

Interfacial Structure at the Quaternary Ammonium-Based Ionic Liquids|Gold Electrode Interface Probed by Surface Enhanced Infrared Absorption Spectroscopy: Anion Dependence of the Cationic Behavior

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Abstract

The interfacial structure at the quaternary ammonium-based ionic liquids(ILs)|gold(Au) electrode interface has been studied using surface enhanced infrared absorption spectroscopy (SEIRAS). Four anions, bis(perfluoroalkanesulfonyl)amide ($C_nC_nN^-$; $n = 0, 1, 2, 4$) have been combined with a quaternary ammonium cation, trioctylmethylammonium (N_{881}^+), to investigate the influence of the perfluoroalkyl chain length of the anion on the behavior of the quaternary ammonium cation at the interface. In addition, to investigate the effect of the alkyl chain length of the quaternary ammonium cations on the cationic behavior, we have also combined a cation with a shorter alkyl chain, tributylmethylammonium (N_{441}^+) with $C_1C_1N^-$. Thus, we have performed SEIRAS measurements at the Au interface of five ILs: $[N_{881}^+][C_nC_nN^-]$ ($n = 0, 1, 2, 4$) and $[N_{441}^+][C_1C_1N^-]$. The four CH stretching bands originating from the quaternary ammonium cations have been individually analyzed, enabling us to reveal the behavior of the quaternary ammonium cations at the interface. The cationic behavior is found to dramatically depend not only on the alkyl chain length but also on the perfluoroalkyl chain length of the counter ion. For $[N_{881}^+][C_4C_4N^-]$ and $[N_{881}^+][C_2C_2N^-]$, octyl chains of N_{881}^+ cannot reach the Au electrode surface at positive potentials because the bulky anions in the first ionic layer on the electrode surface block the approach. Conversely, for ILs with the smaller anions ($[N_{881}^+][C_1C_1N^-]$ and $[N_{881}^+][C_0C_0N^-]$) octyl chains of N_{881}^+ can penetrate into a space in the first ionic layer of small anions. The butyl chains of N_{441}^+ in $[N_{441}^+][C_1C_1N^-]$ cannot reach the surface at positive potentials even across the first ionic layer of the small anions because of their relatively short alkyl chain length.

1 Introduction

Ionic liquids (ILs), which are entirely composed of cations and anions, have various attractive properties such as negligibly low volatility, nonflammability, electrochemical stability, and designability of various physicochemical properties.¹⁻³ ILs are possible candidates as

a new type of electrolyte for electrochemical devices⁴⁻⁶ such as lithium ion batteries,⁷⁻⁹ dye-sensitized solar cells,¹⁰⁻¹² electrical double layer capacitors,¹³⁻¹⁵ and redox flow batteries.^{16,17} To maximize the performance of such devices, it is of crucial importance to understand and control the structure and dynamics of ILs at the electrode interface. Several interface-selective techniques have been used to study the IL|electrode interface, such as x-ray reflectometry,¹⁸⁻²² neutron reflectometry,^{23,24} surface force apparatus,^{25,26} atomic force microscopy,²⁷⁻³⁰ and scanning tunneling microscopy,³¹⁻³³ in addition to theory and simulation.^{3,34-44} These studies have illustrated that IL ions spontaneously form ionic multilayers^{45,46} at the interface and the amount of the ions in each layer depends on the electrode potential. Such a peculiar structure at the IL interface has been found to show ultraslow dynamics⁴⁷⁻⁵¹ and hysteresis.^{20,52-59}

Interface-selective vibrational spectroscopy techniques are powerful tools to study the IL|electrode interface. Baldelli and coworkers used sum frequency generation vibrational spectroscopy (SFG-VS) to conduct pioneering study on the interface between Pt and ILs based on 1-methyl-3-alkylimidazolium ions ($C_n\text{mim}^+$).⁶⁰⁻⁶³ They found that the imidazolium ring of $C_4\text{mim}^+$ lies relatively parallel to the interface at negative potentials while it stands relatively perpendicular at positive potentials.^{60,62,63} Other interface-selective vibrational spectroscopy techniques, infrared absorption spectroscopy (IRAS),⁶⁴ surface-enhanced infrared absorption spectroscopy (SEIRAS),^{58,65} and surface-enhanced Raman spectroscopy (SERS)⁶⁶⁻⁶⁸ have confirmed a similar trend in the orientation of the imidazolium ring. Zhou, Ouchi, and coworkers found, by using SFG-VS at the Pt interface of $[C_4\text{mim}^+]\text{trifluoromethanesulfonate}$ ⁵⁵ and $[C_4\text{mim}^+][C_1C_1N^-]$ ($C_nC_nN^-$: bis(perfluoroalkanesulfonyl)amide),⁵⁷ that the potential dependence of the vibrational bands for the IL anions exhibits hysteresis. They suggested that the hysteresis results from adsorption/desorption of the anions at the first ionic layer. Motobayashi et al. also found such a hysteresis during a potential scan in SEIRAS measurements at the Au interface of $[C_4\text{mim}^+][C_1C_1N^-]$ ⁵⁸ and several other ILs.⁶⁹ Analysis of the vibrational bands for both of the IL cations and anions clarified that during

potential scans, the local ion concentration in the overlayers changes first followed by exchange of ions between the first ionic layer and the overlayers to compensate for the change in the surface charge of the electrode. The results illustrate the existence of an energy barrier for exchange of ions between the first ionic layer and the overlayers.

