

Surface Structure of a Hydrophobic Ionic Liquid Probed by Spectroscopic Ellipsometry

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Abstract

The surface of an ionic liquid, trioctylmethylammonium bis(nonafluorobutanesulfonyl) amide ($[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$) has been studied using spectroscopic ellipsometry at 300 K. The values for δ , which is the phase difference between p-polarized and s-polarized reflection coefficients, deviate from zero to positive values, suggesting that spectroscopic ellipsometry detects surface structures such as surface roughness and surface layers at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface. A model taking into account not only the surface roughness estimated using the capillary wave theory but also ionic multilayers, which was found to exist at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface by a recent x-ray reflectivity study, well reproduces the experimental δ values. Spectroscopic ellipsometry is demonstrated to be a complementary technique to x-ray reflectometry to detect surface structures at ionic liquid interfaces.

I. INTRODUCTION

The surface of ionic liquids (ILs), which are liquid salts and are entirely composed of ions, has been intensively studied to reveal the molecular-level view of the surface of ILs.^{1–29} Thermally induced capillary waves (CWs) exist at the surface of ILs as well as all the soft interface of liquids. CWs are induced by thermal fluctuation of the soft interface. The fluctuated interface feels restoring force whose origin is surface tension of the interface. The amplitude of CWs is in the molecular scale, usually on the order of Å.³⁰ The CW theory proposed by Buff, Lovett, and Stilling³¹ predicts several aspects of CWs including the surface roughness that is the effective surface thickness caused by CWs. For the surface of molecular liquids, the surface roughness experimentally obtained using x-ray reflectivity (XR) measurements, σ_{XR} , well agrees with that from the CW theory, σ_{CW} .^{32,33} For the surface of ILs, $[\text{C}_4\text{mim}^+]\text{BF}_4^-$ and $[\text{C}_4\text{mim}^+]\text{PF}_6^-$ where C_4mim^+ denotes 1-butyl-3-methylimidazolium, Sloutskin et al.⁶ demonstrated the agreement between the XR results and the CW theory, adopting one-box model for the electron-density profile at the surfaces. On the other hand, Jeon et al.¹⁴ suggested that $\sigma_{\text{XR}} < \sigma_{\text{CW}}$ for the surface of the two ILs and found, conversely, that $\sigma_{\text{XR}} > \sigma_{\text{CW}}$ for the surface of another IL, $[\text{C}_4\text{mim}^+]\text{I}^-$. Therefore, the validity of the CW theory to the surface of ILs is still unclear. Recently, we studied the surface of hydrophobic ILs such as trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide ($[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$) by XR and obtained the XR results that do not contradict the CW theory.^{34,35} By analyzing the XR data assuming the surface roughness predicted by the CW theory, we were able to detect ionic multilayers at the surfaces of the hydrophobic ILs and to quantitatively measure the structure of the ionic multilayers. To confirm both the validity of the CW theory at the surface of the hydrophobic ILs and the validity of the structure of the ionic multilayers in a quantitative level, a study by other technique complementary to XR is desirable.

We chose spectroscopic ellipsometry as the complementary technique. Although the wavelength of the light involved in ellipsometry is on the order of hundred nanometers and much larger than a molecular scale, accurate and precise measurements of the phase shift and amplitude ratio of p-polarized and s-polarized light enable us to obtain the molecular-scale information at interfaces.^{36,37} Single-wavelength ellipsometry has been used to analyze the surface roughness at the surface of molecular liquids.^{38–46} For ILs, single-wavelength ellipsometry has been used to determine the thickness of IL films coated on substrates.^{47–51} In the present paper, we will show a spectroscopic ellipsometry study of the surface of $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$. An analysis incorpo-

rating the surface roughness predicted by the CW theory and the ionic multilayers obtained by XR well reproduces the results of spectroscopic ellipsometry, illustrating that both spectroscopic ellipsometry results and XR results do not contradict the CW theory for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface and that spectroscopic ellipsometry can be used to detect surface structures at ionic liquid interfaces.

