

Interfacial Viscosity and Ionic Reorientation Probed Using Electrochemical Surface Plasmon Resonance at the Gold Electrode Interface of Ionic Liquids

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Abstract:

The interfacial dielectric relaxation of ionic liquids (ILs) at the gold electrode interface has been investigated using electrochemical surface plasmon resonance (SPR), by analyzing the SPR response to the potential step for four ILs with the two cations, trioctylmethylammonium and 1-butyl-3-methylimidazolium, and three amide anions, bis(fluorosulfonyl)amide, bis(trifluoromethanesulfonyl)amide, and bis(nonafluorobutanesulfonyl)amide. For all the four ILs, the SPR response to the potential step exhibits a fast relaxation process mainly ascribable to the ionic reorientation, followed by an ultraslow relaxation process ascribable to the ionic translation, with the opposite directions of SPR shift to each other. The ultraslow relaxations by the positive potential steps are always significantly slower than those by the negative steps. The average time constants of the ultraslow relaxation process and the amplitudes of the fast relaxation process are evaluated by the fitting with a multiple exponential function and are compared with the measured bulk viscosity and the dipole moments of each ion. The interfacial viscosity, estimated from the time constants of the ultraslow relaxation process, is several orders of magnitude higher than the bulk viscosity, and the viscosity increase is larger for the ILs composed of smaller ions. The amplitude of the fast relaxation, reflecting the ionic reorientation, is moderately correlated with the dipole moments of counter-ions on the electrode at the pre-step potential.

Keywords: dynamics, electric double layer, Walden plot, dielectric polarization.

1. Introduction

Ionic liquids (ILs) have been attracting attention as a new type of electrolytes for electrochemical devices such as batteries^[1,2] and supercapacitors.^[3-5] The dynamics at the interface of ILs are critical in the performance of electrochemical devices. However, due to the strong Coulomb interaction, high ionic concentration, and complicated ionic structure, ILs show the dynamics at the interface too complicated to be fully clarified yet. Several experimental studies using techniques such as electrochemical impedance spectroscopy (EIS)^[6-8] and X-ray reflectometry (XR)^[9-11] demonstrated that ILs exhibit several orders of magnitude slower dynamics than the conventional electrolytes at the electrochemical interface. Considered as the reason of the slow interfacial dynamics, the solid-like^[12-18] and multilayered^[8,12,14,15,19-26] ordering structure, originated from the dense ionic arrangement at the IL interface, has been revealed using various experimental methods.

The ultraslow relaxation is one of the special and important dynamics in the electric double layer (EDL) at the electrochemical IL interface with water^[27-30] and metal,^[31-35] which does not appear in the conventional electrolytes.^[36] Previous studies using electrochemical surface plasmon resonance (ESPR) revealed the interfacial dielectric relaxations at the gold electrode interface of two ILs, trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide ($[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$)^[35] and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ($[\text{C}_4\text{mim}^+][\text{TFSA}^-]$).^[37] In the potential-step ESPR measurements, the response of SPR angle ($\Delta\theta$) to the potential step was a fast $\Delta\theta$ shift followed by an ultraslow $\Delta\theta$ relaxation on the order of 100 s, which were opposite to each other in the $\Delta\theta$ shift direction, indicating that at least two kinds of dynamics in the dielectric relaxation of EDL structure are separately detected by

ESPR.^[35,38] There are four polarization processes contributing to the dielectric relaxation, which are electronic, distortion, orientation, and ionic polarization, in the order of relaxation time from fast to slow.^[39] The former three polarization are known to occur on the timescale of femtoseconds or picoseconds.^[39] Therefore, the fast $\Delta\theta$ shift is ascribable to fast dielectric relaxation due to the electronic, distortion, and orientation polarization.^[35,38] A recent study using ESPR combined with sequential potential pulse techniques demonstrated that the fast $\Delta\theta$ shift is affected by the compactness of the first ionic layer on the electrode, depending on the pre-step potential.^[38] On the other hand, reflected by the ultraslow relaxation, the ionic polarization in the solid-like EDL structure of ILs occurs on the timescale of 1 s to 100 s, more sluggish than the conventional electrolyte (usually on the timescale of milliseconds), and also showed significant asymmetry of time constants by the potential step direction (positive or negative).^[35,37,38] EIS is often applied on analyzing the EDL charging/discharging process. However, due to the long relaxation time, the current corresponding to the ultraslow relaxation is difficult to be decoupled from the residual current. On the other hand, ESPR is hardly influenced by the residual current. Also, the fast $\Delta\theta$ shift does not originate from the EDL charging/discharging process and therefore such dielectric response cannot be detected by EIS. Thus, ESPR is a unique method to analyze the interfacial dielectric relaxation of ILs.

