodes, and the delay in the formation of double layers. Therefore, for better understand the interfacial behavior of ionic liquids/electrodes system, researchers have started to study the interface using theoretical computational analysis and simulation methods, such as quantum chemistry and molecular dynamics (MD) simulations. These methods can be used to investigate the properties of the ‘electrode/ionic liquid’ interface at the molecular scale. To obtain the distribution of cations and anions on the electrode surface by using the number density distribution, to explain the double-layer structure in the ionic liquids/electrode interface stratification, and explain the experimental phenomena and to verify the theoretical hypothesis.

Recently, researchers investigate the ILs/Au electrode interface from the theoretical point of view. Ruzanov et al [16] combined with density functional theory (DFT) found that [EMIM]BF4 formed a multilayer structure on the Au plane, and the integral and differential capacitances decreased with increasing electrode potential. Sha et al [10] studied various electrochemical properties of 1-butyl-3-methyl-imidazolium hexafluorophosphosphate ([BMIM]BF4) on Au(100) surface, and they also compared with their former work of ionic liquids on graphene surface. It was found that imidazole ionic liquids showed a positive zero charge potential on neutral graphite electrode but a negative zero charge potential on neutral Au electrode, indicating that there are obvious differences between ionic liquids on graphite surface and that on metal surface. Moreover, Au/ionic liquid system has high conductivity, high thermal and chemical stability [17]. Therefore, it is very meaningful and necessary to study the interface of ionic liquid on the surface of Au electrode.

Imidazolium-based ILs have attracted the attention of researchers due to their relatively special structures and properties, such as asymmetric ionic structures, uneven charge distribution, easy to assemble and wide electrochemical window [25]. As the alkyl chain of imidazolyl cations increases, the steric hindrance of the alkyl group increases, the viscosity of the imidazolium ionic liquid becomes larger, and the conductivity becomes smaller [26–30]. Jung et al [18] used the method of molecular dynamics simulation to study the effects of alkyl chain length on interfacial structure of imidazolium-based ILs in graphene supercapacitor of and found that with the increase of alkyl chain length, the interface double-layer structure became loose and the capacitance decreased. Li et al [19] found that the alkyl chain length could tune the compositions and structure of the interfacial layer, using the atomic force microscopy (AFM). Although the ILs/electrode interfacial systems have been studied, seeing from the micro view, we don’t have a deeper understanding of the interfacial behaviors of the system. Also, for some experiments, the current level of technology makes it difficult to achieve the constraints of the stringent laboratory conditions. The ionic liquids/electrode interface can only be characterized by a combination of test methods. In addition, the working environment and the properties of ionic liquids make them hygroscopic, and traditional methods often fail to produce high purity ionic liquids and lack a completely untainted electrode surface, resulting in abnormal results. Therefore, in order to overcome the limitations of traditional experimental methods and to better understand the mechanism of ionic liquid bilayer structure formation, we attempted to model the ‘ionic liquid/electrode’ interface through molecular dynamics simulation, to obtain the specific distribution of anions on the electrode surface and the orientation of cationic imidazole rings in the bilayer, and to discuss the influence of imidazole cation alkyl chain length on the bilayer structure of ionic liquid electrode interface. In addition, by using the molecular dynamics simulations to study the properties of the ‘ionic liquid/electrode’ interface can speed up the research and product selection and greatly reduce the cost of experimental studies.

The outline of this paper is as follows: the model system and simulation methods employed in this study will be given in section 2. Results of molecules dynamics (MD) are compiled in section 3, where interfacial structures and orientations of imidazolium-cations of ILs/Au(100) systems, comprising two Au electrodes and 1-Cn (n = 2, 4, 6)-3-methylimidazolium tetrafluoroborate ionic liquids, the variation on the length of alkyl chain was analyzed. We also give our conclusions in the last section.
2. Simulation details

2.1. Force field
The force field of cations in this work was based on the optimized potential for liquid simulation/all atom OPLS-AA suggested by Jorgensen et al [31, 32] and developed by Lopes et al [33]. Parameters for BF$_4^-$ were obtained from the work of Wu et al [34].

