

Temperature dependence of multilayering at the free surface of ionic liquids probed by X-ray reflectivity measurements

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The effect of the temperature on the surface layering of ionic liquids has been studied for two ionic liquids, trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide ([TOMA⁺][C₄C₄N⁻]) and trihexyltetradecylphosphonium bis(nonafluorobutanesulfonyl)amide ([THTDP⁺][C₄C₄N⁻]), using x-ray reflectivity measurements at 285, 300, and 315 K. Both [TOMA⁺][C₄C₄N⁻] and [THTDP⁺][C₄C₄N⁻] develop multilayers at the surface. The structure of the multilayers at the [TOMA⁺][C₄C₄N⁻] surface shows little temperature-dependent change whereas that at the [THTDP⁺][C₄C₄N⁻] surface clearly becomes diffused with increasing temperature. The different temperature dependence seems to be related to the difference in the recently reported ultraslow dynamics of the interfacial structure of [TOMA⁺][C₄C₄N⁻] and [THTDP⁺][C₄C₄N⁻] at the ionic liquid|water interface.

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I. INTRODUCTION

Multilayering at liquid surfaces (liquid|vapor interfaces) has been revealed to be a general feature of liquid metals^{1–6} and liquid alloys.^{7–12} On the other hand, for molecular solvents evidence of the multilayers at the surfaces has not been obtained^{13–16} except for some organic silicon compounds at low temperatures.^{17–20} For ionic liquids (ILs), which are liquid salts at ambient temperature and are composed entirely of ions, molecular dynamics simulation^{21–27} predicted the existence of multilayers at the IL surface, and x-ray reflectivity (XR)^{28–32} and neutron reflectivity^{33,34} measurements revealed that at least one surface layer exists at the IL surface. Recently, we found that there exists multilayers at the surface of an ionic liquid, trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide ([TOMA⁺][C₄C₄N[−]], Scheme 1).³⁵ The analysis using model fittings suggested that at least four ionic layers are formed without segregation of cations and anions between the layers, with the interlayer distance of 16 Å, extending into the bulk from the surface to the depth of ~60 Å.³⁵

In this paper, the temperature dependence of XR for the surface of the two ILs, [TOMA⁺][C₄C₄N[−]] and trihexyltetradecylphosphonium bis(nonafluorobutanesulfonyl)amide ([THTDP⁺][C₄C₄N[−]], Scheme 1) will be presented. The dynamics of the collective rearrangement of IL-constituent ions at the interface between water and hydrophobic ILs is extremely slow, on the order of min, in response to the change in the phase-boundary potential across the interface.^{36–39} The relaxation time of this ultraslow dynamics depends on ILs; for example, [TOMA⁺][C₄C₄N[−]] shows three times slower dynamics than [THTDP⁺][C₄C₄N[−]].³⁹ The difference of the relaxation time may be reflected from the difference between the structure of the multilayers at the interface of [TOMA⁺][C₄C₄N[−]] and [THTDP⁺][C₄C₄N[−]]. We will show that [TOMA⁺][C₄C₄N[−]] and [THTDP⁺][C₄C₄N[−]] show significantly different temperature dependence of the structure of the multilayers at the surface.

II. EXPERIMENTAL

A. Preparation of ionic liquid

[THTDP⁺][C₄C₄N[−]] was prepared from trihexyltetradecylphosphonium chloride (Aldrich) and hydrogen bis(nonafluorobutanesulfonyl)amide (Wako Pure Chemical Industries) and purified using the same method for [TOMA⁺][C₄C₄N[−]] described elsewhere.³⁵

B. X-ray reflectivity measurement

XR measurements were performed at the beamline BL37XU of SPring-8⁴⁰ using a liquid interface reflectometer.^{41–43} The details of the XR measurements are described elsewhere.³⁵ Briefly, X-ray of 25 keV from the undulator was irradiated to the IL surfaces. The reflected x-ray beam profiles were detected using a two-dimensional pixel array detector (PILATUS 100K) and the bulk scattering was removed from the specularly reflected beam.^{35,42} For the temperature control, a PTFE coated aluminum trough was used instead of the PTFE trough used in our previous study.³⁵ The PTFE coated aluminum trough was set on an aluminum block in which temperature-controlled water was flowed. The lower part of the trough, which has an inner size of 100×60×7 mm³ (width/depth/height, x-ray is in the direction of the long axis), was filled with [THTDP⁺][C₄C₄N[−]] (~40 mL). Temperature was controlled with an accuracy of 1 K.