To further study these interfacial dielectric relaxations of ILs, we focus on the comparison of ions with different volumes and dipole moments, both of which significantly affect the van der Waals and electrostatic interactions between ions and are also related to the electronic, distortion, orientation, and ionic polarization.^[35,38,39] In this letter, we compare the $\Delta\theta$ response of four ILs, which are [C₄mim⁺][FSA⁻],

[C₄mim⁺][TFSA⁻], [TOMA⁺][TFSA⁻], and [TOMA⁺][C₄C₄N⁻], with the two cations, C₄mim⁺ and TOMA⁺, and three amide anions, bis(fluorosulfonyl)amide (FSA⁻), TFSA⁻, and C₄C₄N⁻, with different volume and dipole moment. We will discuss a relationship between the interfacial dielectric relaxation and ionic species of ILs.

2. Experimental

The preparation and purification of ILs were described in our previous works.^[37,38] The two cations, TOMA⁺ and C₄mim⁺, were synthesized as chloride salts, while the three anions, FSA⁻, TFSA⁻ and C₄C₄N⁻, were purchased as lithium salts (Tokyo Chemical Industry for FSA⁻; Kanto Chemical for the other two). To avoid the effect of volatile impurities, ILs were vacuum evacuated for more than 2 h at 60 °C before the measurements. The same ESPR experimental system was used as that described previously.^[35,37,38] A Kretschmann configuration was applied in an SPR apparatus (Springle, Kinetic Evaluation), in which a 670-nm laser beam was irradiated at a 50-nm thick gold film through an SF15 glass (refractive index of 1.6911 at 670 nm). The gold film was used as the working electrode (WE) in a three-electrode cell filled with the ILs in an atmosphere of Ar gas (99.9%), where the counter electrode (CE) was a Pt wire and the quasi-reference electrode (QRE) was an Ag wire coated with AgCl. The Ag/AgCl QRE shows relatively stable potential with small amounts of Ag⁺ and Cl⁻ released from and remaining near the AgCl surface.^[40] The surface area of WE was 0.071 cm². A PC-controlled potentiostat (Autolab Type III) was used to control the potential of WE with respect to that of QRE, denoted as E . The response of SPR, $\Delta\theta_{\text{SPR}}$, was recorded as a function of time, t , where the potential was stepped at $t = 0$. The viscosity of each

IL was also measured with a viscometer (TV-33, Toki Sangyo) at the same temperature as in the ESPR experiments.

To evaluate the volume and dipole moment for each ion, we performed quantum chemical (QC) calculations of an ion in vacuum at the level of b3lyp-gd3bj/6-311+g(d,p). The *cis* and *trans* conformations of anions^[41,42] were individually evaluated. The calculation results are shown in Fig.S1. One can see that the *cis* and *trans* conformations of each anion are almost the same for volume, but significantly different for dipole moment, which affects the orientation polarization. According to our previous MD study for the structure at the electrode interface of [C₄mim⁺][TFSA⁻], the anions on the electrode are almost in the *cis* conformation at positive potentials.^[43] The amide analogs, C₄C₄N⁻ and FSA⁻, are likely to show the same behavior and we assume that the three anions on the electrode at positive potentials have the *cis* conformation. The ionic volume follows the order of TOMA⁺ > C₄C₄N⁻ > C₄mim⁺ > TFSA⁻ > FSA⁻. The dipole moment follows the order of C₄C₄N⁻ (*cis*) > TOMA⁺ > C₄mim⁺ $\approx$ TFSA⁻ (*cis*) > FSA⁻ (*cis*).