The electrode interface of imidazolium-based ILs has been relatively well-studied compared with other kind of ILs such as quaternary ammonium-based ILs focused in the present study. Quaternary ammonium-based ILs have an advantage over imidazolium-based ILs in that they are thermodynamically more stable against reduction, leading to a wider potential window at negative potentials.^{70,71} Because of this advantage, quaternary ammonium-based ILs have been applied to electrical double layer capacitor.¹³ Quaternary ammonium cations are more flexible than $C_n\text{mim}^+$ ions because they have multiple (up to four) flexible alkyl chains compared with one alkyl chain in $C_n\text{mim}^+$ ions (except methyl moiety). Such conformation flexibility would provide them interfacial structure and its potential dependence different from $C_n\text{mim}^+$ ions.

Here, we will report a SEIRAS study of the interface between Au and trialkylmethylammonium bis(perfluoroalkanesulfonyl)amide, $[\text{N}_{\text{mmm1}}^+][\text{C}_n\text{C}_n\text{N}^-]$. SEIRAS uses the enhancement of the IR electric field at the metal surface with nanometer scale roughness for its interface selectivity, and it is suitable to investigate electrical double layer (EDL) because its selectivity thickness is comparable with that of the EDL on the level of several nanometers.^{72,73} In previous studies, SEIRAS has been shown to be a powerful tool to study the structure of not only the first ionic layer but also the overlayers on the Au electrode interface of imidazolium-based ILs.^{58,59,69} In the present paper, we show that the structure and conformation of quaternary ammonium cations at the Au electrode interface are dramatically affected by both the alkyl chain length of the cation and the perfluoroalkyl chain length of the amide anion.

2 Experimental

2.1 Preparation of ILs

The ILs, $[\text{N}_{8881}^+][\text{C}_n\text{C}_n\text{N}^-]$ ($n = 0, 1, 2, 4$), were prepared by mixing $[\text{N}_{8881}^+]\text{Cl}$ (Alfa Aesar) with $\text{Li}[\text{C}_0\text{C}_0\text{N}^-]$ (Nippon Shokubai), $\text{Li}[\text{C}_1\text{C}_1\text{N}^-]$ (Kanto Chemical), $\text{H}[\text{C}_2\text{C}_2\text{N}^-]$ (Central Glass) and $\text{Li}[\text{C}_4\text{C}_4\text{N}^-]$ (Mitsubishi Materials), respectively, followed by washing with water to remove the byproduct (LiCl or HCl). $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]$ was similarly prepared with $\text{Li}[\text{C}_1\text{C}_1\text{N}^-]$ and $[\text{N}_{4441}^+]\text{Cl}$, which was synthesized from iodomethane and tributylamine.⁷⁴ The prepared ILs were purified by column chromatography⁷⁵ and colorless liquids were obtained. The structures of some of the cations and anions used in the present study are shown in Figure 1.

2.2 SEIRAS measurements

The SEIRAS measurements were performed using the same setup as previously reported.^{58,69} The working electrode was a Au film deposited on the flat surface of a semicylinder Si prism by an electroless deposition technique.⁷⁶ The counter and quasi-reference electrodes were Pt mesh and Pt wire, respectively. Before the SEIRAS experiments, the spectroelectrochemical cell filled with an IL was evacuated at 5×10^{-6} Torr at 80 °C overnight to eliminate water and other gaseous contaminants. The SEIRAS measurements were performed at 5×10^{-6} Torr and room temperature. Each SEIRA spectrum at a specific potential is a difference spectrum with respect to the spectrum at a reference potential. The reference spectrum for SEIRAS was recorded after the potential was kept at the initial potential for 200 s and just before the potential scan of cyclic voltammetry (CV). After the measurements, we checked water contents in the ILs by using the Karl Fischer titration and the contents were less than 30 ppm. Even with the low water contents, because of the enhancement effect of SEIRAS, we can detect broad O-H stretching mode of trace water in SEIRA spectra (Supporting Information). The behavior of the mode is similar to that in a recent SEIRAS study on the

IL|Au interface by Motobayashi and Osawa⁵⁹ where more intense band was observed at more positive potentials, suggesting potential-dependent accumulation of water at the interface. They found that the EDL structure and behavior in ILs are basically similar even after small amount of water (700 ppm) is intentionally added into ILs, except for slight acceleration of potential-induced structural change in the EDL.⁵⁹ Their results illustrate that the effect of water on the EDL in ILs is marginal in the level of water contents in the present study.