The x-ray reflectivity normalized by the Fresnel reflectivity, R/R_F can be written as follows under the kinematic approximation,¹³

$$\frac{R}{R_F} = |\phi|^2 \exp \left[-\sigma_{\text{CWT}}^2 Q^2 \right], \quad (1)$$

$$\phi = \int_{-\infty}^{\infty} \frac{d}{dz} \left(\frac{\langle \rho(z) \rangle}{\rho_{\infty}} \right) \exp [iQz] dz, \quad (2)$$

where ϕ is the surface structure factor, z is a displacement along with the surface normal with $z > 0$ for the IL phase, Q is the z component of the scattering vector, $\langle \rho(z) \rangle$ is the intrinsic electron density averaged in the xy direction (along the surface plane) at z , and ρ_{∞} is the electron density in the IL bulk. The Fresnel reflectivity, R_F , was calculated with the density, ρ_{IL} , and formula weight of the IL, and the atomic scattering factors of atoms constituting the IL at 25 keV.^{44,45} A surface roughness due to thermal capillary waves derived from the capillary wave theory, σ_{CWT} , may be written as,^{13,41}

$$\sigma_{\text{CWT}}^2 = \frac{k_B T}{2\pi\gamma} \ln \left(\frac{q_{\text{max}}}{q_{\text{res}}} \right), \quad (3)$$

where k_B is the Boltzmann constant, T is the absolute temperature, γ is the surface tension, and q_{max} and q_{res} , are the lower and upper cutoffs of the thermal capillary wave vector, respectively. The value of q_{max} was estimated from $q_{\text{max}} = \pi/r_{\text{mean}}$,¹³ where r_{mean} is the mean value of radii for the cation and the anion constituting the IL, which are estimated from B3LYP/6-311+G** level calculation by Gaussian 03⁴⁶ (Table 1). Note that this q_{max} value may be overestimated, according to a recent x-ray reflectivity study at the surfaces of water, some short-chain alcohols, and their mix-

tures.⁴⁷ The value of q_{res} was evaluated from the sample-detector distance and the vertical spatial resolution of PILATUS.^{35,41} The values of γ and ρ_{IL} of $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ and $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ were measured using a pendant drop method,⁴⁸ and a density/specific gravity meter (Kyoto Electronics, DA-520), respectively, and are listed in Table 1.

III. RESULTS AND DISCUSSION

A. $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$

Figure 1 shows the plots of $\log(R)$ against Q for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface at 285 K (red squares) and 315 K (blue circles) along with that at 300 K (green triangles) previously reported.³⁵ The experimental plots at 285 and 315 K show a similar tendency to that at 300 K as described below. The plots are lower than the Fresnel reflectivity (solid lines) at the incident angle, θ , smaller than the critical angle, θ_c , which is due to a longer footprint of x-ray at interface than the size of the interface at small θ .⁴⁹ The plots are also lower than the Fresnel reflectivity (solid lines) when $\theta \gg \theta_c$ mainly due to thermal fluctuation of the surface. The plots still deviate from the reflectivity for the thermally fluctuated and structureless surface (dotted lines), which incorporates the contribution of the thermal fluctuation due to capillary waves on the surface estimated using the capillary wave theory (see eqs 1 and 3). The deviation suggests that there exists a certain surface structure at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface.

The common logarithm of the square of the surface structure factors, $\log|\phi|^2$, which are the ratio of the reflectivity plots to the reflectivity for the thermally fluctuated and structureless surface (see eq 1), are plotted against Q^2 in Fig.2. One can see peaks around $Q^2 = 0.13 \text{ \AA}^{-2}$, which are attributable to quasi-Bragg peaks due to the multilayers.³⁵ Little temperature dependence was discernible in this temperature range for the plots. The distorted crystal (DC) model was fitted to the plots, as was the case for data at 300 K.³⁵ Slab (box) model did not reproduce the plots.³⁵ In the DC model, the total electron density profile is a superposition of the gaussian electron density profile in each layer;

$$\frac{\langle \rho(z) \rangle}{\rho_\infty} = \frac{d}{\sqrt{2\pi}} \sum_{n=0}^{\infty} \frac{1}{\sigma_n} \exp \left[\frac{-(z - nd)^2}{2\sigma_n^2} \right], \quad (4)$$

where d is the interlayer distance and σ_n is the line width for the n th layer. The deeper the position of the layer into bulk, the wider the line width of the layer is; $\sigma_n^2 = n\bar{\sigma}^2 + \sigma_0^2$,