2.2. System building
Our MD simulations were performed for IL-electrode systems of three different ILs: 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF$_4$), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) and 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM]BF$_4$), using the GROMACS 5.1.4 package. The initial configurations of ILs/Au(100) binary systems were consisted of ILs bulk phase and two Au electrode in a tetragonal box, as shown in figure 1.

In order to obtain the minimum-energy geometry of three ionic liquids, we performed the quantum-mechanical ab initio calculations by using the GAUSSIAN 09 package at the RHF/6-31+G(d) level. We employed vibrational analysis on ab initio structure to ensure the absence of negative vibrational frequencies, and verify the existence of a true minimum at the same time. The optimized geometry of three ILs was employed in our MD simulation. Each ILs bulk systems consisted with 256 ion pairs. An NPT run using a Berendsen thermostat was followed for 5 ns to obtain ILs bulks, the results of bulk sizes were $34 \times 34 \times 66$ Å$^3$, $34 \times 34 \times 78$ Å$^3$ and $34 \times 34 \times 92$ Å$^3$, for [EMIM]BF$_4$, [BMIM]BF$_4$ and [HMIM]BF$_4$, respectively. There are 432 fixed Au atoms arranged in a face-centered cubic (Fcc) structure with the (100) surface exposed to the ILs in each electrode using the Material Studio package. A slab of vacuum was inserted into the box to neutralize any image charge effects, so the dimensions of the simulation box were 34 Å in the x and y directions and the z-dimensions were fixed to 350 Å for each ILs. Surface charge densities of the positive electrode and negative electrode were set in the total charge of ±8e, where e is an elementary charge.

2.3. Simulation parameters
All MD simulations were carried out at 350 K and at a pressure of 1 bar with a time step of 1 fs. Periodic boundary conditions were applied in all directions with long-range van der Waals tail corrections for both energy and pressure applied for distances larger than 1.4 nm. Long-range Coulomb interactions were addressed using the particle mesh Ewald method with a cutoff of 1.2 nm and a grid spacing of 0.12 nm, and for the neighbor list using a Verlet cutoff scheme [35]. Equilibrium simulations were carried out with 20 ns equilibration, followed by a 10 ns production run from which ensemble averages were computed, trajectory dates were written at every 10 timesteps.

3. Results and discussion

3.1. Mass density profiles of three ILs
In order to investigate the electric double layer structure at the interface between the ionic liquids bulk phase and the planar electrode, the mass density profile normal to the Au surface along z axis for three ionic liquids with different electrode surfaces are neutral (a), negative (b) and positive (c), respectively, as exhibited in figure 2. It illustrates that, the ionic liquid bulk phase has obvious delamination on all electrode surfaces. There are three distinct peaks, which extend to 16 Å from the electrodes surface. This result coincides with results obtained in different RTILs [12, 13]. The peak height of theionic liquid [EMIM]BF$_4$ is higher than that of the other two ionic
liquids, which indicates that the increase of the imidazole chain length will weaken the distribution of the ionic liquids in the first layer to a certain extent.

A clear three-layer structure can be observed on the surface of the neutral electrode, figure 2(a). The heights of the first layer are both higher than the bulk mass density. Moreover, the heights of the first peaks close to the Au interface are 350%, 325% and 290% higher than that of the bulk ILs, for [EMIM]BF₄, [BMIM]BF₄ and [HMIM]BF₄, respectively. This is because the electrode surface has a strong force on the ionic liquid, enhancing the ion adsorption of the ionic liquid on the electrode surface. The first dense layer is produced at a distance of about 0.3 nm, while the second layer is produced at a distance of about 0.8 nm from the pole plate, the peak of the second layer is lower than the peak of the first layer, indicating that the electrode at the location of the second layer has less force on the ionic liquid. However, the height of the first peak decreases as the alkyl chain on the imidazole ring increases and the positions of the peaks of each layer of the three ionic liquids are almost the same. Illustrating that the growth of alkyl chains of imidazolyl ionic liquids reduces the distribution of ionic liquids within the first layer of the electrode surface. The height of the first peak at the negatively charged Au electrode is not different from that at the neutral electrode, but the position of the second peak appears significantly different. At the positive electrode surface, a layering situation different from that of the neutral electrode is shown. Two peaks appeared in the first layer, and the height of the first peak was also decreased. The second peak appeared in the same position as on the surface of the negative electrode. Since the distribution of anion and cation ions at the surface of the positive and negative electrode should be different, the above differences may be caused by the uneven distribution of anions and cations.