3 Results and discussion

3.1 ILs of large anions: $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$ and $[\text{N}_{881}^+][\text{C}_2\text{C}_2\text{N}^-]$

Figure 2a shows a CV at the $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$ |Au interface and Figure 2b shows typical SEIRA spectra in the CH stretching region at several electrode potentials during the positive-going potential scan of the CV, along with the IR spectrum of bulk $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$ measured with the conventional attenuated total reflection (ATR) configuration without the Au film on the Si prism. In the SEIRA spectra, one can see four CH stretching vibrational bands ($\nu(\text{CH})$) originating from N_{881}^+ existing in the EDL at the $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$ |Au interface. The four bands are assigned to the symmetric and asymmetric stretching modes of the CH_2 and CH_3 moieties of N_{881}^+ . Assignment of the four bands is listed in Table 1. In the SEIRA spectra (Figure 2b), one can see a similar trend for all of the four CH stretching bands; at relatively positive (negative) potentials the bands show dips (peaks). The dips mean less absorption at the potentials than at the reference potential (-0.6 V) and can be explained from a simple electrochemical point of view; at relatively positive potentials, N_{881}^+ cations with CH_2 and CH_3 moieties are depleted in the EDL. In contrast, at relatively negative potentials, N_{881}^+ cations accumulate, resulting in peaks in the SEIRA spectra. Thus the SEIRA spectra in Figure 2b are quite reasonable when considering the local concentration of N_{881}^+ in the EDL at the electrochemical interfaces. In Fig.S1 we show SEIRA spectra in the lower wavenumber region during the same measurements exhibiting SO and CF stretching

modes, both of which originate from $\text{C}_4\text{C}_4\text{N}^-$. As expected, the potential dependence of the anion bands in Figure S1 is opposite to that of the cation bands in Figure 2; the anion bands show peaks (dips) at positive (negative) potentials, corresponding to higher (lower) local concentrations of $\text{C}_4\text{C}_4\text{N}^-$ in EDL at the $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]|\text{Au}$ interface.

It should be noted that the behavior of the absorption bands in the SEIRA spectra is determined not only by the local concentration of the IR-active moieties in the EDL but also by their orientation. The orientation dependence of the vibration bands originates from the anisotropic direction (surface normal direction) of the IR electric field induced at the metal interface.^{72,77} The absorption is proportional to the magnitude of the dot product of the transition dipole moment of the vibration bands with the IR electric field. Therefore, when the transition dipole moment is more orientated along the surface normal, the moieties interact more with the IR electric field, leading to more absorption. This mechanism, so called the surface selection rule, has been utilized to obtain information about the interfacial orientation of molecules from SEIRA spectra. The results shown in Figure 2b and Figure S1b seem to suggest that there is no drastic orientation change of both N_{881}^+ and $\text{C}_4\text{C}_4\text{N}^-$ by changing the electrode potential because the relative band intensities do not change with respect to the potential. This is opposite to the case with the electrode interface of C_4mim^+ -based ILs where a drastic orientation change of the C_4mim^+ cation is observed by SEIRAS^{58,65} and SFG-VS.⁶⁰ For C_4mim^+ , the C_4mim^+ cation is orientated with the imidazolium ring relatively parallel to the surface at negative potentials because of the attractive electrostatic interaction between the positive charge on the imidazolium ring and the negative charge induced on the electrode surface. Conversely, at positive potentials, the electrostatic interaction changes from attractive to repulsive, leading to the C_4mim^+ orientation being relatively perpendicular to the surface. The stretching vibration of the imidazolium ring CH with a transition dipole moment parallel to the ring plane shows a stronger absorption band at positive potentials, because it interacts with the surface-normal IR electric field. The peculiarity of imidazolium ions like C_4mim^+ compared with quaternary

ammonium cations like N_{881}^+ is probably because $C_n\text{mim}^+$ has a rigid aromatic moiety with delocalized positive charge. Such a moiety will drastically change the orientation when the surface charge on the electrode is changed. The rigid and positively charged imidazolium ring behaves differently from the flexible and neutral alkyl moieties of quaternary ammonium cations. A flexible moiety can easily change its conformation and orientation depending on its local environment and a neutral moiety is not directly affected by the surface charge on the electrode.

To more quantitatively discuss the behavior of the IR bands in Figure 2b, the intensities of the bands were evaluated by integrating the peaks. The wavenumber ranges for integration of the bands are shown in Figure 2b as the gray background and they are listed in Table 1 along with each assignment. The integration range was chosen to be sufficiently narrow to minimize the influence of overlapping neighboring bands. We did not find any Stark shift beyond the spectral resolution for the vibrational modes of the quaternary ammonium cations in the present study, although the Stark shift was reported for those of the imidazolium ring in $C_n\text{mim}^+$ ions.⁶⁶ Furthermore, the bandwidths of the bands do not vary with the electrode potential. Therefore, this way of integration is quite effective to separately focus on the potential dependence of each band. Voltabsorptograms (potential dependence of the absorption band intensity) for the four CH stretching modes during the potential scan at the $[N_{881}^+][C_4C_4N^-]|Au$ interface are shown in Figure 2c. As qualitatively observed in Figure 2b, one can see that the intensities of the cation-based bands decrease with increasing potentials. Also shown in Figure 2c is the potential of zero charge (E_{pzc} , -0.18 V, vertical dotted line), which was measured using the immersion method.^{51,58,78,79} One can see that the slopes of the plots changes at E_{pzc} ; a gradual slope at $E < E_{pzc}$ and a steep slope at $E > E_{pzc}$ for all of the bands. Because we are unsure whether this change in the slope only results from accumulation and depletion of IL ions in the EDL, not from the orientation effect, we performed a model simulation of the voltabsorptogram for IL ions in the EDL. In the model, we calculated the local concentration of IL cations and anions in the EDL and, by