II. EXPERIMENTAL

A. Preparation of IL

$[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ was prepared and purified as we previously reported.^{34,52} Before ellipsometry measurements volatile impurities in $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ were evaporated under reduced pressure at 60 °C more than 6 hours.

B. Spectroscopic ellipsometry

A spectroscopic phase-modulated ellipsometer (UVISEL-VIS, Horiba) was used. A trough made of stainless steel with the inner diameter of 15 mm and the depth of 10 mm was filled with $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$. The backside interface of $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$, i.e., the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ /steel interface was conically shaped to prevent possible incidence of the backside reflected light to the detector slit. The temperature was controlled to 300 ± 0.1 K by circulating temperature-controlled water through the jacket of the trough. No time dependence of the ellipsometry data due to possible absorption of water from air into $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ was detected, as was in the previous XR measurements of the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface.³⁴ Two parameters, Ψ and Δ , which were used to analyze ellipsometry data, are defined as,

$$\frac{r_p}{r_s} = \tan \Psi e^{i\Delta}, \quad (1)$$

where r_p (r_s) is the reflection coefficient of p-polarized (s-polarized) light at the interface, $\tan \Psi$ is the absolute value of the amplitude ratio and Δ is the phase shift of r_p to r_s . The Ψ and Δ values were measured as a function of the wavelength, λ , over the range from 300 to 600 nm with 4 nm step. The incident angle of the light, θ_{in} , is defined as the angle between the Poynting vector of the incident light from air to the surface and the axis normal to the surface, was 70.0°.

III. RESULTS AND DISCUSSION

A. Ellipsometry results

The Ψ values as a function of λ for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface are shown in Fig. 1a (open circles). The Ψ values decrease with decreasing λ . This is due to the normal dispersion relationship for the refractive index of IL, n_{IL} ; with decreasing λ , n_{IL} increases and the Brewster angle, θ_{B} ($= \tan^{-1} n_{\text{IL}}$), shifts toward θ_{in} (70.0°). For example, at 600 nm $\{n_{\text{IL}}, \theta_{\text{B}}\}$ is $\{1.410, 54.65^\circ\}$ and at 300 nm is $\{1.439, 55.20^\circ\}$, where n_{IL} is from the fitting results to the Ψ data using the Sellmeier model (*vide infra*). The closer θ_{B} is to θ_{in} , the smaller the Ψ value, and when $\theta_{\text{B}} = \theta_{\text{in}}$, Ψ reaches a minimum value around zero (see also Fig. A1c).³⁶

The Ψ values for the surface sandwiched by two homogeneous phases are insensitive to the interfacial structures such as surface roughness and surface layers when (1) the thickness of the interfacial structures is much smaller than λ , and (2) the incident angle is apart from θ_{B} .⁵³ In such a case the Ψ values are approximately equal to those for an ideally flat surface (the Fresnel surface). Because r_{p} and r_{s} (eq 1) for the Fresnel surface are determined only with the refractive indices of the two bulk phases and the incident angle as indicated in eqs 2 and 3, spectroscopic ellipsometry has been used to reveal the dispersion relationship of the refractive index of liquids.^{54–57} The present experimental condition for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface fulfill the above conditions (1) and (2). XR measurements³⁴ at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface revealed that the ionic multilayers extend from the surface to the bulk with a depth of 6 nm, which is much less than the wavelength of the light, 300–600 nm. Also, θ_{B} , which is around 55° depending on λ (*vide supra*), is sufficiently apart from θ_{in} , 70.0° . Therefore, from the Ψ data shown in Fig. 1a, we can evaluate the dispersion relationship of n_{IL} for $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$. The reflectivity coefficients for the Fresnel surface can be written as,⁵⁸

$$r_{\text{p}} = \frac{\frac{1}{n_{\text{air}}} \cos \theta_{\text{in}} - \frac{1}{n_{\text{IL}}} \cos \theta_{\text{IL}}}{\frac{1}{n_{\text{air}}} \cos \theta_{\text{in}} + \frac{1}{n_{\text{IL}}} \cos \theta_{\text{IL}}} \quad (2)$$

