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Analysis of Equilibrium Electrocapillary Curves at the Interface between Hydrophobic Ionic Liquid, Trioctylmethylammonium Bis(nonafluorobutanesulfonyl)amide, and Aqueous Lithium Chloride Solutions[†]

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Electrocapillary curves obtained under the thermodynamic equilibrium at the interface between trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide and aqueous lithium chloride have been analyzed to study the adsorption of Li^+ and Cl^- ions at the interface. The specific adsorption of Li^+ and Cl^- is negligible in almost the entire range of the polarized potential window. At the positive extreme where the excess surface charge density is greater than $3\ \mu C \cdot cm^{-2}$, the deviation of the experimental relative surface excesses of Li^+ and Cl^- from the Gouy's theory was detected. This deviation suggests the coordination of adsorbed bis(nonafluorobutanesulfonyl)amide to Li^+ in the aqueous side of the interface. The double layer capacitance on the ionic liquid side of the interface is deduced to be $125\ \mu F \cdot cm^{-2}$ at the potential of zero charge.

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1. Introduction

Capillarity is an important interfacial property that reflects thermodynamic as well as nonequilibrium properties of fluid interface,[1,2] and has played a central role in surface chemistry and electrochemistry of liquid|gas, liquid|liquid, and liquid|metal interfaces. Remarkable advances have been made in the past 50 years, in particular, with regard to both theoretical and experimental studies of macroscopic as well as molecular pictures of the capillarity.[1,3] However, it seems that the distance between theories and experiments is still substantial in electrocapillarity, that is, the capillarity under the influence of the phase-boundary potential across the interface, where the electrical variables are key parameters and the charge−charge interactions between the ions and between the ion and the electrode are of primary importance.

The first systematic study of electrocapillarity at the mercury|aqueous solution interface was made by Lippmann[4] after the seminal work by Paalzaw in 1858[5] and was followed by Gouy.[6] Since then, thanks to the additional degree of freedom regarding the potential drop across the interface at the mercury|solution interface, the structure of the electrical double layer formed at electrified interfaces was revealed in considerable detail at this interface.[7−9] The study of electrocapillarity at two immiscible electrolyte solutions also dates back to the end of 19th century.[10] In most of the electrified liquid−liquid systems, the interfacial relaxation against the modulation of the phase-boundary potential is fast, typically on the order of milliseconds, in comparison with the observation time, for example, interfacial tension measurements or impedance measurements.

Recently, however, we came across the ultraslow relaxation of the electrical double layer to the change in the phase-boundary potential at the interface between the aqueous electrolyte solution (W) and the ionic liquid (IL), trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide ($[TOMA^+][C_4C_4N^-]$).[11] The time scale of this slow relaxation is on the order of minutes and can be significant in electrochemistry not only at the IL|W interface but at the IL|metal interface, because the slow relaxation is clearly the property of the IL side of the interface. To make a thermodynamically meaningful analysis of electrocapillary curves to obtain thermodynamic quantities, such as excess surface charge density, double layer capacitance, and relative surface excess, well-equilibrated electrocapillary curves are required. Previously, we reported the electrocapillary curves at the nonpolarized interface between the IL, 1-methyl-3-octylimidazolium bis(pentafluoroethanesulfonyl)amide, and an aqueous electrolyte solution.[12] In such a nonpolarized interface, the phase-boundary potential is controlled through the activity of the potential determining ion, and hence the slow relaxation of the double layer structure does not surface. However, electrocapillarity studies using potential modulation techniques at the polarized IL|W interface[13−16] and IL|mercury interface[17−20] can suffer from the hysteresis problem, and hence the data derived should be interpreted with care. Voltammetry at the IL|W and IL|electronic conductor interfaces should also consider the ultraslow relaxation problem.[21]

In this paper, we report the electrocapillarity studies at the electrochemically polarized IL|W interface employing thermodynamically equilibrated interfacial tension to analyze the double layer structure at the IL|W interface.

2. Experimental Section

2.1. Materials. $[TOMA^+][C_4C_4N^-]$ was prepared from trioctylmethylammonium chloride (Tokyo Chemical Industry Co., Ltd., Extra Pure) and hydrogen bis(nonafluorobutanesulfonyl)amide (HC_4C_4N, Wako Pure Chemical Industries, Ltd.) by the method described elsewhere.[11,14,15,22] For purification of the IL, we first washed the IL with water repeatedly and further purified with the method proposed by Earle et al.[23] Water used in this study was purified with a Milli-Q system (Millipore Co.).