combining with surface enhancement factor, we estimated the relative absorbance values of the cation and anion bands depending on the potential (details of the model are described in the Supporting Information). The model voltabsorptograms for N_{8881}^+ and $C_4C_4N^-$ are shown in Figure 3. At both positive and negative potentials far away from E_{pzc} , the slope of the model voltabsorptogram for N_{8881}^+ is gradual. The reason for the former is simple; at $E \gg E_{pzc}$ the EDL is predominantly occupied by IL anions and few IL cations remain in the EDL region (and the SEIRA enhancement region) when E becomes very positive. The latter is because of the lattice saturation,³⁶ that is, at sufficiently negative potentials, IL cations already occupy some of the closest ionic layers and subsequent cations coming from the bulk for charging the electrode cannot approach the electrode where SEIRA enhancement is high. The gradual slope at more negative potentials than E_{pzc} in Figure 2c is likely because of the lattice-saturation effect. The behavior of the anions in Figure S2c is similar, although there is strong hysteresis of the potential dependence of the bands. In Figure 2c and Figure S2c, one can clearly see hysteresis in the potential dependence of the band intensity. Such hysteresis has also been observed in SEIRA spectra at the Au interface of $[C_4mim^+][C_1C_1N^-]$ ⁵⁸ and other ILs,⁶⁹ and originates from the energy barrier for ionic exchange between the first ionic layer and the overlayers in the EDL. Hysteresis was also observed for all of the other quaternary ammonium-based ILs in the present study, indicating the generality of this phenomenon for the electrode interface of ILs (one exception has been confirmed to be $[C_4mim^+][BF_4^-]$.^{58,69})

To investigate the anion dependence of the ionic behaviors at the interface we performed SEIRAS measurements for $[N_{8881}^+][C_2C_2N^-]$, an IL with a smaller anion than $C_4C_4N^-$. $C_2C_2N^-$ has a shorter perfluoroalkyl moiety (perfluoroethyl) than $C_4C_4N^-$ (perfluorobutyl). The voltabsorptograms representing the cationic and anionic behavior are shown in Figure S4. The results are similar to those of $[N_{8881}^+][C_4C_4N^-]$, indicating that the IL anion has no influence on the interfacial structure in this ionic size range.

3.2 ILs of small anions: $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ and $[\text{N}_{881}^+][\text{C}_0\text{C}_0\text{N}^-]$

We performed similar experiments for $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ to further diminish the anion size. Figure 4a and Figure 4b show a CV and SEIRA spectra for the $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface. The four CH stretching bands are discernible in Figure 4b, similar to Figure 2b. Their intensities vary with the potential, but the tendency is different from that in Figure 2b. The intensities of the CH_3 -related bands (2875 and 2960 cm^{-1}) increase with decreasing potential, which is a similar trend to Figure 2b. However, the intensities of the CH_2 -related bands (2850 and 2920 cm^{-1}) decrease in contrast to the $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$ case in Figure 2b. This is also clearly seen in Figure 4c, which shows the band intensity of each band. This opposite tendency for the CH_3 and CH_2 bands indicates that the orientation effect described above surpasses the local concentration change for the $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ case as is the case with C_4mim^+ .^{58,60,65} It should be emphasized here that we observed such a switch of the tendency of the cation bands when we changed the IL-anion, from $\text{C}_4\text{C}_4\text{N}^-$ to $\text{C}_1\text{C}_1\text{N}^-$, illustrating that IL anions affect the interfacial behavior of IL cations. In contrast, the anion bands for $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ shown in Figure S2 exhibit a potential dependence similar to that for $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$ in Figure S1. Therefore, only the N_{881}^+ cations of $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ change their orientation enough with the potential change to be observed in the SEIRA spectra.

This puzzling behavior of $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ was reproduced for $[\text{N}_{881}^+][\text{C}_0\text{C}_0\text{N}^-]$, which is the IL of the smallest anion considered in the present study. The voltabsorptograms representing the cationic and anionic behavior are shown in Figure S5. Therefore, considering all of the data for $[\text{N}_{881}^+][\text{C}_n\text{C}_n\text{N}^-]$, we can conclude that there must be a threshold of the anionic size to change the cationic behavior in SEIRAS from predictable to unpredictable using the simple EDL model.

