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Communication: Coordination structure of bromide ions associated with hexyltrimethylammonium cations at liquid/liquid interfaces under potentiostatic control as studied by total-reflection X-ray absorption fine structure

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Total-reflection X-ray absorption fine structure (TR-XAFS) technique was applied for the first time to an interface between two immiscible electrolyte solutions under potentiostatic control. The hydration structure of bromide ions was investigated at polarized 2-octanone/water interfaces. TR-XAFS spectra at Br K-edge measured in the presence of hexyltrimethylammonium bromide (C_6TAB) were slightly modified depending on the Galvani potential difference ($\Delta_o^w \phi$). The extended X-ray absorption fine structure analysis exposed hydration structure changes of bromide ions at the polarized interface. The coordination structure of bromide ions at the interface could be analyzed as compared with bromide ions dissolved in aqueous solution and Br^--exchanged resin having quaternary ammonium groups. The results indicated that bromide ions were associated with C_6TA^+ at the polarized interface. The relative contribution of ion association form of bromide ions with quaternary ammonium groups was enhanced at a potential close to the ion transfer of C_6TA^+, where the interfacial concentration of C_6TA^+ is increased as a function of $\Delta_o^w \phi$. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4867899]

An interface between two immiscible solutions (ITIES) is a two-dimensional specific reaction field. The interfacial reactions have been extensively studied for separation sciences, synthesis of thin-layer materials, and biochemical applications.[1] Under potentiostatic conditions, the charge transfer reaction across the interface can be controlled as a function of the applied potential.[2] The interfacial reaction often involves adsorption processes of reactants and specific species formed only at the interface.[3] The characterization of interfacial species at the molecular level is thus essential to elucidate the heterogeneous reaction mechanism. The structural analysis such as a solvation structure has, however, rarely been carried out *in situ* at ITIES because of the lack of a suitable technique.

X-ray absorption fine structure (XAFS) is widely used to analyze the molecular structure in various chemical states. Total-reflection XAFS (TR-XAFS) techniques have been applied mainly for thin-layer materials and surface species on chemically modified solid surfaces. In order to characterize the species at soft interfaces,[4] whose concentration is much lower than that of solid surface systems, the TR-XAFS method should be combined with highly sensitive detection techniques such as a total-conversion helium ion yield mode[5] or a fluorescence yield mode.[6] The polarization dependences of TR-XAFS spectrum have also provided valuable insights into the molecular orientation and coordination structure of metal complexes at soft interfaces.[7–9] Recently, the polarized TR-XAFS method was applied to liquid/liquid interfaces, in which a partial dehydration of the axial sites of anionic zinc(II) porphyrin spontaneously adsorbed at the heptane/water interface was directly observed from the polarization dependences of X-ray absorption near-edge structure (XANES) involving a 1s-4p_z transition for a square planar metal complex.[10] The interfacial association between alkylammonium surfactants and bromide ions was also measured at the heptane/water interface.[11,12]

In the present study, the TR-XAFS technique was applied for the first time to the liquid/liquid interface under potentiostatic control. The electrochemical studies at ITIES have mostly been carried out by means of the water/1,2-dichloroethane (DCE) and water/nitrobenzene (NB) systems. In those systems, valuable electrochemical parameters such as standard transfer potential correlated to the Gibbs free energy of transfer and partition coefficient are available for a variety of ionic species. Schlossman and co-workers have