The mass density distribution of the ionic liquid shows a clear double layer structure on the surface of the electrode. The strong interaction between the ions of the ionic liquid and the electrode surface is indicated, making the ionic liquid more inclined to adsorb on the electrode surface, forming a dense two-layer structure. Therefore, the distribution of anion and cation ions at the surface of the electrodes would be further discussed in the next section.
3.2. Number density of cations and anions

In order to obtain the distribution of anions and cations in the ionic liquid bilayer structure and the effect of the charged electrode on the anions and cations of the ionic liquid, we made the number density distribution of anions and cations to compare the force of the electrode on anions and cations. The results of number density distribution of three ILs are shown in Figure 3. There were some differences in the EDL structures, due to the different alkyl chain length of the cations. In general, as the alkyl chain rising, the number of anions and cations in the first layer decreases. This should be due to the growth of the cationic alkyl chain, which increases the volume of the cations and takes up more space. Results of ionic liquid [EMIM]BF₄ on the surface of neutral electrode is shown in figures 3(a) and 2(d), it can be seen that the first peak of [EMIM]⁺ starts to appear at 3.3 Å from the electrode, while the peak of anion appears later at 3.7 Å from the electrode, but the peak of anion is slightly higher than the cation. It indicates that cations are closer to the electrode surface than anions, but there are more anions than cations in the first layer. Same trends have been found in [BMIM]BF₄ and [HMIM]BF₄, as shown in figure 3. It is important to note that the second peak of the anion number density distribution of the ionic liquid [HMIM]BF₄ on the surface of the neutral electrode appeared earlier than the other two ionic liquids.

Figures 3(b) and (e) shows the distribution of cations and anions at positive electrode. The peaks of the anions became taller and thinner, indicating that the number of anions accumulated in the first layer was increasing, while the peak height of the cations was reduced, but the presence of cations was still observed in the first layer. Which is consistent with simulation studies with ionic liquids [BMIM]PF₆ and Au electrode [10]. The cation first peak height of the three ionic liquids are almost the same, but the order of the peak heights of the anions is [EMIM]⁺ > [BMIM]⁺ > [HMIM]⁺. Which means that the increase of alkyl chain length obviously affects the distribution of anions on the surface of positively charged electrode, and the number of anions in the first layer decreases with the rising of chain length. Compared with the surface of the positive electrode, the distribution of anions and cations in the first layer of the negative electrode surface is significantly different. No anion distribution was observed in the first layer, indicating that only cations were present in the first layer. Alternating layers of ions and ions are formed.

3.3. Orientation of cations at the interface

To obtain more details of the interfacial solvent layer and to explain the special distribution of ionic liquids [HMIM]BF₄ in figure 3(d), orientations of imidazolium ring plane to the electrode surface are analyzed, as show in figure 4. Probability distribution P(θ_ring) of the angle θ_ring between the electrode surface and normal vector of imidazolium ring plane in the first layer of ILs were examined. The results of angle distribution of P(θ_ring) in three ionic liquids with respect to different electrodes are illustrated in figure 4. It can be seen that the orientations of [EMIM]BF₄ and [BMIM]BF₄ imidazole rings on the neutral electrode surface are significantly
different from that of [HMIM]BF₄. As the alkyl chain becomes longer, the imidazole ring tends to be parallel to the electrode surface. There are two peaks of \( P(\theta_{\text{ring}}) \) in the former two ionic liquids, the imidazolium ring of [EMIM]⁺ trend to be at 98° and 119°, but the imidazolium ring of [BMIM]⁺ trend to be at 65° and 85°. What is more, we only found one peak in [HMIM]BF₄. Compared with the structure of ionic liquids/graphene system, the arrangement of imidazole cations on the surface of Au electrode is much more well-ordered. This may be attributed to the higher interaction energy between the Au(100) electrode and ions in our system compared with the graphene electrode.