2.2. Measurements of Density and Viscosity. The density of $[TOMA^+][C_4C_4N^-]$ was measured with an Ostwald-type pycnometer at 25 ± 0.5 °C. Literature values were used for the density values of aqueous LiCl solutions for calculating interfacial tension (γ) using a pendant-drop method.

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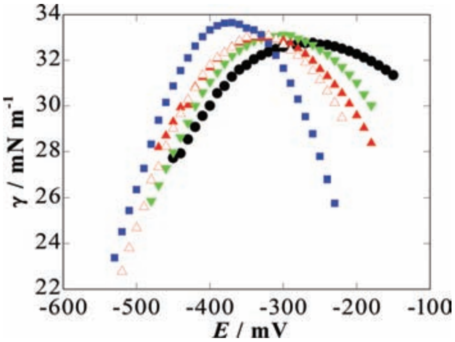

Figure 1. Equilibrated electrocapillary curves at the interface between $[\mathrm{TOMA}^+][\mathrm{C_4C_4N}^-]$ and an aqueous LiCl solution at 25 °C. The concentration of LiCl in W is ●, 0.01; ▼, 0.05; △, 0.1; ▲, 0.2; and ■, 1.0 $\mathrm{mol \cdot dm^{-3}}$.

2.3. Interfacial Tension Measurements. The potential drop across the interface was controlled using a four-electrode configuration together with a potentiostat (HA1010mA1A, Hokuto Denko), as described elsewhere.[11] The cell configuration is,

$$\mathrm{Ag/AgCl}\left|\begin{array}{c}0.05\ \mathrm{mol\cdot dm^{-3}\ LiCl}\\ +\\ 0.05\ \mathrm{mol\cdot dm^{-3}\ Li[C_4C_4N]}\\ \mathrm{(W2)}\end{array}\right|\begin{array}{c}[\mathrm{TOMA^+}][\mathrm{C_4C_4N^-}]\\ \mathrm{(IL)}\end{array}\left|\begin{array}{c}a\ \mathrm{mol\cdot dm^{-3}\ LiCl}\\ \mathrm{(W1)}\end{array}\right|\mathrm{Ag/AgCl} \qquad \mathrm{(I)}$$

where $\mathrm{Li[C_4C_4N]}$ is lithium bis(nonafluorobutanesulfonyl)amide and a in phase (W1) was 0.01, 0.02, 0.05, 0.1, 0.2, or 1.0. The interface between IL and W1 is the polarized interface, while that at W2 and IL is the nonpolarized. The ohmic drop due to the residual resistance uncompensated by the potentiostat was compensated for using a positive feedback method.

The interfacial tension was measured using video-imaging of a pendant drop of the IL in the aqueous solution. The details of the video imaging and data processing have been described elsewhere.[24] Equilibrium electrocapillary curves were obtained by the potential step method. The cell potential, E, was stepped from the positive end of the potential window to the negative direction by 10 mV intervals. The video image 1 min after each potential step was employed for constructing an equilibrium electrocapillary curve. Our detailed analysis of the time dependence of the interfacial tension at this interface indicates that the time to reach the 90 % of the equilibrium interfacial tension after the potential step is less than 30 s.[25]

3. Results and Discussion

3.1. Equilibrium Electrocapillary Curves. Figure 1 shows equilibrium electrocapillary curves at five different concentrations of LiCl. The increase in the LiCl concentration results in three noticeable changes in the appearance of the curves. First, the curvature of the curves becomes larger. Second, the potential of zero charge (pzc) shifts to the negative direction of E. Third, the γ at the pzc increases with the LiCl concentration. All of these features are characteristic to the case when the ions in W do not specifically adsorb at the interface, as have been seen at the interface between nitrobenzene and an aqueous LiCl solution[26] and also at the IL|W interface,[14] where the IL consists of tetrahexylammonium and bis(trifluoromethanesulfonyl)amide ($[\mathrm{THA}^+][\mathrm{C_1C_1N}^-]$) ions. The increase in γ at the pzc with LiCl concentration is a clear indication of the negative adsorption of Li^+ and Cl^- at the pzc and the presence of an ion-free inner layer at the aqueous side of the interface.[14,26]

