

A wide electrochemical window at the interface between water and a hydrophobic room-temperature ionic liquid of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

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Ionic liquids composed of a hydrophobic anion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB⁻), and various aromatic and aliphatic ammonium, have been prepared. TFPB salts of *N*-octadecylisoquinolinium (C₁₈Iq⁺) and trioctylmethyammonium (TOMA⁺) show low melting points of 31 and 36°C, respectively, whereas TFPB-based ionic liquids of 1-alkyl-3-methylimidazolium with the alkyl chain length of 5–12 show melting points lower than 90°C. The [C₁₈Iq][TFPB]|water(W) and [TOMA][TFPB]|W interfaces have the polarized potential window (ppw) of 0.8 V at 56°C, which is twice as wide as the ppw at the interface between W and a room-temperature ionic liquids of bis(perfluoroalkylsulfonyl)imide so far reported. The extension of the ppw by more than 0.4 V to the positive direction enables voltammetric measurements of the ion transfer of relatively hydrophobic anions such as bis(trifluoromethylsulfonyl)imide and bis(pentafluoroethylsulfonyl)imide, and of hydrophilic cations such as tetraethylammonium and acetylcholine ions.

Introduction

It has been demonstrated recently that the interface between a hydrophobic room-temperature ionic liquid (RTIL) and an aqueous electrolyte solution can be electrochemically polarizable.¹⁻⁶ When the polarized potential window (ppw) is wide enough, e.g., 200 mV or so, the transfer of ions across the RTIL|water(W) interface can be studied voltammetrically.^{2, 3} The widest ppw so far reported is 0.4 V and ions voltammetrically measurable in the ppw are limited to moderately hydrophobic cations and moderately hydrophilic anions such as 1-methyl-3-octylimidazolium (C_8mim^+)² and SCN^- .³ The positive end of the ppw so far reported is limited by the dissolution of the moderately hydrophobic anions constituting the RTIL, such as bis(perfluoroalkylsulfonyl)imide, into W.^{1, 2, 4, 5} To study the transfer of more hydrophobic anions or hydrophilic cations across the RTIL|W interfaces, RTILs of more hydrophobic anions are required to extend the potential window at the RTIL|W interfaces to the positive direction where the potentials of the W phase is more positive with respect to that of the RTIL phase. RTIL-W two-phase systems with a wider ppw are desirable for studies in view of physical chemistry, such as the structure of the electrical double layer,⁷ the kinetics of interfacial charge transfer,⁸ and also in view of analytical chemistry, such as, liquid-liquid extraction of ions⁹⁻¹¹ and ion-selective electrodes with nonvolatile membrane phases.

In the present paper, we report RTILs composed of a hydrophobic anion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($TFPB^-$), and various aromatic and aliphatic ammonium. $TFPB^-$ has been known as an anion with strong hydrophobicity,¹² little nucleophilicity¹³ and high chemical stability.¹⁴ A few attempts have been made to prepare ionic liquids composed of $TFPB^-$ and C_2mim^+ ¹⁵ and C_4mim^+ .^{16, 17} The melting point (T_m) of $[C_4mim][TFPB]$ was 100~110°C,^{16, 17} and T_m of $[C_2mim][TFPB]$ is estimated to be higher than that of $[C_4mim][TFPB]$ judging from the tendency of T_m of a series of $[C_nmim]BF_4$ ($n=0-18$).¹⁸ To apply hydrophobic $TFPB^-$ to RTIL for RTIL-W two-phase systems, $TFPB^-$ -based ionic liquids with much lower T_m are desirable. Two $TFPB^-$ -based RTILs we describe in this paper have T_m lower than 40°C, and the wide ppw of 0.8 V at the RTIL|W interfaces with extremely low solubility in W. These features make these RTILs suitable

to applications of the RTIL-W two-phase systems for analytical chemistry as well as physical chemistry.