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studied the ion condensation and distribution properties of monovalent ions at electrified water/DCE interfaces by X-ray reflectivity analysis, in which the incident X-ray at ∼30 keV was introduced to the interface through an upper aqueous phase.[13–15] For X-ray absorption spectroscopy, however, the incident X-ray introduced to the interfacial region, whose energy is restricted by the absorption edge of a target atom and much smaller (e.g., 13.5 keV for the Br K-edge) than that for X-ray reflectivity, is considerably attenuated by an upper solution phase. For instance, the attenuation lengths of X-ray at 13.5 keV for water, DCE and NB are calculated as 4.9, 0.48, and 6.4 mm, respectively.[16] The 2-octanone/water and 2-heptanone/water interfaces have been developed for ITIESs with low toxicity.[17,18] In particular, 2-octanone provides a wider polarizable potential window compared with 2-heptanone. A longer attenuation length (i.e., 12 mm at 13.5 keV) is also suitable for the XAFS study. The TR-XAFS experiments were thus performed at the 2-octanone/water interface. The composition of electrochemical cell and the TR-XAFS cell are schematically shown in Fig. 1. The supporting electrolytes were 2×10^{-3} mol dm^{-3} bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB) for the upper organic phase and 2×10^{-3} mol dm^{-3} sodium bromide for the aqueous subphase, respectively. BTPPATPFB was prepared by metathesis of bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl) (Aldrich, >97%) and lithium tetrakis(pentafluorophenyl)borate (LiTPFB) ethyl ether complex (TCI, ≥70%). Hexyltrimethylammonium bromide (C$_6$TAB) and 2-octanone were of GR grade (TCI, >98%). All other reagents were of analytical grade. The aqueous solutions were prepared with purified water from a Milli-Q system (Millipore, Simpli Lab-UV). The 2-octanone/water interface was polarized by a four-electrode potentiostat equipped with a positive feedback circuit for *iR* compensation (Hokuto Denko, HA1010mM1A). The platinum counter (CE) and reference electrodes (RE: Ag/AgTPFB with a Luggin capillary and Ag/AgBr) in both organic and aqueous phases were placed not on the optical path. The TR-XAFS measurement was performed at the undulator beamline BL39XU of SPring-8 (Hyogo, Japan). The TR-XAFS cell was made of polychlorotrifluoroethylene resin (PCTFE). The incident X-ray beam (0.020 mm (height) × 2.0 mm (width)) was introduced to the interface through the upper organic phase under the total-reflection condition. The critical angle for the 2-octanone/water system is ∼0.66 mrad at Br K-edge and the angle of incidence (α_i) was $0.49 \leq \alpha_i \leq 0.51$ mrad in all measurements. The footprint of X-rays at the 2-octanone/water interface was calculated as 40 mm × 2 mm at $\alpha_i = 0.50$ mrad. The fluorescent X-ray from the interfacial region was detected by a seven-element silicon drift detector (SDD) (Ourstex). A Se filter (Exafs Materials, $\mu t = 6$ at Br K-edge) was used in order to reduce the background scattering. The detector window was in close proximity to the interface (<2 mm) so as to minimize the attenuation of the fluorescent signal through the organic phase. The cell windows for the incident X-ray and the detector were 0.038 mm thick polyimide (Kapton) film and 0.025 mm thick fluorinated ethylene propylene (FEP) film, respectively. A quartz frame with only the top
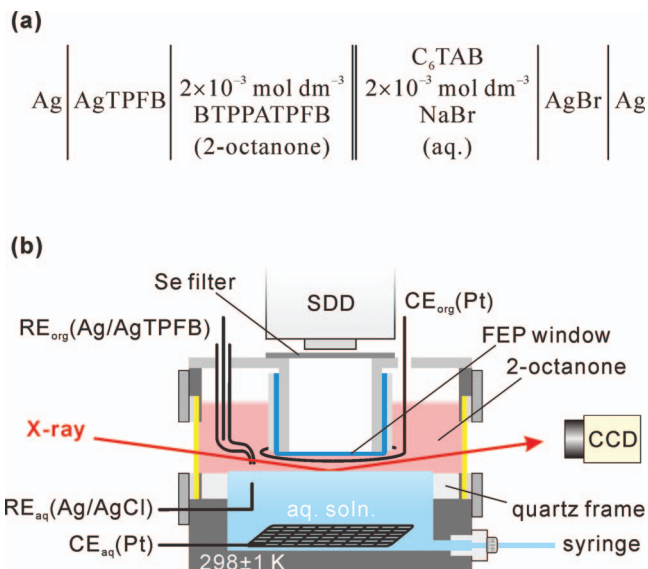

FIG. 1. (a) Composition of the electrochemical cell and (b) schematic drawing of the TR-XAFS cell.

face coated with hydrophobic dimethylsilane was placed in between two phases to form a flat-top convex meniscus. A flatness of the interface (60 mm × 40 mm) was controlled by expanding the aqueous solution volume with a syringe pump. The reflected X-ray beam was continuously monitored by a CCD camera in order to confirm the total-reflection condition. The TR-XAFS cell was thermostated at 298 ± 1 K.