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 DC model assumes no segregation of cations and anions between layers; the number of cations is equal to that of anions in each layer. The fitted parameters of the DC model to the plots are listed in Table 2. The d and σ_0 values at the three temperatures are the same within the experimental errors. The $\bar{\sigma}$ values show weak but detectable temperature dependence; the lower the temperature, the more the multilayers extend into bulk from the surface. The intrinsic electron density profiles in Fig.3, which are reproduced from the DC model with the fitted parameters, show little temperature dependence. Such negligibly small temperature dependence was found for the multilayers at the surface of liquid gallium at 293-433 K.⁵⁰ It is likely that $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ has a transition temperature range between layered surface and layerless surface higher than 285-315 K. One might expect that the Q^2 values at the peaks in Fig. 2 are located at $(2\pi/d)^2$ but actually the Q^2 values are $0.13 \text{ \AA}^{-2}$ and smaller than $0.16 (= (2\pi/15.5)^2) \text{ \AA}^{-2}$. This discrepancy is due to the decay feature of the multilayer structure from the surface to the bulk; the distance between neighboring two local maxima in the electron density profile is longer than d (Fig. 3).

B. $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$

Figure 4 shows the plots of $\log(R)$ against Q for the $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface at 285 K (red squares), 300 K (green triangles), and 315 K (blue circles). Similar to the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface, the $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface showed the deviation of the plots from the reflectivity for the thermally fluctuated and structureless surface (dotted lines). However, the deviation is less prominent at high temperature (315 K, blue circles) compared with that at low temperature (285 K, red squares). The plots of $\log \phi^2$ against Q^2 for the $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface at 285 (red squares), 300 (green triangles), and 315 (blue circles) K are shown in Fig.5. The temperature dependence of the plots is clearly seen; the higher the temperature, the lower the peak height. Similar to the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface, the slab model did not reproduce the experimental plots. The DC model was fitted to the plots as shown in solid lines and the fitted parameters are listed in Table 2. The d values are around $15 \text{ \AA}$ and greater than $\sim 10 \text{ \AA}$, the diameter of THTDP^+ and $\text{C}_4\text{C}_4\text{N}^-$ estimated assuming the spherical shape for the ions (Table 2). Taking into account that the shape of the ions is not spherical (Scheme 1) and the greater d value than the estimated diameter, we presume that, at the surface of $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$, ions are likely

to be orientated with their long axis preferentially in parallel to the surface normal, as is the case with at the surface of $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$.³⁵ Regarding the σ_0 and $\bar{\sigma}$ values, the σ_0 values are greater but the $\bar{\sigma}$ values are smaller at higher temperatures. This tendency means that the topmost layer becomes less ordered with increasing temperatures but the lower layers become less ordered with decreasing temperatures. The intrinsic electron density profiles are shown in Fig.6, which clearly illustrates the disordering of the topmost layer at higher temperatures. The temperature dependence of the structure of the multilayers at the surface of liquids was reported for liquid mercury,⁵¹ where not sharp but gradual change between layered surface and layerless surface was observed. The transition temperature region for the $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface is likely to be around 285-315 K.

A question is why $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ shows clear temperature dependence of the structure of the multilayers whereas $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ does not. Systematic studies with other ILs will be needed for clearer discussion but the following is our postulate at the present stage. The positive charge in THTDP^+ is buried in the long four alkyl chains (three hexyl and one tetradecyl chains), in contrast to that in TOMA^+ which is surrounded by three octyl chains but one short methyl group (see Scheme 1 for the structure of the ions). Therefore, electrostatic interaction between THTDP^+ and $\text{C}_4\text{C}_4\text{N}^-$ should be weaker than that between TOMA^+ and $\text{C}_4\text{C}_4\text{N}^-$ due to the lesser accessibility of $\text{C}_4\text{C}_4\text{N}^-$ to the positive charge in THTDP^+ hindered by the long chains. The electrostatic interaction between charged parts of ions seems to play an important role for forming the multilayers at liquid surfaces. The weaker electrostatic interaction between ions in $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ than in $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ would be responsible to the lower transition temperatures for the structure of the multilayer at the $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface.

