

Wide Polarized Potential Windows at the Interface between Water and an Ionic Liquid, Tetraheptylammonium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

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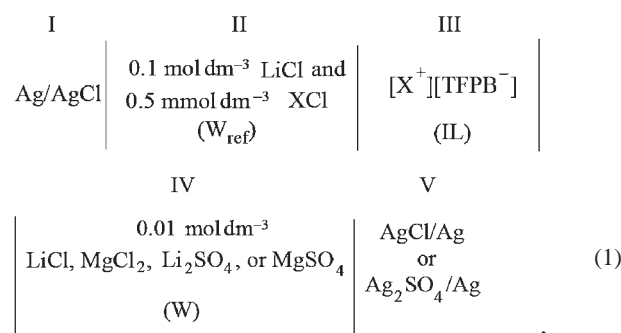
(Received June 25, 2007; CL-070680; E-mail: kakiuchi@scl.kyoto-u.ac.jp)

Wide polarized potential windows against interfacial ion transfer are available at the interface between a hydrophobic ionic liquid (IL), tetraheptylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($[\text{THpA}^+][\text{TFPB}^-]$) and an aqueous electrolyte solution (W) of MgSO_4 . The width of the potential window, 1.1 V at 60 °C, enables electrochemical studies of charge transfer at the IL/W interface for a variety of ions and redox couples.

When an ionic liquid (IL) is sufficiently hydrophobic, the interface between the IL and an aqueous electrolyte solution (W) can be electrochemically polarizable to allow us to use conventional electrochemical methods, such as voltammetry for studying equilibrium and nonequilibrium properties of charge transfer and other interfacial properties in IL–W two-phase systems.^{1–5} The wider the potential window, the larger the degree of freedom we have in choosing the subject of electrochemical studies at the IL/W interface. Using a very hydrophobic anion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB^-) as the IL constituting anion, the wide window of about 0.8 V at 56 °C was achieved.⁴ The transfer of moderately hydrophilic cations and hydrophobic anions such as choline⁴ and bis(trifluoromethylsulfonyl)imide⁴ ($\text{C}_1\text{C}_1\text{N}^-$), and the facilitated transfer of alkali metal ions across the IL/W interface were successfully studied at this interface.⁵ To detect the transfer of various cations and anions across the IL/W interface, an even wider polarized potential window is preferable. In this paper, we report a wide polarized potential window of 1.1 V at 60 °C at the micro interface between tetraheptylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($[\text{THpA}^+][\text{TFPB}^-]$) and an aqueous MgSO_4 solution. The window is 0.3 V wider than that at the *N*-octadecylisoquinolinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($[\text{C}_{18}\text{Iq}^+][\text{TFPB}^-]$)/W interface.⁴

N-tetradecylisoquinolinium chloride (C_{14}IqCl) was synthesized by mixing isoquinoline (Aldrich) and 1-chlorotetradecane (Aldrich) at 140–150 °C for 20 h. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) was synthesized using a procedure similar to that previously reported.⁶ $[\text{THpA}^+][\text{TFPB}^-]$ and *N*-tetradecylisoquinolinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($[\text{C}_{14}\text{Iq}^+][\text{TFPB}^-]$) were prepared following a procedure as described elsewhere.⁴ The melting point of $[\text{THpA}^+][\text{TFPB}^-]$ was 58–59 °C. $[\text{C}_{14}\text{Iq}^+][\text{TFPB}^-]$ was liquid at room temperature. The electrochemical cell in the present study is represented as Cell(1), where $\text{X} = \text{THpA}$ or C_{14}Iq . In this cell, the interface between phase II and III is electrochemically nonpolarized, and the III and IV is the polarized interface. The potential of the right-hand-side terminal of the cell with respect to the left is hereafter denoted as E . When W contains LiCl or MgCl_2 an Ag/AgCl electrode was employed as the reference electrode (V). In the case of Li_2SO_4 or MgSO_4

electrode was employed. The current due to the flow of cations from W to IL was taken to be positive. Cyclic voltammograms were recorded at the micro IL/W interface formed at the tip of a glass pipette.⁴ The phase IV (W) was filled in a micropipette⁴ whose inner diameter at the tip was $1 \pm 0.3 \mu\text{m}$. The phase II (W_{ref}) was in a glass tube, whose inner diameter was 0.5 mm. For ion-transfer studies, tetrabutylammonium chloride (TBACl), NaClO_4 , and NaSCN were dissolved in W, and the concentrations were 1 mmol dm^{-3} . All voltammetric measurements were made at 60 °C.