The cyclic voltammograms and the negative-going linear sweep volt-SPR-grams, both measured using the ESPR cell at 10 mV s⁻¹, are shown in Fig.S2 for the four ILs. The sigmoidal $\Delta\theta$ curves (Fig.S2b) measured with this slow scan rate to the negative direction show quasi-static behavior, reflecting the potential dependence of the EDL structure.^[37,43] At the positive (negative) edge of the sigmoidal curves, the SPR angle is nearly constant for all the four ILs, indicating that the first ionic layer on the electrode is occupied only by the anion (cation) at the positive (negative) potentials. Here, we chose 0 V and -1.2 V as the common step potentials for all the four ILs to investigate the interfacial dielectric relaxation when the cations (anions) in the first ionic layer are all

replaced by the anions (cations). All the negative potential steps are from 0 V to -1.2 V and held at -1.2 V for 300 s, while the positive ones are on the opposite and held at 0 V for 1000 s, a longer time due to the slower dynamics by positive steps.^[35,37,38]

3. Results and Discussion

Fig.1 shows the responses of SPR angle after the negative (Fig.1a) and positive (Fig.1b) potential steps at $t = 0$ at the interface between gold and the four ILs. All the shown curves are the average of three potential steps. For the negative steps on all the four ILs, $\Delta\theta_{\text{SPR}}$ decreases, whereas $\Delta\theta_{\text{SPR}}$ increases for the positive steps. The positive (negative) $\Delta\theta_{\text{SPR}}$ shift generally corresponds to the increase (decrease) in the interfacial refractive index. The results indicate that, for all the four ILs, the structure of EDL at 0 V has a higher refractive index than that at -1.2 V, reflecting a higher local refractive index for the anion layer than the cation layer.^[43] The total amount of the $\Delta\theta_{\text{SPR}}$ shift after the relaxation is determined by the difference between the two interfacial refractive indices at the two potentials (0 V and -1.2 V), reflecting both the local concentration and electronic polarizability of cations and anions.^[43] Fig.1 clearly shows that the dynamics after the positive potential steps are slower than the negative ones, indicating that the formation of EDL structure at 0 V takes more time than that at -1.2 V for the four ILs.^[38]

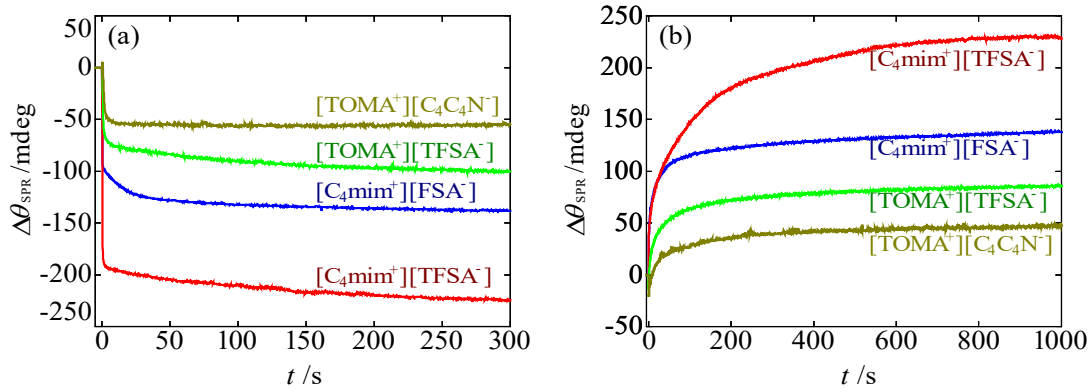


Figure 1. Responses of SPR angle to (a) the negative potential steps from 0 V to -1.2 V and (b) the positive potential step from -1.2 V to 0 V at $t = 0$. All the shown data are the average of three steps.