Such multilayers are likely to be related to the specific dynamics of the IL interfaces. Recently, we demonstrated that the response of interfacial tension at the IL|water interface to the change in the phase-boundary potential is extremely slow, on the order of minutes.³⁶⁻³⁹ Such an ultraslow response is likely to be due to the slow collective rearrangement of ions in the electrical double layer formed at the IL side of the interface. The response rate is IL dependent; for example, $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ shows three-times slower dynamics than $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$, although the response is extremely slow for both ILs. The difference in the rates is likely to be related to be the different transition temperatures between layered and layerless surfaces for $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ and $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$.

IV. CONCLUSIONS

Multilayering of liquid at the solid interface is ubiquitous in liquid metals,^{52–54} molecular solvents^{55–61} and ionic liquids.^{62–69} This type of layering is brought about by the solid surface, which is rigid and usually charged. This is not the case at the liquid|air interface (liquid surface). Liquid metals and liquid alloys generally form multilayers at the free surface, whereas for ionic liquids and molecular solvents clear detections of the multilayers have been rarely reported.³⁵ We reported, in the present paper, that [TOMA⁺][C₄C₄N[–]] and [THTDP⁺][C₄C₄N[–]] have highly ordered multilayers at the free surface. The temperature dependence of the XR data for the two ILs revealed that the structure of the multilayers at the IL surface depends on the ions constituting the ILs. The structure of the multilayers at the IL surface should reflect the structure of the multilayers at electrochemical interfaces such as ionic liquid|water interface^{36–39} and ionic liquid|solid electrode interface⁷⁰ where ultraslow dynamics was recently observed.

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TABLE I. Parameters used for the analysis of the XR data.

Ionic liquid	r_c (Å)	r_a (Å)	T (K)	γ (mN m ⁻¹)	ρ_{IL} (g cm ⁻³)
[TOMA ⁺][C ₄ C ₄ N ⁻]	5.24	4.63	285	22.4±0.1	1.289±0.001
			300	22.0	1.269
			315	20.6	1.251
[THTDP ⁺][C ₄ C ₄ N ⁻]	5.55	4.63	285	23.8	1.230
			300	23.5	1.213
			315	22.9	1.193

TABLE II. Parameters obtained by fitting the curve from the DC model to XR data.

Ionic liquid	T (K)	d (Å)	σ_0 (Å)	$\bar{\sigma}$ (Å)
[TOMA ⁺][C ₄ C ₄ N ⁻]	285	15.66 ± 0.13	5.15 ± 0.05	3.29 ± 0.06
	300	15.45 ± 0.10	5.08 ± 0.04	3.35 ± 0.04
	315	15.54 ± 0.12	5.14 ± 0.05	3.52 ± 0.04
[THTDP ⁺][C ₄ C ₄ N ⁻]	285	15.5 ± 0.3	4.46 ± 0.06	4.67 ± 0.18
	300	14.9 ± 0.3	4.77 ± 0.06	3.93 ± 0.22
	315	15.06 ± 0.18	5.25 ± 0.08	3.36 ± 0.09

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Figure captions

Scheme 1: Structure of the ions constructing $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ and $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$.

Fig. 1: Plots of x-ray reflectivity (R) versus Q for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface at 285 (red squares), 300 (green triangles) and 315 (blue circles) K with error bars of one standard deviation. The solid and dotted curves are the Fresnel reflectivity and the reflectivity for thermally fluctuated but structureless surface, respectively. The data at 285 and 300 K are vertically shifted for the clarity.

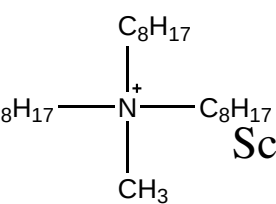
Fig. 2: $\log(\phi^2)$ vs. Q^2 plots at 285 (red squares), 300 (green triangles), and 315 K (blue circles) for the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface. The solid curves are from the model fittings with the DC model to the plots.

Fig. 3: Intrinsic electron density profiles at the $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface using the parameters obtained from the fitting of the DC model listed in Table 2 at 285 (red), 300 (green) and 315 (blue) K.

Fig. 4: Plots of x-ray reflectivity (R) versus Q for the $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface at 285 (red squares), 300 (green triangles) and 315 (blue circles) K with error bars of one standard deviation. The solid and dotted curves are the Fresnel reflectivity and the reflectivity for thermally fluctuated but structureless surface, respectively. The data at 285 and 300 K are vertically shifted for the clarity.

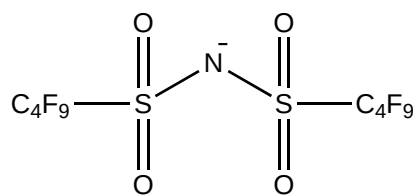
Fig. 5: $\log(\phi^2)$ vs. Q^2 plots at 285 (red squares), 300 (green triangles), and 315 K (blue circles) for the $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface. The solid curves are from the model fittings with the DC model to the plots.