$$r_{\text{s}} = \frac{n_{\text{air}} \cos \theta_{\text{in}} - n_{\text{IL}} \cos \theta_{\text{IL}}}{n_{\text{air}} \cos \theta_{\text{in}} + n_{\text{IL}} \cos \theta_{\text{IL}}}, \quad (3)$$

where $n_{\text{air}} = 1.000$ and θ_{IL} is the angle of the refracted light in IL, which is related to other parameters via the Snell's law: $\cos \theta_{\text{IL}} = \sqrt{1 - (\frac{n_{\text{air}} \sin \theta_{\text{in}}}{n_{\text{IL}}})^2}$. The Sellmeier model⁵⁹ for the dispersion of

refractive index for non-light absorbing materials was used for n_{IL} ;

$$n_{\text{IL}} = \sqrt{A + B \frac{\lambda^2}{\lambda^2 - \lambda_0^2}}. \quad (4)$$

The eqs 1-4 were used for the fitting of the Sellmeier model to the Ψ data. The obtained fitting parameters, A , B and λ_0 are listed in Table 1 and the fitted curve is shown in Fig.1a (solid blue line). The curve from the Sellmeier model well reproduced the Ψ data. To examine the validity of the Sellmeier model, the refractive indices of $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ were measured at 450, 480, 546, and 589 nm by using a multi-wavelength refractometer (DR-M2, Atago) and the Ψ values were similarly calculated using eqs 1-3 at the 4 wavelength values. The calculated Ψ values shown as solid black squares in Fig.1a agree with the experimental Ψ data, indicating that the Sellmeier model is adequate to n_{IL} for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ bulk at least in the range 450-589 nm and that there is no thick interfacial layer whose thickness is comparable to the wavelength at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface.

Wavelength dependence of the Δ values for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface are shown in Fig.1b (open circles). The Δ values are nonzero and positive in this wavelength range. The Fresnel surface gives zero value of Δ (dotted black line), which was calculated using eqs 1-4 and the fitted parameters for the Sellmeier model in Table 1. The nonzero Δ reflects that detectable interfacial structures such as surface roughness and surface layers exist at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface (see also Fig.A1b). The Δ values increase with decreasing λ , contrary to Ψ . This tendency can be explained by the normal dispersion of n_{IL} similarly to Ψ ; with decreasing λ , θ_{B} shifts toward θ_{in} , and when $\theta_{\text{B}} = \theta_{\text{in}}$, Δ is 90° .³⁶

B. Comparison of experimental Δ with that from the ionic multilayer model

To quantitatively discuss the nonzero Δ values, electron density profile obtained using XR measurements³⁴ was used. The intrinsic electron density profile, $\rho(z)$, normalized by the bulk electron density, ρ_{bulk} , for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface is written, using the distorted crystal model, which was originally proposed to represent multilayers at the surface of liquid metals,^{60,61} as,

$$\bar{\rho}_{\text{IM}}(z) = \frac{d}{\sqrt{2\pi}} \sum_{n=0}^{\infty} \frac{1}{\sigma_n} \exp\left(\frac{-(z - nd)^2}{2\sigma_n^2}\right), \quad (5)$$

where $\bar{\rho}_{\text{IM}}(z) = \rho(z)/\rho_{\text{bulk}}$, z is a displacement axis along with the surface normal with $z > 0$ for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ phase and $z < 0$ for the air phase, d is the interlayer distance, σ_n is the line width for the n th layer and $\sigma_n^2 = n\bar{\sigma}^2 + \sigma_0^2$, where σ_0 is the line width for the top most (0th) layer and $\bar{\sigma}$ is a factor of the widening of the distribution. The values obtained by the fitting of the distorted crystal model to XR data are: $d = 15.45 \pm 0.10 \text{ \AA}$, $\sigma_0 = 5.08 \pm 0.04 \text{ \AA}$ and $\bar{\sigma} = 3.35 \pm 0.04 \text{ \AA}$.³⁴ Dashed dotted blue line in Fig.2a is the profile of $\bar{\rho}_{\text{IM}}(z)$ for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface. At least four ionic layers are formed at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface with the interlayer distance of $16 \text{ \AA}$, extending into the bulk from the surface to the depth of $60 \text{ \AA}$.