A cyclic voltammogram at the interface between $[\text{C}_{14}\text{Iq}^+][\text{TFPB}^-]$ and an aqueous $0.01 \text{ mol dm}^{-3} \text{ LiCl}$ solution is shown in Figure 1 (curve a). The width of the polarized poten-

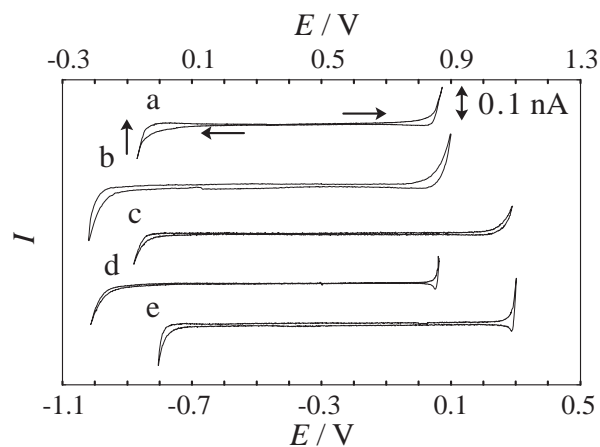


Figure 1. Cyclic voltammograms at the microinterface between $[\text{C}_{14}\text{Iq}^+][\text{TFPB}^-]$ and an aqueous $0.01 \text{ mol dm}^{-3} \text{ LiCl}$ solution (a), and between $[\text{THpA}^+][\text{TFPB}^-]$ and an aqueous solution of $0.01 \text{ mol dm}^{-3} \text{ LiCl}$ (b), Li_2SO_4 (c), MgCl_2 (d), or MgSO_4 (e) at 60 °C. The inner diameter of the micropipette tip: $1 \mu\text{m}$. The voltage scan was made from the middle of the polarized potential window to the positive at the scan rate of 0.02 V s^{-1} .

tial window was 0.85 V, which is comparable to those at $[\text{C}_{18}\text{Iq}^+][\text{TFPB}^-]/\text{W}$ and trioctylmethylammonium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate ($[\text{TOMA}^+][\text{TFPB}^-]/\text{W}$) interfaces (0.8 V).⁴ In fact, C_{18}Iq^+ and TOMA^+ are much more hydrophobic than C_{14}Iq^+ .⁷ The similarity in the width of the polarized potential windows suggests that the potential at the negative ends is independent of the hydrophobicity of the anions constituting the ILs and is determined by the transfer of Cl^- from W to IL. Figure 1b shows a cyclic voltammogram at the interface between $[\text{THpA}^+][\text{TFPB}^-]$ and an aqueous 0.01 mol dm⁻³ LiCl solution. The width of the polarized potential window was 0.95 V, which is 0.1 V wider than that at $[\text{C}_{14}\text{Iq}^+][\text{TFPB}^-]/\text{W}$ interface. This difference of the polarized potential window is similar to that between $[\text{THpA}^+][\text{C}_2\text{C}_2\text{N}^-]/\text{W}$ and $[\text{C}_{14}\text{Iq}^+][\text{C}_2\text{C}_2\text{N}^-]/\text{W}$ interfaces⁸ and indicates a stronger affinity of Cl^- with C_{14}Iq^+ , C_{18}Iq^+ , or TOMA^+ than that with THpA^+ in these IL bulks.^{4,8}

Increasing the concentration of LiCl in W decreased the polarized potential window at both positive and negative ends at the $[\text{THpA}^+][\text{TFPB}^-]/\text{W}$ interface (data are not shown). This fact shows that the positive and negative ends are limited by the transfer of Li^+ and Cl^- from W to the IL, respectively. It is then possible to extend the polarized potential window by using more hydrophilic ions in W. Curves c, d, and e in Figure 1 show cyclic voltammograms at the interface between $[\text{THpA}^+][\text{TFPB}^-]$ and aqueous 0.01 mol dm⁻³ Li_2SO_4 , MgCl_2 , and MgSO_4 solutions, respectively. The widths of the polarized potential windows are 1.0 (curve c), 1.05 (curve d), and 1.1 (curve e) V. The positive currents more sharply increased when the aqueous solution contains Mg^{2+} (Figure 1 curves d and e), whereas the negative currents more sharply decreased when SO_4^{2-} exists in W (Figure 1 curves c and e). It is likely, therefore, that the positive and negative ends of the windows are limited by the transfer of these ions in W from W to IL.