Fig. 6: Intrinsic electron density profiles at the $[\text{THTDP}^+][\text{C}_4\text{C}_4\text{N}^-]$ surface using the parameters obtained from the fitting of the DC model listed in Table 2 at 285 (red), 300 (green) and 315 (blue) K.

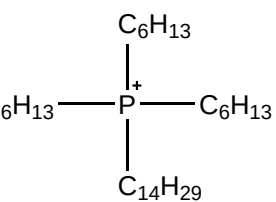


TOMA⁺

Scheme 1 (Nishi et al.)



C₄C₄N⁻



THTDP⁺

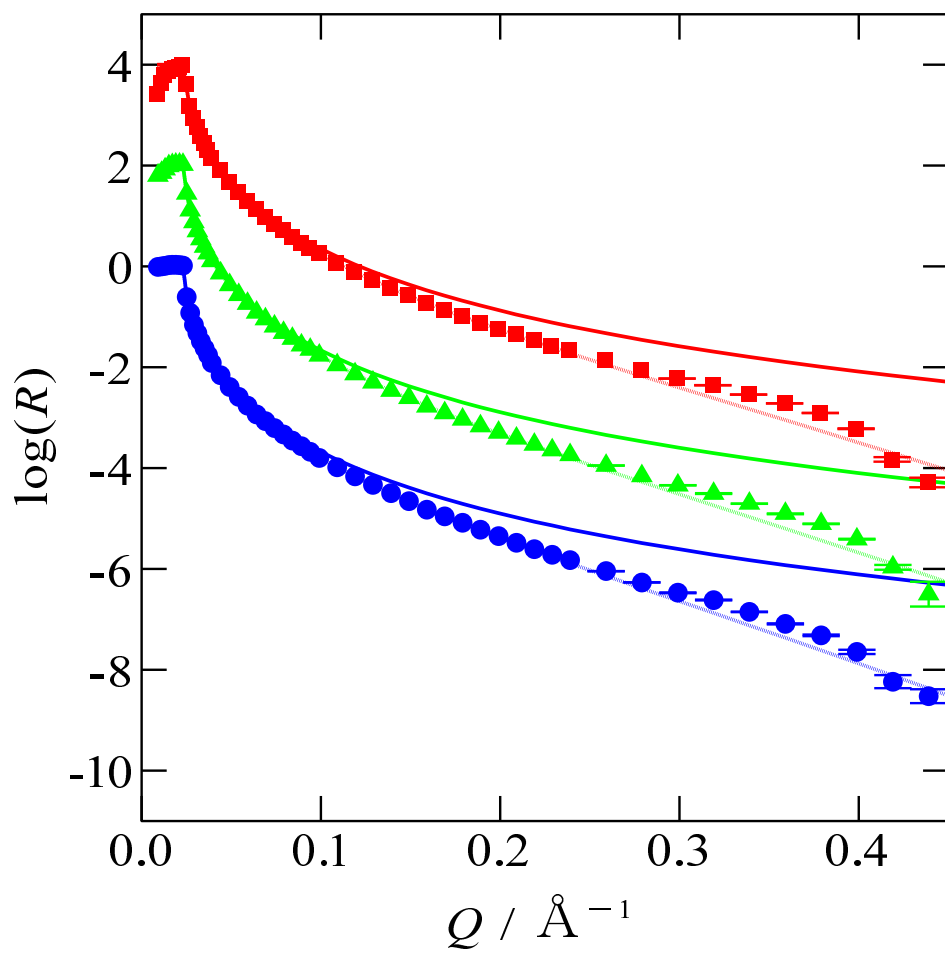


Fig.1 (Nishi et al.)