Every liquid surface is thermally fluctuated at ambient temperature due to CWs. The fluctuation smears the intrinsic density profiles when the density is averaged in the surface tangential direction. Ellipsometry detects not the intrinsic density but the smeared density profile.⁶² The surface roughness due to CWs, σ_{cw} , may be estimated from a modified version of the CW theory³¹ proposed by Meunier,⁵³ who took into account the mode coupling between CWs, which is neglected in the original CW theory, as,

$$\sigma_{\text{cw}}^2 = \frac{k_B T}{4\pi\gamma} \ln \left(\frac{\gamma\lambda^2}{3\pi k_B T} \right), \quad (6)$$

where k_B is the Boltzmann constant and γ is the surface tension. Note that σ_{cw} is a function of λ , because light is only sensitive to the CWs whose wavelength is shorter than λ .⁵³ The σ_{cw} values were calculated with the γ value, 21.9 mN m^{-1} ,³⁴ measured using a pendant drop method.⁶³ For example, σ_{cw} is 4.03 and $4.28 \text{ \AA}$ when λ is 300 and 600 nm , respectively. We obtain the thermally fluctuated density profile, $\langle \bar{\rho}_{\text{IM}}(z) \rangle$, by convolving the intrinsic density profile with a gaussian distribution whose variance is σ_{cw}^2 :

$$\begin{aligned} \langle \bar{\rho}_{\text{IM}}(z) \rangle &= \int_{-\infty}^{\infty} \left\{ \frac{1}{\sqrt{2\pi}\sigma_{\text{cw}}} \exp \left(-\frac{(z-\zeta)^2}{2\sigma_{\text{cw}}^2} \right) \right\} \bar{\rho}_{\text{IM}}(\zeta) d\zeta \\ &= \frac{d}{\sqrt{2\pi}} \sum_{n=0}^{\infty} \frac{1}{\sigma'_n} \exp \left(\frac{-(z-nd)^2}{2\sigma_n'^2} \right), \end{aligned} \quad (7)$$

where $\sigma_n'^2 = n\bar{\sigma}^2 + \sigma_0'^2$ and $\sigma_0'^2 = \sigma_0^2 + \sigma_{\text{cw}}^2$. The thermally fluctuated density profile at 300 nm is shown in Fig.2a as solid blue line. Comparing the thermally fluctuated density profile with the intrinsic density profile (dashed dotted blue line), one can see that the ionic multilayers are diffused due to the thermal fluctuation.

The local refractive index $n(z)$ at z may be obtained by the Lorentz-Lorenz effective medium

approximation,^{64,65}

$$\frac{n^2(z) - 1}{n^2(z) + 2} = \langle \bar{\rho}(z) \rangle \frac{n_{\text{IL}}^2 - 1}{n_{\text{IL}}^2 + 2}. \quad (8)$$

Since there is no analytical solution for r_p and r_s (for Ψ and Δ) from the surface having such $n(z)$ profile, we numerically calculated them using the Abelès matrix method for a stratified interface.⁶⁶ The $n(z)$ profile from $z = -4\sigma'_0$ to $+5d_{\text{DC}}$ was digitized with a step thickness of $\sigma'_0/10$ to 160 steps, each of which has uniform refractive index. The digitized $n(z)$ profile at 300 nm is shown in the inset of Fig.2a. The calculated Ψ and Δ are shown in Fig.1a and 1b as solid blue curves. Both calculated Ψ and Δ well agree with the experimental points over $300 \leq \lambda \leq 600$ nm with no adjustable parameters. This agreement between ellipsometry and XR suggests that the assumption of the applicability of the CW theory to the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface made for the XR data^{34,35} is valid. The curve for Ψ from this ionic multilayer model in Fig.1a perfectly overlaps that for the Fresnel surface, again suggesting that Ψ is insensitive to the surface structures if the thickness is much smaller than λ . Note that it is impossible to uniquely determine the density profile only by ellipsometry, since ellipsometry is only sensitive to the integral of a function of $n(z)$ with respect to z .⁶² Therefore, with fitting parameters, other models such as one-box and two-box models (Fig.A1) could explain the present results, although models other than the ionic multilayer model contradict the XR results.³⁴