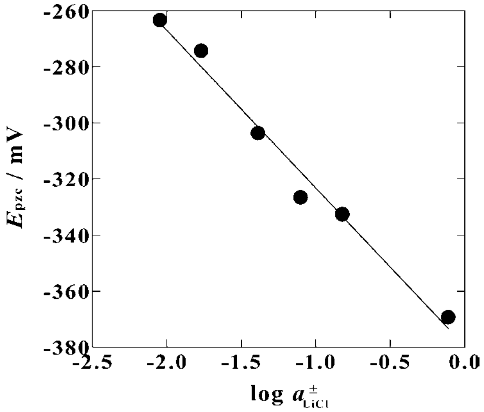

Figure 2. Plot of the potential of zero charge as a function of the common logarithm of the mean activity of LiCl.

3.2. Potential of Zero Charge. Two possible causes of the shift of the pzc with the LiCl concentration are conceivable: the shift of the potential of the Ag/AgCl electrode on the right-hand side of cell (I) and the specific adsorption of Li^+ or Cl^- at the interface. The pzc values from Figure 1 are plotted in Figure 2 as a function of the logarithm of the mean activity of LiCl in W. The least-squares regression of the straight line to these points is shown as a solid line. The slope of this line, 56 mV, is close to 59 mV expected for the nernstian response of the Ag/AgCl electrode, and the shift is mainly ascribed to the change in the potential of the Ag/AgCl electrode. In other words, Li^+ and Cl^- ions do not appreciably adsorb at the interface at the pzc.

At the pzc, the IL phase is electrically neutral, and half of the ions at the surface of $[\mathrm{TOMA}^+][\mathrm{C_4C_4N}^-]$ facing the aqueous phase must be TOMA^+. The fact that there is no appreciable specific interaction between TOMA^+ and Cl^- at the interface, in the form of an interfacial ion-pair,[15] may look surprising because, unlike tetrahexylammonium, TOMA^+ (same as tricaprylmethylammonium, Aliquat 336, methyl tri-*n*-octylammonium) has been used as an anion exchanger and phase transfer catalyst, that is, a lipophilic cation that can extract anions into the nonaqueous phase in solvent extraction, ion sensing with liquid membrane-type ion sensors, or liquid−liquid two-phase organic synthesis.[27−29]

It seems that at the interface the positively charged part of TOMA^+ is not exposed to the aqueous phase, so that the direct contact of Cl^- in the aqueous side of the interface is not favorable. In contrast, in ion pair extraction, the electroneutrality in the organic phase or in a plasticized membrane is the primary driving force for the interaction of TOMA^+ with anions.[30] We note that the term specific interaction, used in the double layer studies at the electrified interface, connotes an interaction that cannot be described in terms of simple electrostatic interactions.[7,8]

3.3. Double Layer Capacitance. In the presence of ultraslow relaxation at the IL|W and IL|electronic conductor interfaces, thermodynamically defined double layer capacitance,

$$C_{\mathrm{dl}} = -\left(\frac{\partial^2 \gamma}{\partial E^2}\right)_{T,P,\mu} \qquad (1)$$

is not accessible through alternating current voltammetry,[21] which is powerful, otherwise.

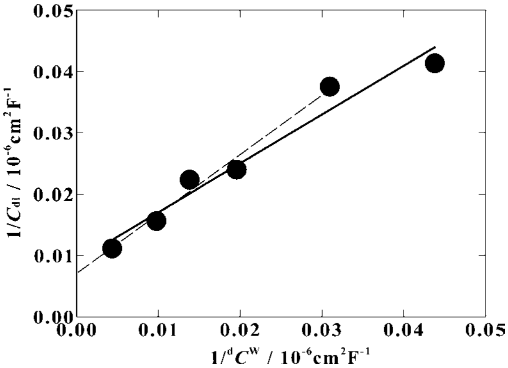

Figure 3. Plot of the measured double layer capacitance vs the reciprocal of the diffuse double layer capacitance calculated from the Gouy theory at the potential of zero charge at different concentrations of LiCl in the aqueous phase.