Cyclic voltammograms (CVs) at the 2-octanone/water interface are displayed in Fig. 2. The Galvani potential difference ($\Delta_o^w \phi \equiv \phi^w - \phi^o$) was estimated by taking a value of −0.01 V for the formal transfer potential ($\Delta_o^w \phi^{o\prime}$) of tetrapropylammonium (TPA$^+$).[17] The present electrochemical cell provided a polarizable potential window of ∼0.38 V width (-0.28 V $\leq \Delta_o^w \phi \leq 0.10$ V) (Fig. S1 in the supplementary material).[19] The positive and negative limits of the potential window could be attributed, respectively, to the transfer of TPFB$^-$ and BTPPA$^+$ across the interface. The quasi-reversible voltammetric responses with the peak separation of ∼60 mV for a monovalent cation were observed for C$_6$TA$^+$ by using a small conventional four-electrode cell with an interfacial area of 1.8 cm^2 (Fig. 2(a)). The formal transfer potential of C$_6$TA$^+$ was determined as $\Delta_o^w \phi^{o\prime}_{C_6TA^+} = 0.02$ V. It should be noted that the total concentration of C$_6$TAB in the aqueous subphase was less than 1×10^{-3} mol dm^{-3}, which is much lower than the critical micelle concentration (CMC), 0.495 mol dm^{-3}.[20] In the case of the TR-XAFS cell, the ion transfer current drastically increased because of the large interfacial area (24 cm^2) (Fig. 2(b)). The potentiostatic condition for TR-XAFS measurements with a stable *iR* compensation was therefore restricted to $\Delta_o^w \phi < 0$ V by the transfer of C$_6$TA$^+$. In addition, the CVs exhibit a significant increase in the capacitive current at negative potentials associated with the adsorption of C$_6$TA$^+$ at the interface. C$_6$TAB is known to act as a surfactant and form the ion-associate with anionic species at liquid/liquid interfaces.[10]

The TR-XAFS spectra at the Br K-edge were successfully obtained at polarized 2-octanone/water interfaces
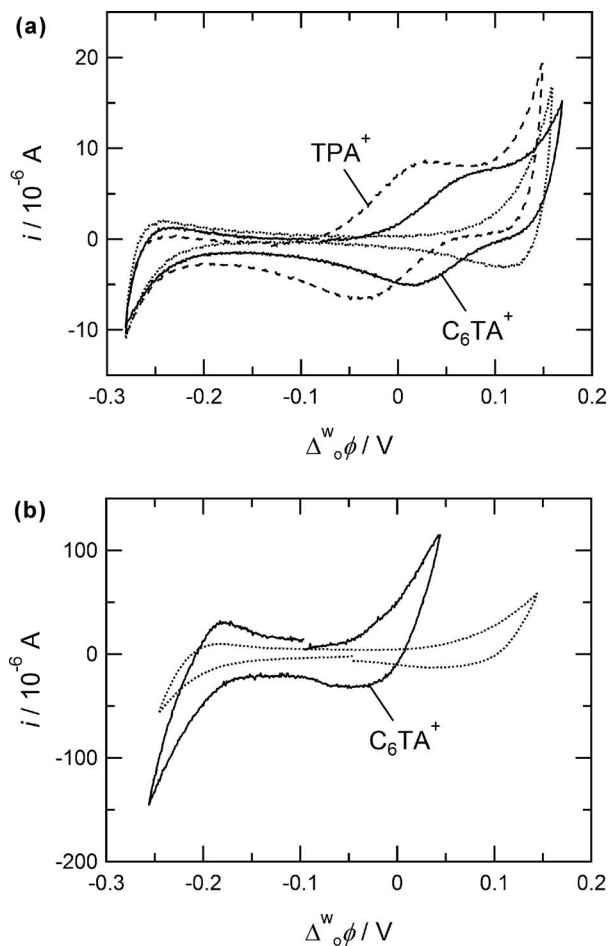
(a)

(b)

FIG. 2. Typical CVs measured for (a) 1.0×10^{-4} mol dm^{-3} C$_6$TA$^+$ and TPA$^+$ (small cell) and (b) 1.0×10^{-3} mol dm^{-3} C$_6$TA$^+$ (TR-XAFS cell) at the 2-octanone/water interface. The dotted lines refer to CVs in the absence of alkylammonium cations. The potential sweep rate was 10 mV s^{-1}.