Here, we consider the interfacial structure of the puzzling results for $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ and $[\text{N}_{881}^+][\text{C}_0\text{C}_0\text{N}^-]$, that is, the ILs of the smaller anions. When $E \ll E_{\text{pzc}}$, N_{881}^+ will be preferentially located in the first ionic layer, forming a “cation layer”. Because the positive charge is localized around the N atom in N_{881}^+ , the positively-charged N atom in the first ionic layer

will be attracted to the negatively-charged Au surface. Therefore, N_{881}^+ has an orientation with the methyl group pointing toward the surface and oppositely the three long octyl chains against the surface (the $[N_{881}^+][C_1C_1N^-]$ case in Figure 6a). In such an orientation, the octyl chains are relatively directed along the surface normal, and the transition dipole moments for the two CH_2 bands are directed along the surface, leading to less interaction with the IR electric field and therefore less absorption. This view can explain why relatively low absorption of the CH_2 bands was observed at negative potentials (Figure 4c). At positive potentials, the first ionic layer is occupied by the small anions. Taking into account the increase in the CH_2 band intensity at positive potentials, the octyl chain of N_{881}^+ is likely to be inserted into the first anionic layer (Figure 6b). A recent MD simulation study of the interface between a graphene electrode and $[N_{228}^+][C_1C_1N^-]$ ⁴³ supports this view, where the authors found that the octyl chain of N_{228}^+ in the second ionic layer is inserted into the first $C_1C_1N^-$ layer at a positive potential. Similar insertion of the octyl chains of N_{881}^+ into the first anionic layer would be the cause of the increase of the intensities of the CH_2 bands at positive potentials (Figure 4c).

Some questions remain about the potential dependent behavior of N_{881}^+ . First, why do the CH_3 bands not exhibit behavior similar to the CH_2 bands for $[N_{881}^+][C_1C_1N^-]$ and $[N_{881}^+][C_0C_0N^-]$? At negative potentials, the CH_3 moiety next to the N atom of N_{881}^+ will be close to the electrode surface, contributing to the high absorbance of the CH_3 bands. The other three CH_3 moieties at the terminus of the octyl chains of N_{881}^+ would make some contribution to the absorbance. At positive potentials, the small anions form the first ionic layer and the CH_3 moiety next to the N atom will not show the high absorbance because of the distance of the first anionic layer thickness from the electrode surface. Some of the octyl chains would be inserted into the first anionic layer, but not all of them. This is probably the reason why the CH_3 band behavior is predictable with the EDL model (Figure 4c). Second, how about the behavior of N_{881}^+ in $[N_{881}^+][C_4C_4N^-]$ and $[N_{881}^+][C_2C_2N^-]$ (ILs of the bulkier anions), after we see drastic difference for the bands of N_{881}^+ in $[N_{881}^+][C_1C_1N^-]$ and

$[\text{N}_{881}^+][\text{C}_0\text{C}_0\text{N}^-]$? For $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$ and $[\text{N}_{881}^+][\text{C}_2\text{C}_2\text{N}^-]$, the ILs are based on a bulkier anion than $\text{C}_1\text{C}_1\text{N}^-$ or $\text{C}_0\text{C}_0\text{N}^-$, and it would be difficult to realize such alkyl chain insertion because the bulkier anions are easily fully packed in the first ionic layer at moderate potentials (Figure 6c). Moreover, the bulkier-anion layer is thicker than the smaller-anion layer, blocking octyl chain penetration to the bottom of the first anionic layer where the surface enhancement is high. For $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$ (Figure 2c) and $[\text{N}_{881}^+][\text{C}_2\text{C}_2\text{N}^-]$ (Figure S4), the barrier formed by the bulky anionic layer would make the voltabsorptogram predictable with the EDL model (Figure 3).

3.3 IL of a short-chain cation: $[\text{N}_{441}^+][\text{C}_1\text{C}_1\text{N}^-]$

We assumed that insertion of the octyl chains into a space in the first $\text{C}_1\text{C}_1\text{N}^-$ layer is the cause of the peculiar voltabsorptograms for $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ (Figure 4c). To examine the validity of this assumption, we adopted N_{441}^+ , quaternary ammonium cation with a shorter alkyl chain than N_{881}^+ , and studied the behavior of the cation at the Au interface of $[\text{N}_{441}^+][\text{C}_1\text{C}_1\text{N}^-]$ by SEIRAS. We expected that the shorter chains would fail to reach the electrode surface even when they are inserted into the first $\text{C}_1\text{C}_1\text{N}^-$ layer at positive potentials, losing the peculiar behavior $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$ exhibited. Figures 5b and 5c show the potential dependence of the SEIRA spectra and their band intensities of N_{441}^+ at the $[\text{N}_{441}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface, respectively, and Figure S5 shows anion SEIRA spectra. The potential dependence of the four CH bands reverts to simple behavior like that for $[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$. The butyl chains are probably inserted into the $\text{C}_1\text{C}_1\text{N}^-$ layer, however, they are too short to penetrate to the bottom of the $\text{C}_1\text{C}_1\text{N}^-$ layer (Figure 6d).

4 Conclusions

The behavior of quaternary ammonium cations at the electrode interface of quaternary ammonium-based ILs is significantly affected by the anion structure, depending on their

own alkyl chain length. This finding was made possible by utilizing SEIRAS, an interface-selective vibrational spectroscopy technique and, furthermore, by individually investigating each CH stretching vibration mode of quaternary ammonium cations.