It has been well-established that the structure of the diffuse part of the double layer is well-described by the Gouy's model at least for a 1:1 electrolyte, except for the overestimation of the outer Helmholtz potential.[7,31,32] We calculated the double layer capacitance on the aqueous side of the interface, C_{dl}^{W}, using the Gouy's theory, and examined if the following simple model of the total double layer capacitance holds.

$$\frac{1}{C_{dl}} = \frac{1}{C_{dl}^{IL}} + \frac{1}{C_{dl}^{i}} + \frac{1}{C_{dl}^{W}} \tag{2}$$

where C_{dl}^{i} is the capacitance in the inner part of the double layer.

Figure 3 is the plot of the measured C_{dl} at the pzc for six concentrations of LiCl with the Gouy's model. The least-squares straight line is shown as the solid line. The slope of this curve is 0.8. However, if we neglect the point at the lowest LiCl concentration examined, 0.01 mol·dm^{-3}, where the error in the numerical secondary differentiation is the largest, the slope becomes unity (dashed line). From the intercept of this plot, the sum, $1/C_{dl}^{IL} + 1/C_{dl}^{i}$, is about 0.08 cm^2 μ·F^{-1}. Assuming that C_{dl}^{i} is large, we obtain 125 μF·cm^{-2} for the value of C_{dl}^{IL}. According to the Oldham's model of the electrical double layer at the IL–metal interface, the Gouy's model applies for the capacitance at the pzc. Then, $C_{dl}^{IL} = \varepsilon/\delta$, where ε is the permittivity of the IL and δ is the Debye length, defined by

$$\delta = \sqrt{\frac{RT\epsilon}{2F^2c}} \tag{3}$$

where R is the gas constant, T the absolute temperature, F the Faraday constant, and c the molar concentration of the electrolyte in the IL phase. In the present case, the density at 25 °C and the molecular weight of [TOMA$^+$][C$_4$C$_4$N$^-$], 1.281 g·cm^{-3} and 948.9 g·mol^{-1}, give $c = 1.350$ mol·dm^{-3}. From the value 125 μF·cm^{-2}, the relative dielectric constant in the diffuse part of the double layer in [TOMA$^+$][C$_4$C$_4$N$^-$] is calculated to be 17.4 at 25 °C. This value is comparable to 15.2 measured by microwave dielectric spectroscopy for an IL composed of smaller ions, 1-ethyl-3-methylimidazolium and trifluoromthylsulfonate.[33]

3.4. Relative Surface Excesses of Li$^+$ and Cl$^-$. To obtain the double layer structure at the potentials other than the pzc, we first calculated the relative surface excess of Li$^+$, $\Gamma_{Li^+/W}$, from the concentration dependence of γ at a given potential. The relative surface excess of Cl$^-$, $\Gamma_{Cl^-/W}$, was obtained from $\Gamma_{Li^+/W}$ using the condition of electroneutrality in W. The relative surface excess of ion i (i = Li$^+$ or Cl$^-$) is defined by

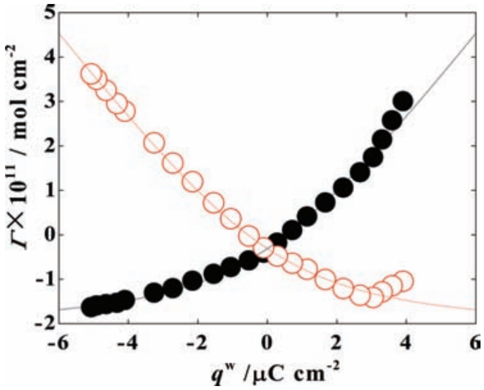

Figure 4. Relative surface excesses of Li$^+$ and Cl$^-$ as a function of excess surface charge density in the aqueous phase for 0.1 mol·dm^{-3} LiCl. Solid lines are calculated using Gouy's diffuse double layer theory and are corrected for the ion-free inner layer.

$$\Gamma_{i/W} = \Gamma_{i} - \frac{x_{LiCl}}{x_{W}}\Gamma_{W} \tag{4}$$

where Γ_i is the surface excess of i, x_{LiCl} and x_W are the mole fractions of LiCl and water, and Γ_W is the surface excess of water. Experimentally obtained relative surface excesses of Li$^+$ (filled circles) and Cl$^-$ (open circles) are plotted in Figure 4 at $a = 0.1$ as a function of the excess surface charge density in W, q^W, which was evaluated from the first derivative of the electrocapillary curve in Figure 1.