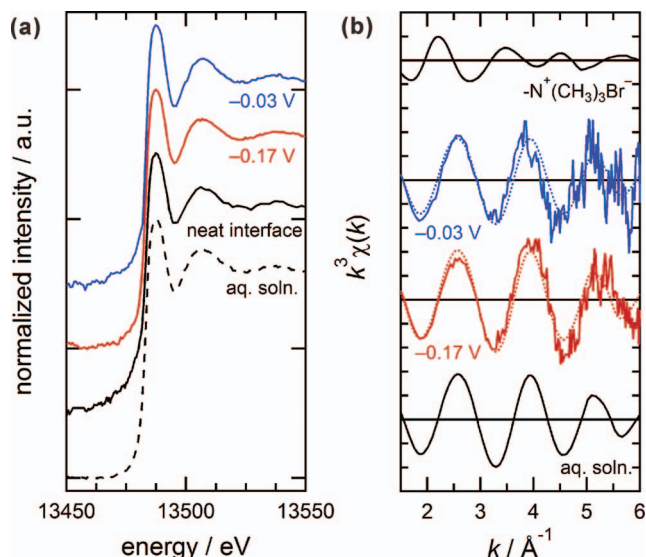FIG. 3. (a) TR-XAFS and (b) $k^3\chi(k)$ spectra for Br K-edge measured at polarized 2-octanone/water interfaces ($\Delta_o^w\phi = -0.03$ V and -0.17 V). (a) The black solid and dashed lines refer to the neat interface without adding C$_6$TAB and 2×10^{-3} mol dm^{-3} NaBr in water. (b) The dotted lines refer to the fitting-curves obtained from the linear combination of $k^3\chi(k)$ spectra for Br$^-$-exchanged resin powder (Amberlyst A-26) and 1 mol dm^{-3} LiBr aqueous solution measured in transmission mode.

(Fig. 3). The standard Gibbs free energy of ion transfer $\left(\Delta G_{tr}^{w\to o}\right)$ for bromide ions was reported as 40.1 kJ mol^{-1}, which corresponds to $\Delta_o^w\phi_{Br^-}^\circ = -0.42$ V.[17] The large negative value of $\Delta_o^w\phi_{Br^-}^\circ$ indicates that the bromide ions are not transferred across the 2-octanone/water interface within the potential window. Indeed, when the X-ray beam did not irradiate the interface and passed through the upper organic phase at ~1 mm from the interface, the fluorescence intensity dropped drastically to a negligibly small value. The TR-XAFS spectra thus reflect the bromide ions located in an evanescent field generated at the aqueous side of the interface, e.g., the penetration depth is calculated as ~17 nm ($\alpha_i = 0.50$ mrad). The XANES spectra observed at both -0.03 V and -0.17 V were analogous to the spectra measured at the neat interface in the absence of C$_6$TAB (Fig. 3(a)), indicating no drastic differences in the coordination structure of bromide ions at the interface in the presence of C$_6$TA$^+$. Nevertheless, the signal-to-noise level of the fluorescence X-ray signals from the interfacial region was apparently improved in the presence of C$_6$TAB. On the other hand, the EX-AFS analysis highlighted the buried changes in the TR-XAFS spectra as a function of $\Delta_o^w\phi$, i.e., the significant phase shift of $k^3\chi(k)$ data was observed at $k > 3$ Å^{-1} (Fig. S2(a) in the supplementary material).[19] XAFS spectrum was analyzed by

a curve-fitting based on a single-shell model with Br$\cdots$HO parameters calculated with FEFF ver. 8.2, where the O$\cdots$H distance was fixed as 0.95 Å (Fig. S2(b) in the supplementary material).[19] As summarized in Table I, the structural parameters for Br$^-$ at the interface were apparently modified from the hydrated bromide ion in water ($N = 6.0$ and $r = 3.25$ Å). The relative coordination number (N') with respect to the hexahydrated form in water and Br$\cdots$O distance (r/Å) were 3.8 and 3.32 Å at -0.03 V, whereas 4.3 and 3.17 Å at -0.17 V. The r values were analogous to that of the aqueous species (3.25 Å) within experimental error. The smaller N' values might correspond to the partial dehydration of bromide ions associated with $-$N$^+$(CH$_3$)$_3$ groups at the interface. The EX-AFS R-factors (>0.2) for the quality of fit, however, indicate that the single-shell Br$\cdots$O structure is not successfully adapted to the structural analysis for the interfacial species. In the present condition, two-possible coordination structures could be proposed for the bromide ions in the interfacial region: hexahydrated form in similar to aqueous species and ion association form with C$_6$TA$^+$.[21] In order to estimate the contribution from two-possible structures, the $k^3\chi(k)$ data measured at the polarized interface were decomposed by the regression analysis with the linear combination of $k^3\chi(k)$ spectra for hexahydrated bromide ions in water and the Br$^-$-exchanged resin (powder):[22,23]