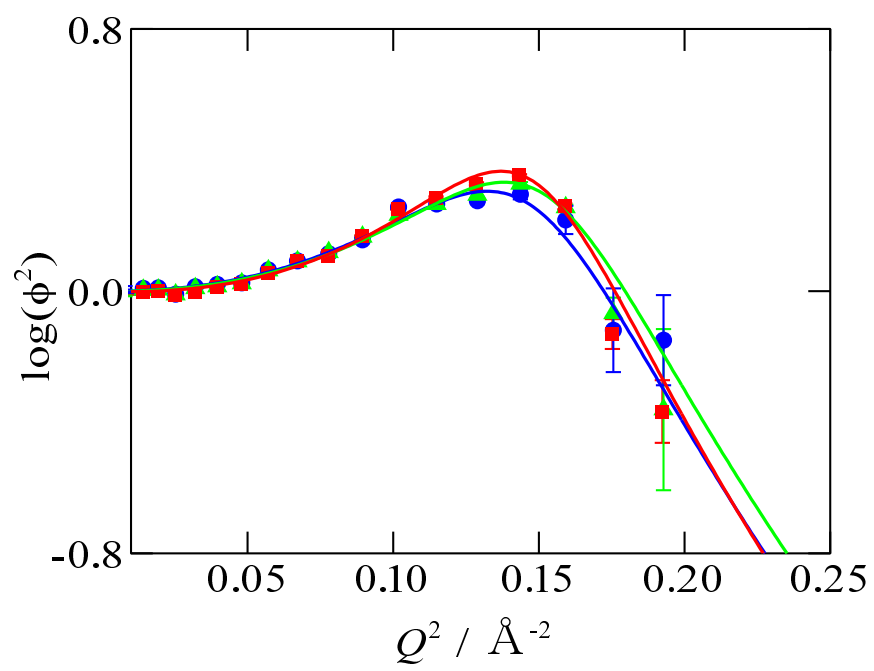


Fig.2 (Nishi et al.)

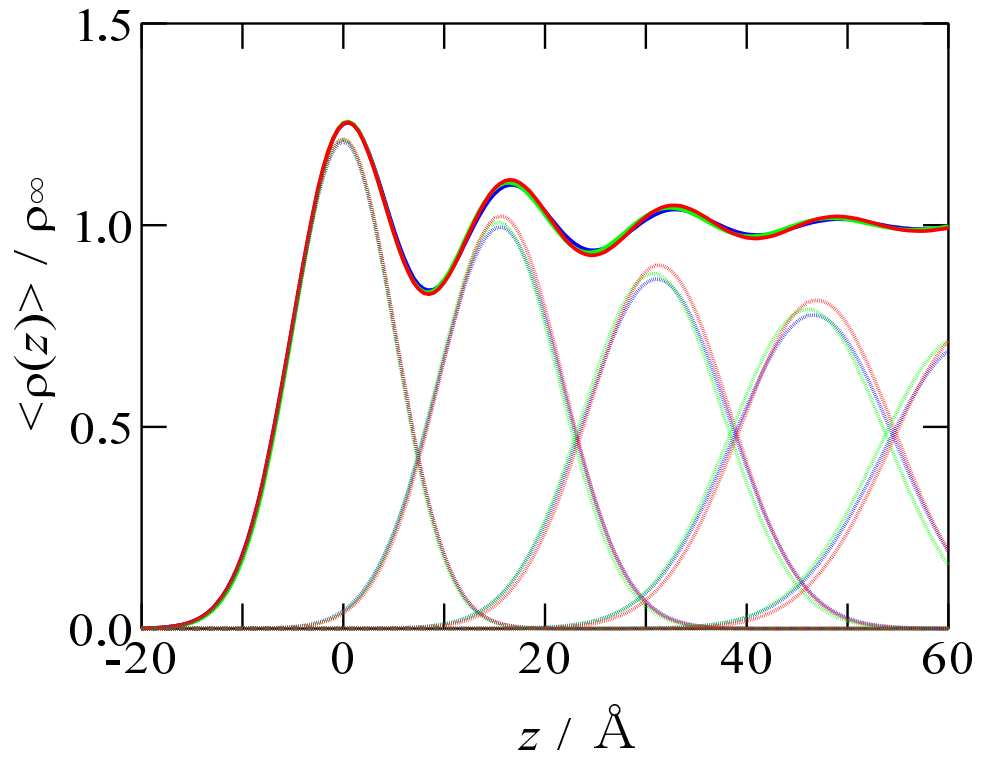


Fig.3 (Nishi et al.)