As shown in figure 4(b) only one peak can be observed on the surface of the neutral electrode for the ionic liquid [HMIM]BF₄. Indicating that the distribution of [HMIM]BF₄ was more concentrated on the surface of the neutral electrode, the cations are arranged more regularly and there is more space for the small anions. So the second peak of the anions in the ionic liquid [HMIM]BF₄ appears earlier than the ionic liquid, which just explained the second peak in figure 3(d).

The charged electrodes have effects on the imidazole cations, so that the cations are rearranged on the electrode surfaces. Combining the findings of section 3.2, the number of first layer cations increases at the positive electrode surface, as shown in figure 3(b). The cations are rearranged in a certain order, making a denser arrangement of the cations on the surface of the electrode. On the negative surface, the number of negative ions increases and there are a few cations in the first layer. The crowded anions tend to have imidazole rings parallel to the electrode surface. Thus, the cation is distributed parallel to the imidazole ring on both the anode and cathode surfaces of the electrode. No matter the positive and negative electrode surfaces, the second peak disappears and leaving only one peak for [EMIM]BF₄ and [BMIM]BF₄. Due to the electrostatic interaction between the charged electrodes and the ions, the orientation of the imidazole cations on the surface of the charged electrodes is affected, and the imidazole ring is more inclined to be parallel to the electrode surface, which influence the ion distribution.

3.4. Snapshots of ILs in the first layer

Snapshots in figure 5 show representative configurations of cations in the first solvent layers in the presence of neutral electrodes. It can be clearly observed that the number of anions and cations in the first layer changes significantly. As the chain length increases, the number of cations and anions decreases, and the imidazole ring tends to be parallel to the surface.
4. Conclusion

The electrical double layer structures at Au(100) electrode in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF$_4$), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) and 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM]BF$_4$) have been studied by using the MD Gromacs package. All ionic liquids have a significant layered structure within the distance 16 Å from the electrode surface. The distribution of the three ionic liquids is similar, but the increasing of alkyl chain reduces the distribution of the ionic liquids in the first layer. Specifically, the number of anions in the first layer on positive electrode decreases with the increase of alkyl chain significantly. But for the systems of negative and neutral electrodes, the increase of alkyl chain leads to the decrease of cations and anions in the first layer.

From the results of the orientation distribution of the imidazole ring on the electrode surface in the first layer, it can be seen that the imidazole ring tends to be distributed parallel to the surface of the neutral electrode, but the [EMIM]$^+$ and [BMIM]$^+$ shows two peaks, the [HMIM]$^+$ shows one peak. It means that the arrangement of [HMIM]$^+$ cations in the first layer is more regular and the packing is tightly, which results in a decrease in the distribution of the anion in the first layer. This is due to the increase of the alkyl chain, which increases the steric hindrance of the cations. At the same time, the second peak of the anions is closer to the electrode. The charging of the electrode causes the imidazole ring near the electrodes to be rearranged and more inclined to be arranged parallel to the plate.

These results may help researchers better understand the structure-dependent properties of the imidazolyl ionic liquid / Au(100) electrode interfaces. In practical applications, such results help experimenters to study imidazolyl ionic liquid and gold electrode interfaces. Our results have important implications for the selection of ionic liquids as electrolytes, especially for the selection of cations. In the future study, we will earn to the influence of the interfacial structure of the electrochemical properties (capacitance, charge density, potential, etc) of the ionic liquid on the electrode surface.

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