Figure 2 shows cyclic voltammograms for the transfer of tetrabutylammonium (TBA^+ , curve a), ClO_4^- (curve b), and SCN^- (curve c) across the $[\text{THpA}^+][\text{TFPB}^-]/\text{W}$ interface at the scan rate of 0.02 V s⁻¹. Plateau currents were observed for all curves in Figure 2. Such steady-state voltammograms have also been found at $[\text{C}_{18}\text{Iq}^+][\text{TFPB}^-]/\text{W}$ ⁴ and tetrahexylammonium bis(trifluoromethylsulfonyl)imide ($[\text{THxA}^+][\text{C}_1\text{C}_1\text{N}^-]/\text{W}$)⁹ interfaces and have been ascribed to the tapered shape of the micropipette.^{4,9} We evaluated the half-wave potentials, $E_{1/2}$, at the scan rate of 0.02 V s⁻¹ for the transfer of TBA^+ , ClO_4^- , and SCN^- across the interface, which are -0.70, -0.75, and -0.81 V, respectively. The values of $E_{1/2}$ for SCN^- and ClO_4^- differ by 0.06 V, which is comparable to the value of 0.1 V at the nitrobenzene/W interface at 25 °C.¹⁰ The transfer of TBA^+ and ClO_4^- has been found at $[\text{THxA}^+][\text{C}_1\text{C}_1\text{N}^-]/\text{W}$ interface⁹ and that of SCN^- at tetraoctylammonium 2,4,6-trinitrophenolate/W interface at 25 °C.² The transfer of these moderately hydrophobic cation and moderately hydrophilic anions were successfully observed when the ILs composed of the hydrophobic symmetric quaternary ammonium, such as THpA^+ .

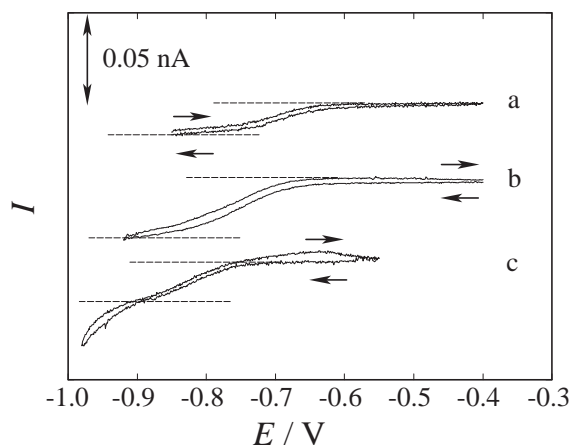


Figure 2. Cyclic voltammograms for the ion transfer of (a) ClO_4^- , (b) TBA^+ , and (c) SCN^- from W to IL side at the interface between $[\text{THpA}^+][\text{TFPB}^-]$ and an aqueous 0.01 mol dm⁻³ LiCl solution at 60 °C. The concentrations of the anion in W were 1 mmol dm⁻³, and the scan rate was 0.02 V s⁻¹. The dashed lines show the level of zero currents and limiting currents.

In conclusion, a wider polarized potential window of 0.95 V at the IL/W interface has been achieved by suppressing the facilitated transfer of Cl^- . By using more hydrophilic ions for supporting electrolyte in W, such as Mg^{2+} and SO_4^{2-} , the widest polarized potential window over 1 V has been observed. This wide potential window enables us to observe the transfer of the moderately hydrophilic SCN^- and ClO_4^- and hydrophobic TBA^+ across the IL/W interface and provides a voltammetric means for studying the ion transfer for a range of anions and cations at the same interface and also the electron transfer for a variety of redox couples.

References

- 1 T. Kakiuchi, N. Tsujioka, *Electrochem. Commun.* **2003**, 5, 253.
- 2 H. Katano, H. Tatsumi, *Anal. Sci.* **2003**, 19, 651.
- 3 R. Ishimatsu, F. Shigematsu, T. Hakuto, N. Nishi, T. Kakiuchi, *Langmuir* **2007**, 23, 925.
- 4 N. Nishi, S. Imakura, T. Kakiuchi, *Anal. Chem.* **2006**, 78, 2726.
- 5 N. Nishi, H. Murakami, S. Imakura, T. Kakiuchi, *Anal. Chem.* **2006**, 78, 5805.
- 6 H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1984**, 57, 2600.
- 7 S. Tanaka, Y. Kitazumi, A. Suzuki, Y. Matsuoka, N. Nishi, T. Kakiuchi, in preparation.
- 8 R. Ishimatsu, N. Nishi, T. Kakiuchi, *Langmuir* **2007**, 23, 7608.
- 9 N. Tsujioka, S. Imakura, N. Nishi, T. Kakiuchi, *Anal. Sci.* **2006**, 22, 667.
- 10 B. Hundhammer, S. Wilke, *J. Electroanal. Chem.* **1989**, 266, 133.