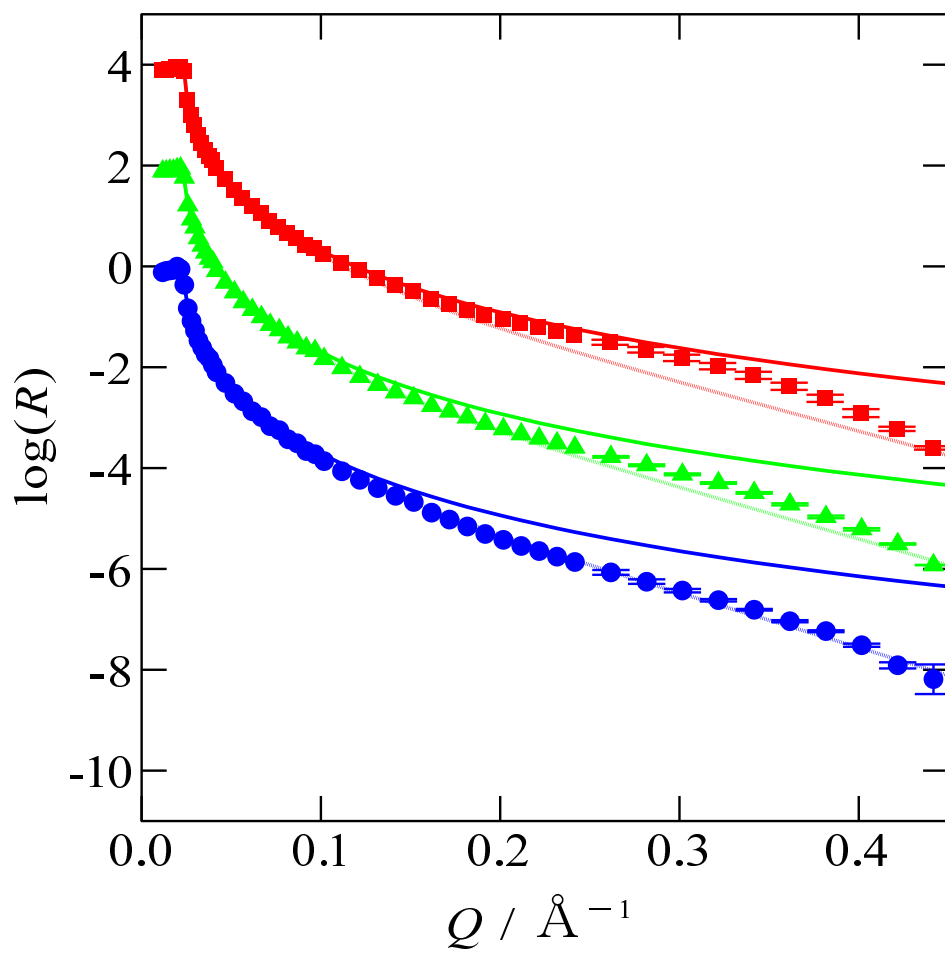


Fig.4 (Nishi et al.)

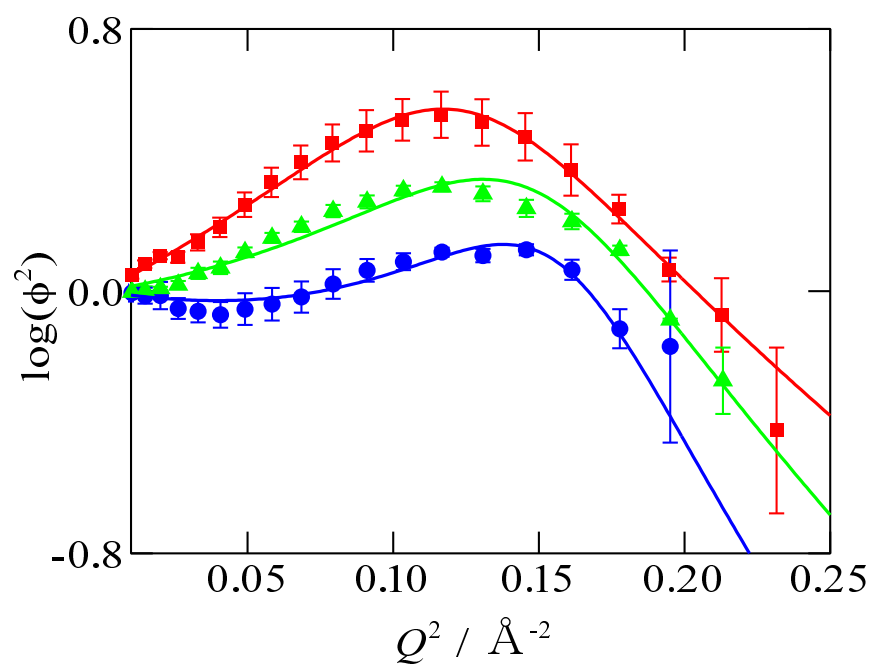


Fig.5 (Nishi et al.)