By taking a closer look at Δ one can see slight deviation between the calculated curve and the experimental data; at short λ the curve is lower than the data. Three possible reasons of the deviation are: (1) non-negligible imaginary part of refractive index for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ bulk, making a positive contribution to Δ , (2) anisotropy of the refractive index at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface, and (3) wavelength dependence of the amplitude of CWs slightly different from that predicted by the CW theory. For the reason (1), we measured the imaginary part of the refractive index for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ bulk using an absorption spectrophotometer. The value is at a maximum 5×10^{-6} at 300 nm, which is negligible and only contributes to Δ with $+0.0004^\circ$. For the reason (2), if the TOMA^+ and $\text{C}_4\text{C}_4\text{N}^-$ ions at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface are preferentially orientated, it may lead to anisotropy of the refractive index at the surface, as is the case with the surface of liquid crystal 5CB (4'-Pentyl-4-biphenylcarbonitrile) in the isotropic phase slightly above the critical temperature to the nematic phase.⁶⁷ Although several studies have suggested the orientation of ions at the surface of other ILs,^{1,2,4,8,11,14,15,22,23} the orientation of TOMA^+ and $\text{C}_4\text{C}_4\text{N}^-$ at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface has not been revealed. By using a method for the

calculation of the reflection coefficients for anisotropic surface³⁷ we checked the possible effect of the anisotropy. The greater z component of refractive index, n_z , than the tangential component, n_{xy} , was found to lead to higher Δ . However, the rising of Δ occurred for all the wavelength of 300 ~ 600 nm, different from the present situation where at only short λ the model calculation deviates from the experimental values. Therefore anisotropy cannot fully explain the deviation. For the reason (3), deviations of the CW amplitude from the CW theory have been reported by theoretical studies,^{68,69} although the deviations are discernible from much higher wavevector (q) than q for 300-600 nm wavelength.

C. Comparison of experimental Δ with that from the error function model

To access the extent of the validity of the ionic multilayer model, we also calculated Ψ and Δ for the surface without ionic multilayers. The intrinsic density profile for such surface, $\bar{\rho}_{\text{EF}}(z)$, may be represented with an error function,

$$\bar{\rho}_{\text{EF}}(z) = \frac{1}{2} \left\{ 1 + \text{erf} \left(\frac{z}{\sqrt{2}\sigma_{\text{EF}}} \right) \right\}, \quad (9)$$

where $\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) dt$ and σ_{EF} is the intrinsic interfacial roughness due to molecular (ionic) structure. We shall refer this model to the error function model hereafter. We assumed that σ_{EF} is equal to $\sigma_0 = 5.08 \text{ \AA}$. The σ_{EF} value is comparable to $4.94 \text{ \AA}$, the mean value of radii for TOMA^+ and $\text{C}_4\text{C}_4\text{N}^-$ calculated by the molecular orbital calculation.³⁴ Taking into account the tendency of the underestimate of the ionic radii for the molecular orbital calculation,⁷⁰ the σ_{EF} value is probably smaller than the actual ionic radii for TOMA^+ and $\text{C}_4\text{C}_4\text{N}^-$. For the surface of molecular liquids, the intrinsic interfacial roughness was evaluated by XR to be comparable to^{32,71} and smaller than^{32,33} the radii of the molecules. The density profile thermally fluctuated by CWs for the error function model can be obtained with the convolution similar to that adopted for the ionic multilayer model;