The solid lines are relative surface excesses of Li$^+$ and Cl$^-$ calculated using the Gouy's model and have been corrected for the second term of the right-hand side of eq 4 assuming that the density of water at the inner layer is the same as that of the bulk W phase and that the inner layer has the thickness of a monomolecular film of water. In the range, $q^W < 3$ μC·cm^{-2}, the experimental points are well-represented by the theoretical curves, which in fact means that the Gouy's model satisfactorily explains the adsorption behavior of Li$^+$ and Cl$^-$ not only at the pzc but at the charged interface. When $q^W \geq 3$ μC·cm^{-2}, the deviation from the Gouy's model is clearly seen in Figure 4. In this range of q^W, the IL side is negatively charged, and Li$^+$ is attracted to the interface. The deviation from the curve suggests the presence of a specific interaction of Li$^+$ with the IL, in particular, C$_4$C$_4$N$^-$. It is likely that C$_4$C$_4$N$^-$ ions are aligned at the interface with their hydrophilic sulfonyl moieties protruding into the W phase. These sulfonyl moieties can coordinate to Li$^+$ in the W side of the interface, as has been observed in the binding of C$_1$C$_1$N$^-$ ions in the IL phase.[34]

The specific adsorption or interaction of Li$^+$ in W and the IL is conditional; that is, it depends on the phase-boundary potential. We found previously that Li$^+$ does not undergo specific interaction with C$_1$C$_1$N$^-$ at the interface between [THA$^+$][C$_1$C$_1$N$^-$] and an aqueous LiCl solution.[14] Because of the narrower potential window at the [THA$^+$][C$_1$C$_1$N$^-$]|W interface, the experimental determination of the adsorption was possible only up to $q^W = 1$ μC·cm^{-2}, where the driving force for bringing Li$^+$ in W to the proximity of adsorbed C$_1$C$_1$N$^-$ ions is weaker.

Regarding the specific adsorption of Cl$^-$, we showed previously that Cl$^-$ is specifically adsorbed at the surface of the IL, *N*-tetradecylisoquinolinium bis(pentafluoroethanesulfonyl)amide, presumably by forming an interfacial ion pair.[15] The ion pairing takes place also in the bulk IL phase between Cl^- and *N*-tetradecylisoquinolinium, resulting in the narrowing of the potential window.[15] The absence of the specific adsorption of Cl^- at the $[\mathrm{TOMA}^+][\mathrm{C_4C_4N}^-]|\mathrm{W}$ interface in the present study shows that the specific interaction between Cl^- and TOMA^+ is negligible up to $q^{\mathrm{W}} = -5.5\ \mu\mathrm{C}\cdot\mathrm{cm}^{-2}$. This accords with the similar widths of the polarized window between $[\mathrm{TOMA}^+][\mathrm{TFPB}^-]$ and between $[\mathrm{C_{18}Iq}^+][\mathrm{TFPB}^-]$,[35] where $[\mathrm{TFPB}^-]$ and $[\mathrm{C_{18}Iq}^+]$ stand for tetrakis[3,5-bis(trifluoromethyl)phenyl]borate and *N*-octadecylisoquinolinium, respectively.

4. Conclusions

The importance and necessity of using thermodynamically reasonable electrocapillary curves have been demonstrated. In a system showing very slow relaxation at the fluid interface, on the order of minutes, the capillarity is an indispensable means to elucidate the thermodynamic properties of the interface. The analysis of the thermodynamically equilibrated electrocapillary curves has revealed that the specific adsorption of Li^+ and Cl^- ions at the $[\mathrm{TOMA}^+][\mathrm{C_4C_4N}^-]|\mathrm{W}$ interface is negligible, except at the positive end of the polarized potential window. The Gouy's model for the diffuse part of the double layer satisfactorily describes the surface excesses of Li^+ and Cl^- ions. These facts suggest that the ultraslow dynamics at the interface is not caused by the specific interaction of ions at the interface, but with the properties of the IL side of the interface.

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