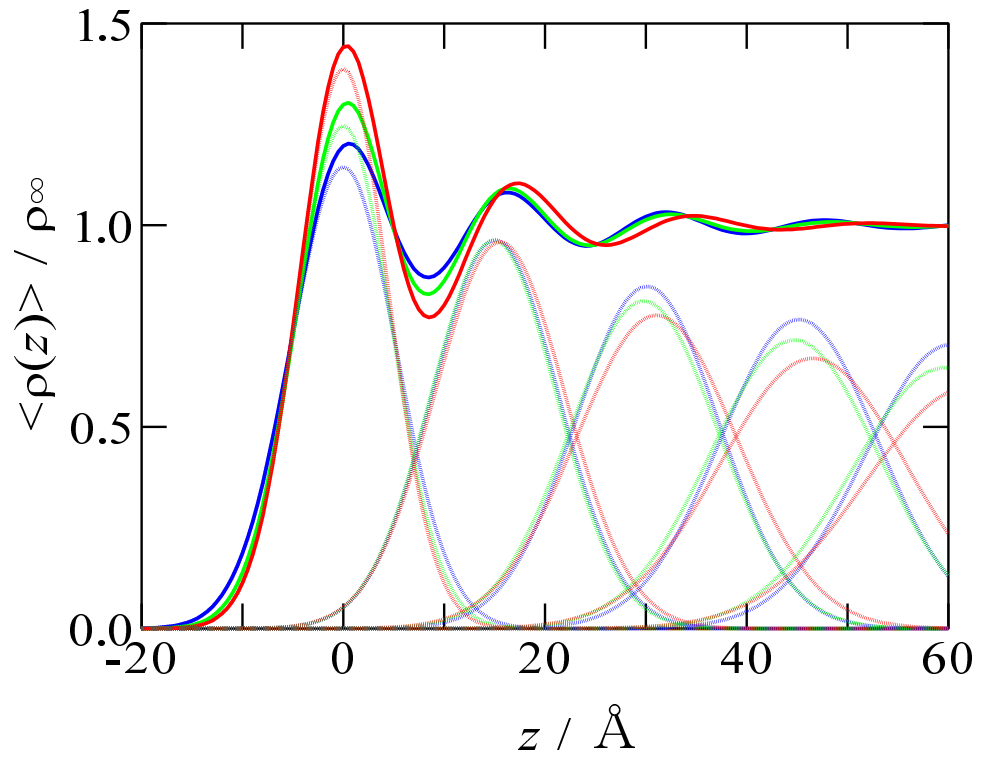


Fig.6 (Nishi et al.)

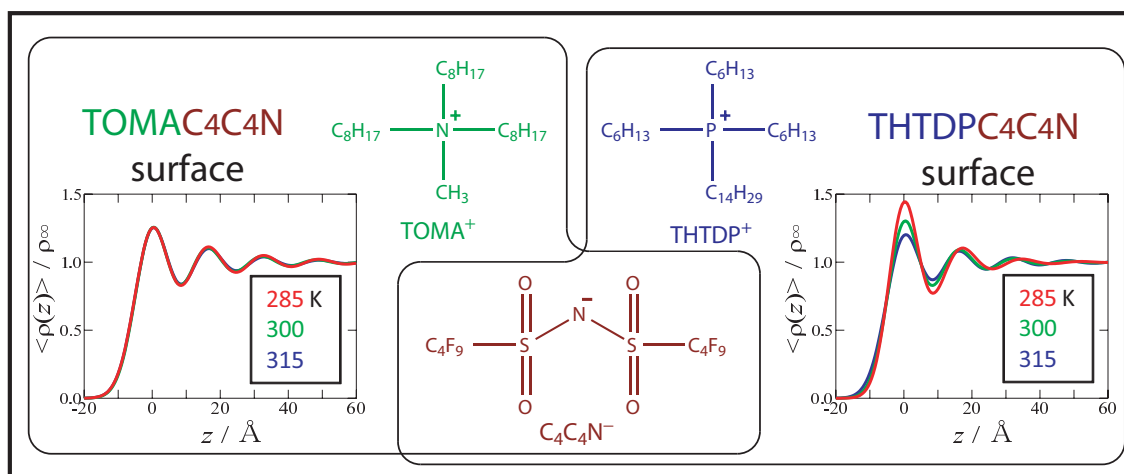


Table of Contents Graphic (Nishi et al.)