$$\begin{aligned} \langle \bar{\rho}_{\text{EF}}(z) \rangle &= \int_{-\infty}^{\infty} \left\{ \frac{1}{\sqrt{2\pi}\sigma_{\text{cw}}} \exp \left(-\frac{(z-\zeta)^2}{2\sigma_{\text{cw}}^2} \right) \right\} \bar{\rho}_{\text{EF}}(\zeta) d\zeta \\ &= \frac{1}{2} \left\{ 1 + \text{erf} \left(\frac{z}{\sqrt{2}\sigma'_{\text{EF}}} \right) \right\}, \end{aligned} \quad (10)$$

where $\sigma'_{\text{EF}}^2 = \sigma_{\text{EF}}^2 + \sigma_{\text{cw}}^2$. The thermally fluctuated density profile is shown in Fig.2b as dashed red line along with the profile for the ideally flat surface as dotted black line. Similar to the ionic

multilayer model, Ψ and Δ for the error function model were calculated using eqs 8 and 10, and with the digitization of $n(z)$ from $-4\sigma'_{\text{EF}}$ to $+4\sigma'_{\text{EF}}$ with a step thickness of $\sigma'_0/10$ to 80 steps. The calculated Ψ curve overlaps those from the ideally flat surface and from the ionic multilayer model (Fig. 1a, blue solid line). The calculated Δ curve is shown in Fig. 1b as red dashed line. The Δ curve is higher than that for the ionic multilayer model (blue solid line) and overestimate the Δ values. The lower Δ values for the ionic multilayer model than those for the error function model are ascribable to the existence of a ionic layers whose density is higher than that for bulk and also the sharp transition of the density from air to liquid at the surface due to the topmost ionic layer (see figs. 2a and 2b and also Fig. A1b). The fact that a model combining ionic multilayers and the CW theory well reproduce the ellipsometry results supports the presence of the ionic multilayers detected by XR measurements in a quantitative level and the validity of the CW theory for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface.

IV. CONCLUSIONS

The spectroscopic ellipsometry results are consistent with those by XR measurements for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface. The Δ values obtained by spectroscopic ellipsometry can be used to discuss the existence of the ionic multilayers at the surface of ILs. The ionic multilayers at the surface of ILs have been detected by XR only for the ILs composed of relatively large ionic species.^{34,35} For ILs composed of small ions, the quasi-Bragg peak due to the ionic multilayers is located at a high transfer momentum and is difficult to be detected. The analysis in the present study by spectroscopic ellipsometry can be used for the surface of the ILs composed of small ions, to detect surface structures and to further confirm the validity of the analysis. One of another interesting targets is the buried IL|water interface where the detection of molecular-level information by XR is also relatively difficult. At the buried IL|water interface slow relaxation of the interfacial structure to an electric potential change was observed,^{52,72-74} which is probably due to multilayering of the IL side of the interface.

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Supporting Information Available: : Numerical calculation results of Ψ and Δ as a function of the incident angle for simple density profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>

TABLE I. Fitted parameters to Ψ using the Sellmeier model for the refractive index of the [TOMA⁺][C₄C₄N⁻] bulk with the standard error

A	B	λ_0 (nm)
1.86 ± 0.03	0.11 ± 0.03	205 ± 15

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Figure captions

Fig. 1: Wavelength dependence of (a) Ψ and (b) Δ for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface. Open circles are the experimental data. Solid blue lines are from the ionic multilayer model. Dashed red lines are from the error function model. Dotted black lines are from the flat surface model. Note that, in (a), solid, dashed and dotted lines overlap each other. Solid black squares in (a) are from the measured refractive index of the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ bulk and the flat surface model. (Inset in (a)) The dispersion relationship of the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ bulk obtained by the fitting with the flat surface model (dotted black line) and measured using a multi-wavelength refractometer (black squares).

Fig. 2: (a) Intrinsic electron density profile for the ionic multilayers at $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface (dashed dotted blue line) and the density profile thermally fluctuated by CWs (solid blue line). (b) density profiles for the error function model (dashed red line) and for the flat surface model (dotted black line). (Inset in (a)) Digitized refractive index profile at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ at 300 nm obtained from the intrinsic electron profile (a).