The alkyl chains of the quaternary ammonium cations are inserted into a space in the first anionic layer. The neutral alkyl chains act as space-filling moieties, which probably have a loose structure and can be replaced by redox species coming from the IL bulk much more easily than the charged parts of IL ions forming the first ionic layer. Such replacement of the moieties of IL ions by redox species will be of crucial importance to reveal the kinetics and mechanisms of electrode reactions in ILs, especially in electrodeposition⁸⁰ and lithium-ion batteries,⁴⁴ where the redox species have to penetrate the first ionic layer and reach the interface so that they can deposit at the interface and transfer across the interface, respectively. A SEIRAS study of several quaternary ammonium-based ILs with different alkyl chain lengths containing redox species would further clarify the role of the alkyl chains.

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Supporting Information Available

SEIRA spectra of the anion bands ($[\text{N}_{881}^+][\text{C}_4\text{C}_4\text{N}^-]$, $[\text{N}_{881}^+][\text{C}_1\text{C}_1\text{N}^-]$, and $[\text{N}_{441}^+][\text{C}_1\text{C}_1\text{N}^-]$, voltabsorptograms of the cation and anion bands for $[\text{N}_{881}^+][\text{C}_2\text{C}_2\text{N}^-]$ and $[\text{N}_{881}^+][\text{C}_0\text{C}_0\text{N}^-]$, details of the EDL model, and SEIRA spectra for the water stretching region.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

Table 1: Assignment of CH stretching vibration modes.

Symbol	Mode	Peak position (cm^{-1})	Integration region (cm^{-1})
$\nu_s(\text{CH}_2)$	symmetrical stretching of CH_2	2850-2866	2843-2862
$\nu_s(\text{CH}_3)^a$	symmetrical stretching of CH_3	2871-2880	2868-2881
$\nu_{as}(\text{CH}_2)$	asymmetrical stretching of CH_2	2928-2938	2914-2940
$\nu_{as}(\text{CH}_3)$	asymmetrical stretching of CH_3	2965	2953-2976

^a Fermi resonance of $\nu_s(\text{CH}_3)$ should be around at $2915\text{-}2924\text{ cm}^{-1}$ but is weak and overwhelmed by the $\nu_{as}(\text{CH}_2)$ band.

Figure captions

Fig. 1 Structures of some of the ions of the ILs in the present study.

Fig. 2 (a) Cyclic voltammogram at 2 mV s^{-1} and (b) SEIRA spectra at the $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]|\text{Au}$ interface and the IR spectrum of bulk $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]$. The SEIRA spectra were recorded at the potentials shown as solid circles in (a) during the CV. The reference spectrum for the SEIRAS was taken before the potential scan at the initial potential (-0.6 V). (c) Voltabsorptograms at the $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]|\text{Au}$ interface for the four CH stretching vibrational bands: $\nu_s(\text{CH}_2)$ (solid diamonds), $\nu_s(\text{CH}_3)$ (open diamonds), $\nu_{\text{as}}(\text{CH}_2)$ (solid squares), and $\nu_{\text{as}}(\text{CH}_3)$ (open squares).

Fig. 3 Model voltabsorptogram for the electrode interface of $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]$.

Fig. 4 (a) Cyclic voltammogram at 2 mV s^{-1} and (b) SEIRA spectra at the $[\text{N}_{8881}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface and the IR spectrum of bulk $[\text{N}_{8881}^+][\text{C}_1\text{C}_1\text{N}^-]$. The SEIRA spectra were recorded at the potentials shown as solid circles in (a) during the CV. The reference spectrum for the SEIRAS was taken before the potential scan at the initial potential (-0.8 V). (c) Voltabsorptograms at the $[\text{N}_{8881}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface for the four CH stretching vibrational bands: $\nu_s(\text{CH}_2)$ (solid diamonds), $\nu_s(\text{CH}_3)$ (open diamonds), $\nu_{\text{as}}(\text{CH}_2)$ (solid squares), and $\nu_{\text{as}}(\text{CH}_3)$ (open squares).

Fig. 5 (a) Cyclic voltammogram at 2 mV s^{-1} and (b) SEIRA spectra at the $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface and the IR spectrum of bulk $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]$. The SEIRA spectra were recorded at the potentials shown as solid circles in (a) during the CV. The reference spectrum for the SEIRAS was taken before the potential scan at the initial potential (-0.8 V). (c) Voltabsorptograms at the $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]|\text{Au}$ interface for the four CH stretching vibrational bands: $\nu_s(\text{CH}_2)$ (solid diamonds), $\nu_s(\text{CH}_3)$ (open diamonds), $\nu_{\text{as}}(\text{CH}_2)$ (solid squares), and $\nu_{\text{as}}(\text{CH}_3)$ (open squares).

Fig. 6 Schematics of the interfacial structures of the quaternary ammonium based ILs at the Au interface for (a,b) $[\text{N}_{8881}^+][\text{C}_1\text{C}_1\text{N}^-]$, (c) $[\text{N}_{8881}^+][\text{C}_4\text{C}_4\text{N}^-]$, and (d) $[\text{N}_{4441}^+][\text{C}_1\text{C}_1\text{N}^-]$ at (a) $E < E_{\text{pzc}}$ and (b-d) $E > E_{\text{pzc}}$.