$$\chi_{obs} = \alpha\chi_{hyd} + \beta\chi_{resin}, \qquad (1)$$

where χ_{obs}, χ_{hyd}, and χ_{resin} are the χ spectra measured for the interface at given potentials, for 1 mol dm^{-3} LiBr aqueous solution and for Br$^-$-exchanged quaternary-ammonium resin having $-$N$^+$(CH$_3$)$_3$ groups (Amberlyst A-26, Rohm and Hass) (Fig. 3(b)), respectively, measured in transmission mode. The proportional factors α and β refer to the contributions from χ_{hyd} and χ_{resin}. It was reported that $-$N$^+$(CH$_3$)$_3$

TABLE I. Structural parameters based on the single-shell model and regression analysis with Eq.(1) for bromide ions associated with hexyltrimethylammonium cations at polarized 2-octanone/water interfaces.

	2-octanone/water interface[a]		Hydrated Br$^-$ (1 mol dm^{-3} LiBr)[b]	Br$^-$-exchanged resin (powder)[b,c]
	−0.03 V	−0.17 V		
r/Å	3.32	3.17	3.25	3.53
N'[d]	3.8	4.3	6	4.27
σ/Å[e]	0.15	0.14	0.18	0.20
R-factor	0.241	0.202	0.019	
$\alpha{:}\beta$[f]	88:12	94:6		

[a]The concentration of C$_6$TAB was 1.0×10^{-3} mol dm^{-3}.
[b]XAFS experiments were carried out in transmission mode.
[c]Literature values from Ref. 22.
[d]N' for Br$^-$ in water was assumed to be 6.
[e]The Debye-Waller factor.
[f]The relative contribution from hydrated Br$^-$ (α) and Br$^-$ associated with $-$N$^+$(CH$_3$)$_3$ groups (β) (Eq. (1)).

groups preferentially interact with bromide ions in the anion exchange resin,[22] whereas the coordination structure of the bromide ions in dried tetraalkylammonium bromide powder includes the contribution of not only $-$N$^+$(CH$_3$)$_3$ groups but also other neighboring molecules.[24,25] The $k^3\chi(k)$ data for the Br$^-$-exchanged resin as a component is, therefore, appropriate to estimate the contribution of ion association between bromide ions and $-$N$^+$(CH$_3$)$_3$ groups. The N' and r values for the Br$^-$-exchanged resin were reported as 4.27 and 3.53 Å, respectively.[22] The relative contributions to the interfacial spectrum from two components ($\alpha{:}\beta$) were calculated as 88:12 (R-factor = 0.060) at −0.03 V and 94:6 (R-factor = 0.040) at −0.17 V, respectively. The results indicate that the coordination structure of bromide ions in the interfacial region was slightly modified from the bulk aqueous species. The ion association with quaternary-ammonium seems to be enhanced at the potential close to $\Delta_o^w \phi_{C_6TA^+}^{\circ\prime}$. The interfacial concentration of surface active ions is generally controlled as a function of $\Delta_o^w \phi$ and maximized at its transfer potential,[26,27] hence a higher interfacial concentration of C$_6$TA$^+$ at −0.03 V could induce the effective interaction with bromide ions at the interface.

In this work, the TR-XAFS measurement of the coordination structure of bromide ions associated with hexyltrimethylammonium cations at ITIES was carried out under potentiostatic conditions by employing the custom-built spectroelectrochemical cell and relatively transparent organic solvent (2-octanone). The EXAFS analysis elucidated slight changes in the average coordination structure of bromide ions in the interfacial region depending on $\Delta_o^w \phi$. Although the application of the present setup to lower energy absorption edges includes some difficulties resulting from a considerable attenuation of the incident beam and fluorescence signal, the TR-XAFS technique is quite useful to characterize a specific coordination structure at ITIES.

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