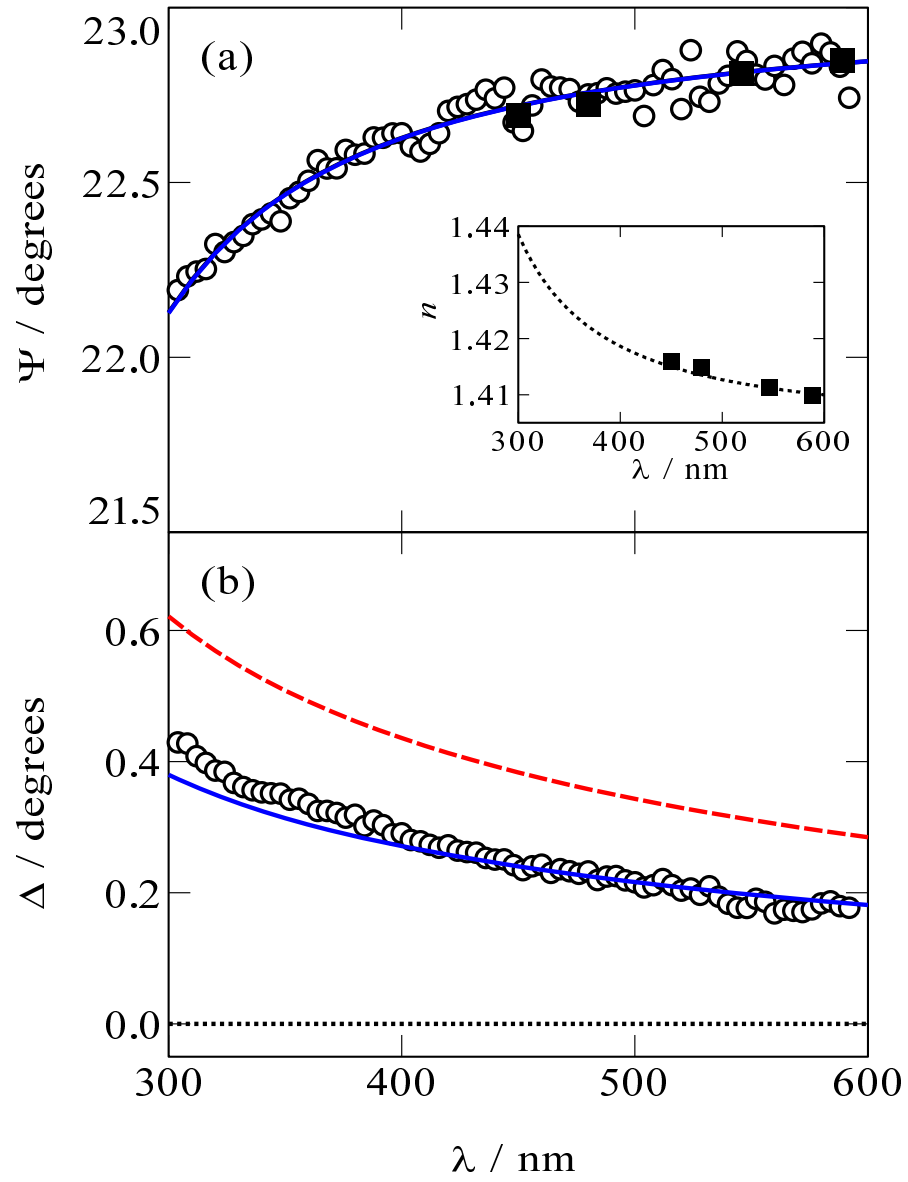


Fig.1 (Nishi et al.)