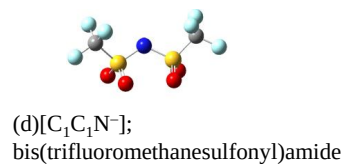
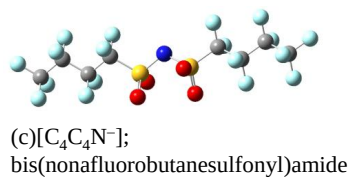
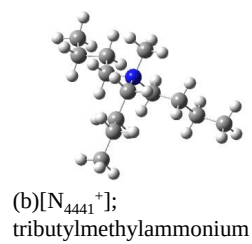
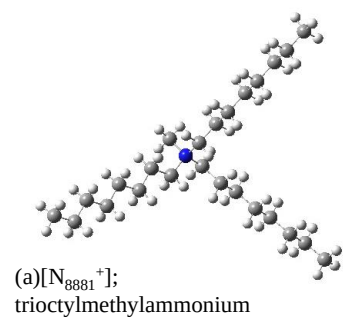


Fig.1 (Nishi et al.)

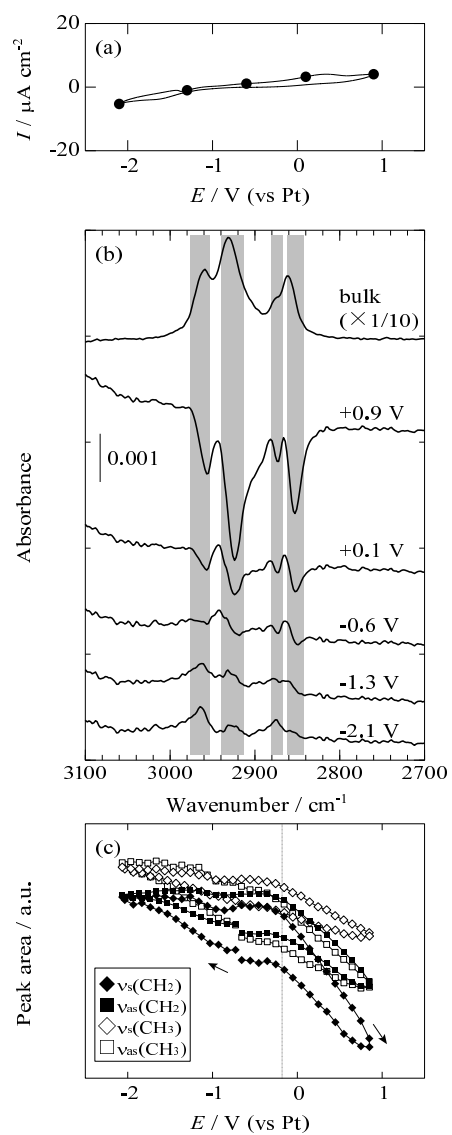


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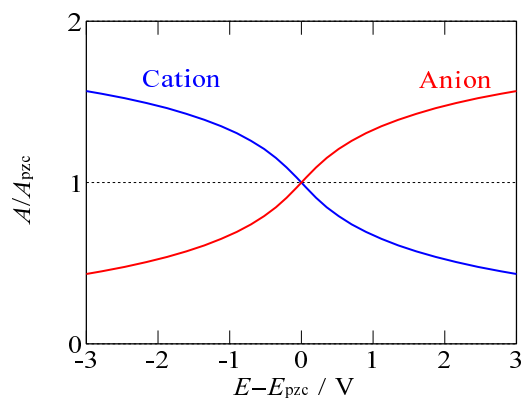


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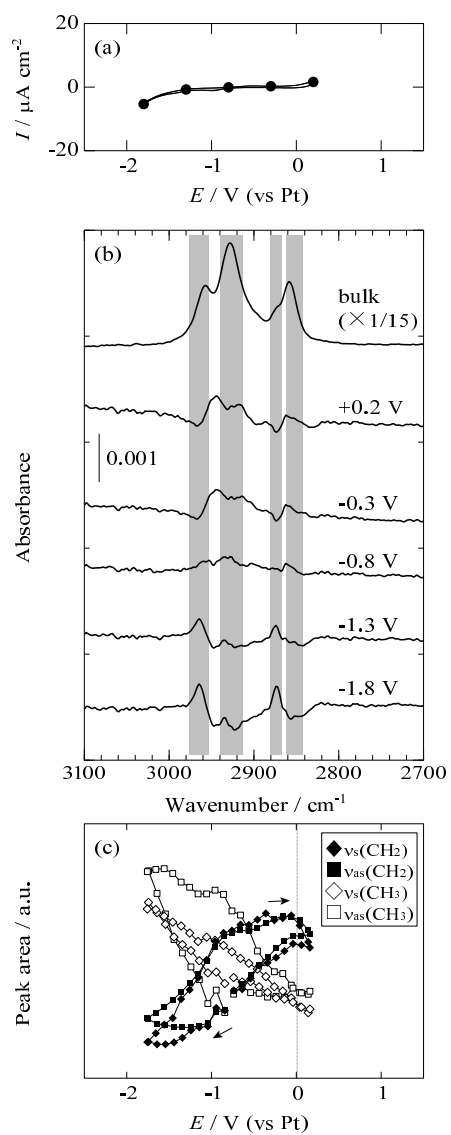