To quantitatively evaluate the interfacial dielectric relaxation, we used the fitting with a multiple exponential function expressed as follows:

$$\Delta\theta(t) = H(t) \left[\Delta\theta_f + \sum_{i=1}^n \Delta\theta_{si} \left\{ 1 - \exp\left(-\frac{t}{\tau_i}\right) \right\} \right] \quad (1)$$

where $H(t)$ is the unit step function and $\Delta\theta_f$ is the $\Delta\theta$ shift due to the fast components of interfacial dielectric relaxation such as electronic, distortion, and orientation polarization. For relatively viscous two ILs ([TOMA⁺][TFSA⁻] and [TOMA⁺][C₄C₄N⁻]), the fast $\Delta\theta$ shift was smeared due to the time constant of the electrochemical cell, up to $t = 0.2$ and 0.7 s, respectively, and therefore, the first several data points (shown as the open circles in Fig.S3) were excluded from the fitting process. $\Delta\theta_{si}$ and τ_i are the $\Delta\theta$ shift and the relaxation time constants of each slow relaxation component i . We used the triple or quadruple exponential function ($n = 3$ or 4), because in the interfacial dielectric relaxation of ILs, τ has a broad distribution, well represented as a lognormal distribution function^[35] and therefore cannot be represented by the simplest single exponential function. It

should be noted that each of the relaxation components in the model does not correspond to any specific physical processes. Further increase in n led to two τ_i with similar values and large standard errors, which is a symptom of overfitting. The average time constant of the interfacial dielectric relaxation, τ_{ave} , was evaluated as:

$$\log \tau_{\text{ave}} = \frac{\sum_{i=1}^n \Delta \theta_{si} \log \tau_i}{\sum_{i=1}^n \Delta \theta_{si}} \quad (2)$$

In the fitting, the fitting weight of $1/t$ is multiplied for negative steps, while that of $1/t^{1/2}$ is multiplied for positive steps, to focus on the early part where most of the SPR angle shift occurs. All the experimental data and fitted curves are shown in Fig.S3. The fitted results, $\Delta \theta_f$, $\Delta \theta_{si}$, and τ_i , are listed in Table S1. The evaluated values of $\Delta \theta_f$ and τ_{ave} are listed in Table 1.

Table 1. Fitted results of fast shift components and ultraslow relaxation time constants.

	Negative Step		Positive Step	
	$\Delta \theta_f$ /mdeg	τ_{ave} /s	$\Delta \theta_f$ /mdeg	τ_{ave} /s
[C4mim ⁺][FSA ⁻]	15.6	0.32	-2.0	11
[C4mim ⁺][TFSA ⁻]	16.1	0.34	-5.6	49
[TOMA ⁺][TFSA ⁻]	44.0	1.2	-20.7	23
[TOMA ⁺][C4C4N ⁻]	48.2	1.0	-31.4	23

The average time constant, τ_{ave} , in Table 1 clearly shows that the interfacial dielectric relaxations for all the four ILs by the positive steps are more than one order of magnitude slower than those by the negative steps, which agrees with our previous studies.^[35,37,38] In a MD simulation study on [C4mim⁺][TFSA⁻] on the electrode, when

the first ionic layer is fully occupied by [TFSA⁻] (at positive potentials), the layering structure is ordered with an obvious boundary between the first and second ionic layers, whereas such an orderedness is unobservable when the first ionic layer is occupied by C₄mim⁺ at negative potentials (see Fig.S4).^[43] Therefore, the structure of EDL seems more solid-like at positive potentials than that at negative potentials for these ILs with amide anions. Hence, as the potential goes positive, the anion-rich ionic layer is likely to be more viscous, which is probably the reason why the interfacial dielectric relaxation by the positive steps is slower.

The ultraslow relaxation is ascribable to the ionic translation, which is significantly affected by the viscosity. Therefore, we measured the bulk viscosity of the four ILs. The measured bulk viscosities, η , and the experimental temperature for the four ILs in the ESPR experiments are listed in Table S2. τ_{ave} by both the negative and positive steps tends to be smaller for ILs with smaller η on the whole, except an outlier: τ_{ave} of [C₄mim⁺][TFSA⁻] for the positive step. The existence of the outlier suggests that the situation is not simple; the interfacial viscosity is not simply predictable from known parameters such as the bulk viscosity. Rather, many factors would complicatedly affect the ionic translation in the EDL behind the interfacial viscosity: the electrostatic interaction of ions with the surface charge on the electrodes, inter-ionic interaction between neighboring ions in the EDL that has an ionic composition different from the bulk (cation-enriched and anion-depleted, or vice versa), and two-dimensional geometry constraint, to name a few. Aside from the outlier, the difference in τ_{ave} for the four ILs is still significantly smaller than that in η . Fig.S5 shows the plots of $\log\tau_{\text{ave}}$ against $\log\eta$. The least regression lines shown in Fig.S5 were obtained assuming that the two kinds of the dataset, for positive and negative steps, have the same slope but different intercepts