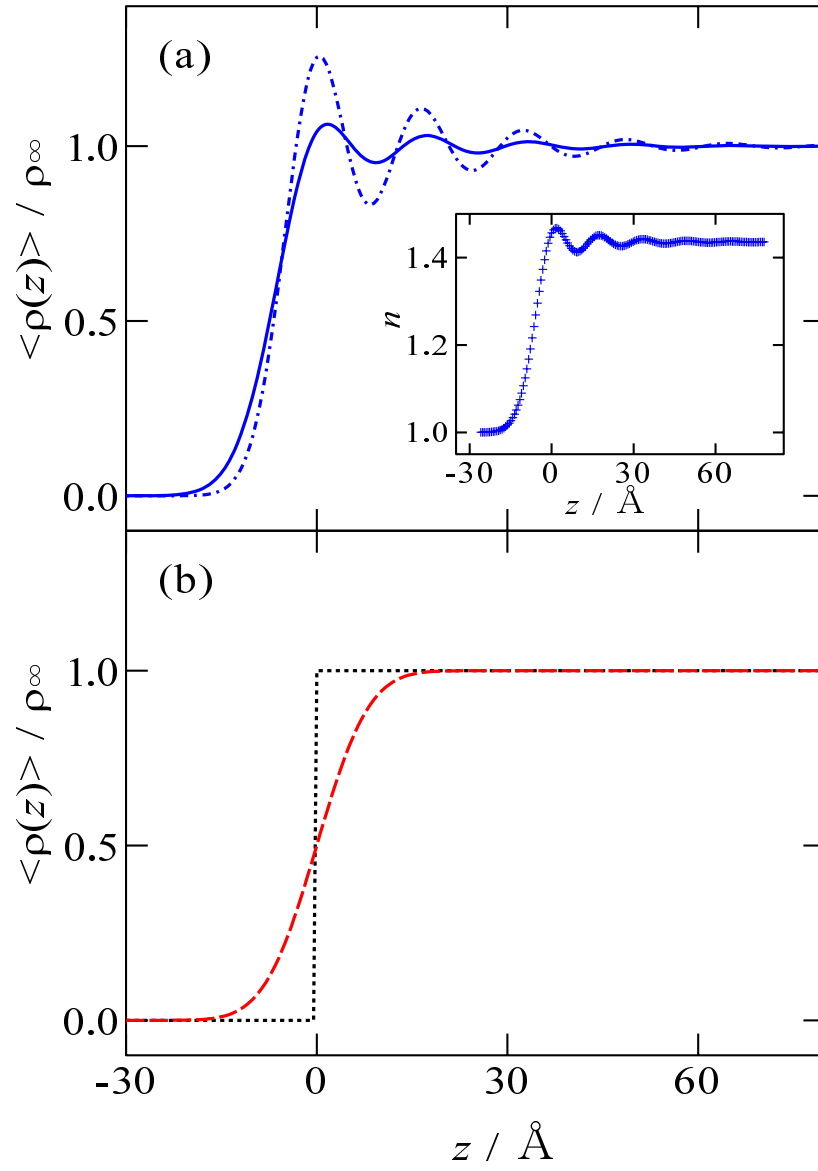


Fig.2 (Nishi et al.)

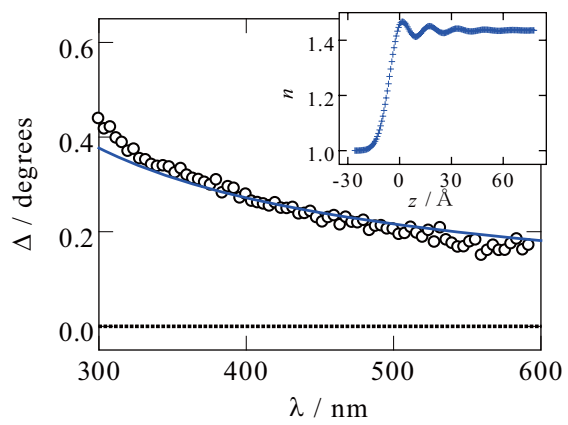
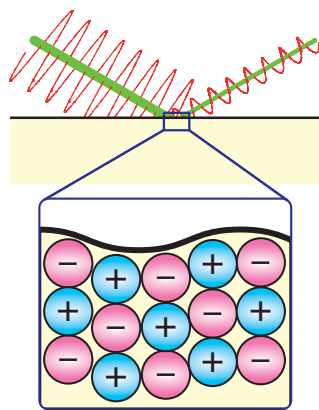


Table of Contents Image (Nishi et al.)