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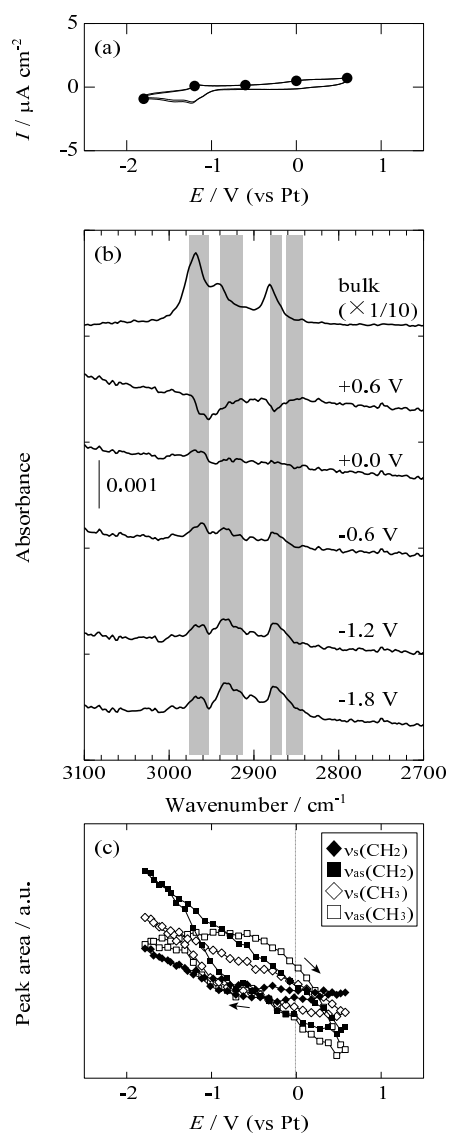


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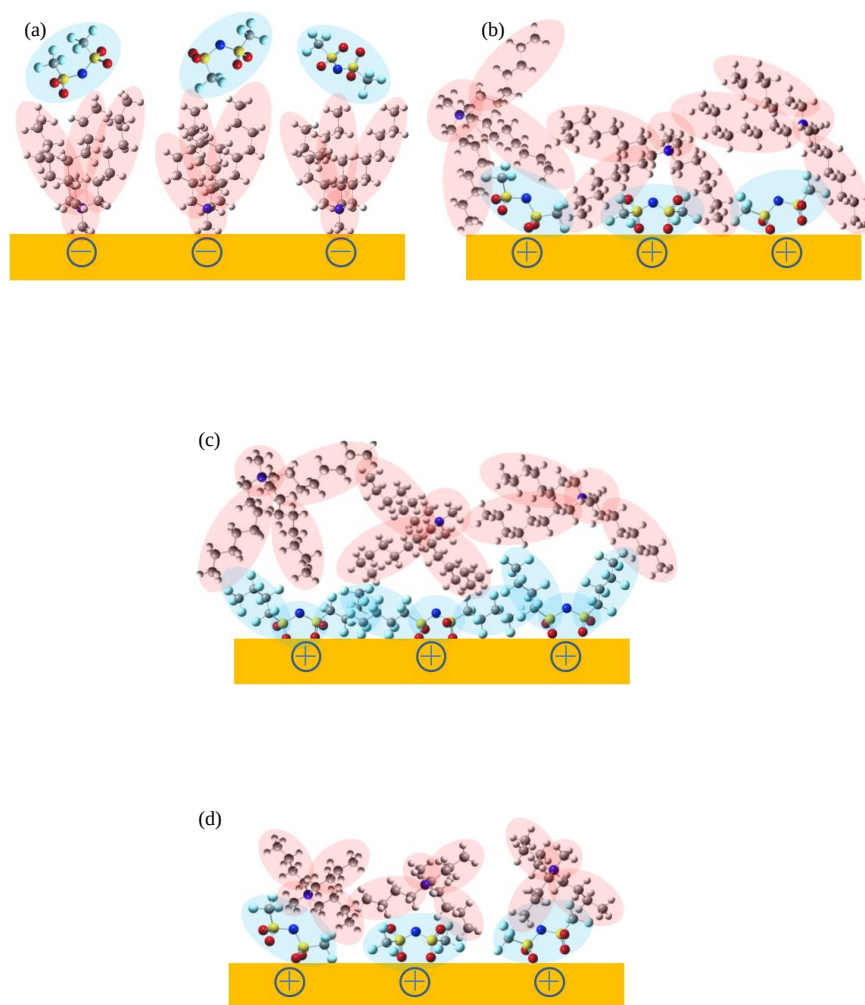


Fig.6 (Nishi et al.)

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TOC Graphic