and also by neglecting the outlier. The slope, 0.28 ± 0.02 , was sufficiently smaller than unity, meaning a weak dependence of the interfacial viscosity on the bulk viscosity. In other words, this weak dependence indicates that the viscosity increase for the interfacial solid-like structure compared with the bulk is higher for small-ion ILs, as will be further discussed below.

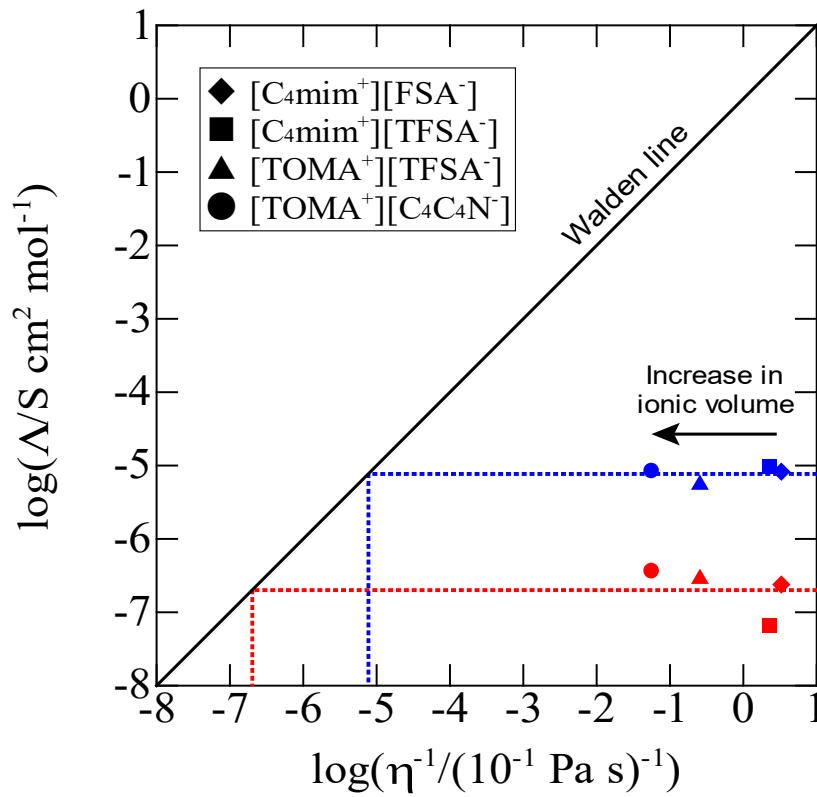


Figure 2. “Interfacial” Walden plot for the four ILs by positive steps (red points) and negative steps (blue points). The horizontal dotted lines are at the average $\log \Lambda$ for four ILs, which meet the Walden line at the left side and then go down as the vertical dotted lines to semi-quantitatively estimate the interfacial viscosity for the four ILs.

In the interfacial dielectric relaxation induced by the electrode potential perturbation, the time constant, τ_{ave} , can be expressed as an RC function:

$$\tau_{\text{ave}} = RC_{\text{dl}} \quad (3)$$

where R is the resistance and C_{dl} is the differential capacitance for the solid-like EDL structure at the IL|gold interface, written as:

$$R = \frac{md}{A\sigma} \quad (4)$$

$$C_{\text{dl}} = \frac{\varepsilon_0 \varepsilon A}{d/2} \quad (5)$$

where d is the ionic diameter, m is the number of the ionic layer in the solid-like structure, A is the working area of the electrode, σ is the conductivity, ε and ε_0 are the relative and vacuum permittivity, respectively. Here σ can be expressed with the ionic concentration, c , and the molar conductivity, Λ , at the interface:

$$\sigma = \Lambda c \quad (6)$$

Hence, we can evaluate Λ with the fitted results of τ_{ave} in Table 1 as:

$$\Lambda = 2m \frac{\varepsilon_0 \varepsilon}{c \tau_{\text{ave}}} \quad (7)$$

Although m is likely to be IL-dependent, we simply assume $m = 1$, which means that the extent of the solidification of the first ionic layer is far beyond the overlayers. ε is weakly IL-dependent for ILs with ionic structures similar to those in the present study,^[44] and we set $\varepsilon = 12$. We also assume that the interfacial ionic concentration, c , equals the bulk one, although c slightly increases at potentials far from the potential of zero charge.^[43] It should be noted that, although these parameters (m , ε , c) are semi-quantitatively input, they do not affect the conclusion of this analysis, extremely high interfacial viscosity described below, which originates from the high values of τ_{ave} .

Taking the logarithm of η^{-1} and the evaluated interfacial molar conductivity, Λ , we draw the “interfacial” Walden plot in Fig.2. In the Walden plot, all the points are far down away from the “ideal” Walden line (solid line) for electrolytes, and by either the

positive or negative steps, the molar conductivity, Λ , is likely to be the same for all the four ILs. This is because the weak dependence of $\log \tau_{\text{ave}}$ on $\log \eta$ (Fig.S5) is canceled out by the concentration, c , in eq 7; $\log(c\tau_{\text{ave}})$ vs $\log \eta$ plots now have no η dependence with a slope of -0.01 ± 0.06 , as shown in Fig.S6. By drawing horizontal lines (dotted lines) from the points to the Walden line in Fig.2, we can estimate the interfacial viscosity, which is on the order of 10^4 Pa·s for the negative steps, and on the order of 10^5 Pa·s for the positive steps. A similar increase in the interfacial viscosity was reported at the gas interface of soap solutions^[45] and globular proteins solutions,^[46] but the extent is significantly smaller than the cases with ILs at the solid interface^[14,15,18] including the present study. Also, the significantly higher interfacial viscosity shows no dependence on the ionic volume for these four amide-based ILs. In other words, for both the negative and positive steps, there is a more significant difference in viscosity between the interface and the bulk for the ILs with smaller ions, which can form the ionic layers with a more compact structure. Another plausible reason is the specific adsorption of C4mim^+ on the electrode, as discussed below, which will contribute to the high interfacial viscosity for the two small-ion ILs investigated in the present study.

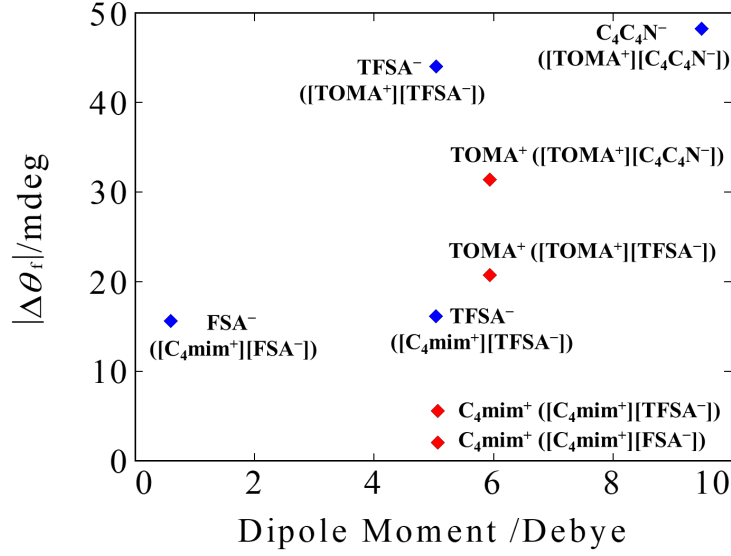


Figure 3. Plots of $|\Delta\theta_f|$ against the calculated dipole moments of the dominant counter-ions in the first ionic layer for the negative (blue points) and positive (red points) potential steps. The labels are in the format of “counter-ion (IL)” against the electrode polarization.

To investigate the effect of ionic reorientation on the fast $\Delta\theta$ shifts, we compared the fitted results with the dipole moment evaluated by QC calculations. In our previous works,^[35,38] the fast $\Delta\theta$ shift was ascribed to be induced by the ionic rotation, and the SPR response was demonstrated to be affected by the first ionic layer. At 0 V, the pre-step potential of negative steps in Fig.3, the first ionic layer is saturated by anions, hence the fast shifts are dominated by the anionic behaviors (electronic, distortion, and orientation polarization). For the same reason, at -1.2 V, the pre-step potential of positive steps, the fast shift indicates the behaviors of cations. Fig.3 shows $|\Delta\theta_f|$ as a function of the calculated dipole moments of the ions in the first ionic layer by both the negative and positive steps. For the two ILs composed of small ions, $[\text{C}_4\text{mim}^+][\text{FSA}^-]$ and $[\text{C}_4\text{mim}^+][\text{TFSA}^-]$, the absolute values of $\Delta\theta_f$ are always smaller than those of large ions,

$[\text{TOMA}^+][\text{TFSA}^-]$ and $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$. Taking all the 8 points into account, we evaluated the correlation coefficient to be 0.52. Although the number of sample points is not large in such a statistical analysis, the correlation coefficient suggests a moderate correlation between the two parameters. The values of the dipole moment were evaluated for an ion in vacuum, which is significantly different from the circumstances of ions in the densified EDL structure. In a strong electric field, ions are forced to take a certain orientation and the electronic distribution can be distorted, therefore in that case the dipole moment is presumed to be larger than the evaluated results by the QC calculation, which is considered as the reason why the correlation is not strong, but can roughly explain the amplitude of fast relaxation in Fig.3. For the negative steps (blue diamonds in Fig.3), the fast $\Delta\theta$ shifts follow the order of $[\text{C}_4\text{mim}^+][\text{FSA}^-] < [\text{C}_4\text{mim}^+][\text{TFSA}^-] \ll [\text{TOMA}^+][\text{TFSA}^-] < [\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$, mainly caused by *cis*-anions in the first ionic layer and also affected by cations in the overlayers. For the positive step of $[\text{TOMA}^+][\text{TFSA}^-]$ and $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ (red diamonds in Fig.3), the fast $\Delta\theta$ shifts are mainly caused by the reorientation of TOMA^+ in the first ionic layer, which has a smaller dipole moment than $\text{C}_4\text{C}_4\text{N}^-$ (*cis*), resulting in smaller value than those by the negative steps. However, for both $[\text{C}_4\text{mim}^+][\text{FSA}^-]$ and $[\text{C}_4\text{mim}^+][\text{TFSA}^-]$, the significantly smaller $|\Delta\theta_f|$ by positive steps deviate from the explanation of the reorientation of C_4mim^+ . If we excluded the two points related to C_4mim^+ , the correlation coefficient increased to be 0.67, further demonstrating the correlation between the two parameters. The small $|\Delta\theta_f|$ values of the two points might be because the imidazole ring of C_4mim^+ chemically interacts with the gold surface, where the rotation is frozen and/or its dipole moment is lost compared with in-vacuum QC situation.

4. Conclusions

In the present study, the interfacial dielectric relaxation of four ILs, $[\text{C}_4\text{mim}^+][\text{FSA}^-]$, $[\text{C}_4\text{mim}^+][\text{TFSA}^-]$, $[\text{TOMA}^+][\text{TFSA}^-]$, and $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$, were investigated using potential-step ESPR at the gold electrode interface. By the data fitting of the multiple exponential function, the time constants of ultraslow relaxation and the amplitudes of fast $\Delta\theta$ shift were evaluated. The analysis of the time constants with an “interfacial” Walden plot revealed that ILs have extremely high interfacial viscosity at the solid electrode interface and that the ILs with smaller ions tend to form a more solidified EDL structure. The absolute value of fast $\Delta\theta$ shift, $|\Delta\theta_{\text{f}}|$, is moderately correlated with the dipole moments of ions in the first ionic layer, except for the significantly small value for C_4mim^+ , indicating that the ionic reorientation of C_4mim^+ is frozen by the chemical interaction with the gold surface.

Acknowledgements

This work was partly supported by JSPS KAKENHI (No. 21H02046) and Izumi Science and Technology Foundation (2020-J-071).

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