Experimental

NaTFPB was synthesized using a procedure similar to that previously reported by Nishida et al.¹⁴ from 3,5-bis(trifluoromethyl)bromobenzene and sodium tetrafluoroborate. Chloride or bromide salts of 1-alkyl-3-methylimidazolium ($C_n\text{mim}^+$, $n=2,4,5,6,7,8,10$, and 12) and *N*-alkylisoquinolinium ($C_n\text{Iq}^+$, $n=12$ and 18) were synthesized as follows.¹⁹ An equimolar mixture of 1-bromoalkane or 1-chloroalkane, and *N*-methylimidazole or isoquinoline was kept at 120°C for several hours. The reaction product was washed with ethylacetate under reflux for three times. Trioctylmethylammonium chloride (TOMACl) and *N*-dodecylpyridinium chloride ($C_{12}\text{PyCl}$) were purchased from Dojindo Laboratories and Tokyo Chemical Industry Co., Ltd, respectively. An aqueous solution of hydrogen bis(pentafluoroethylsulfonyl)imide ($\text{HC}_2\text{F}_5\text{SO}_2\text{N}$), was purchased from Central Glass Co., Ltd. All other chemicals purchased were used as received.

TFPB-based ionic liquids were prepared by mixing a methanol solution of NaTFPB with that of an equimolar amount of RX , where R^+ denotes a hydrophobic cation described above and X^- a chloride or bromide anion. Methanol was removed using a rotary evaporator. To remove NaX from the viscous mixture of ionic liquids, RTFPB, and NaX , the mixture was repeatedly washed with deionized water until X^- was not detected by adding an aqueous AgNO_3 solution in the washing. The residual water and methanol in the ionic liquid were then evaporated using a vacuum pump at the temperature above T_m of each ionic liquid. $[\text{C}_{18}\text{Iq}][\text{C}_2\text{F}_5\text{SO}_2\text{N}]$, a hydrophobic RTIL,²⁰ was similarly prepared. T_m of RTILs were measured using a differential scanning calorimeter (Pyris Diamond DSC, Perkin-Elmer) or a micro melting-point apparatus (MP-S3, Yanako).

Density (d), viscosity (η), conductivity (κ) and solubility of water in the water-saturated RTILs ($S_{w/R}$) were measured with a pycnometer, an oscillation type viscometer (VM-10A-M, CBC Materials), a conductometer (CM-117, Kyoto Electronics), and a Karl Fischer moisturemeter (CA-21, Dia Chemical), respectively. The solubility of

RTILs in water ($S_{R/W}$) was measured from UV absorbance of water saturated with the RTILs.

Cyclic voltammograms (CVs) were recorded to measure the ion transfer across the RTIL|W interface. The interface was formed at the end of a micropipette with the inner diameter of several micrometers (typically 2 μm). A borosilicate glass capillary (o.d.: 1 mm, i.d.: 0.5 mm) was pulled using a micropipette puller with a heat coil (PC-10, Narishige) to prepare a micropipette having desired shape and radius. The two-electrode electrochemical cell employed is represented as:

I	II	III	IV	V	VI	VII
Ag	AgCl	100 mM Li_2SO_4 1 mM CCl (W_{ref})	[C][TFPB] (RTIL)	100 mM LiCl (W)	AgCl	Ag

where mM denotes mmol dm^{-3} and C^+ denotes C_{18}Iq^+ or TOMA^+ . Ions for ion transfer measurement were dissolved in W as a salt of hydrophilic counter ions. The scheme of the cell for cyclic voltammetry is shown in Figure 1. The RTIL was filled in a vial of 10 mm inner diameter. The vial was set in a cell with a water jacket. The aqueous solution (W) and the reference aqueous solution (W_{ref}) were filled in the micropipette and a glass tube (o.d.: 1 mm, i.d.: 0.5 mm), respectively. An Ag/AgCl electrode was inserted in the micropipette. Similarly, another Ag/AgCl was inserted in the glass tube. The micropipette and the glass tube were inserted in the RTIL in the vial. The polarized interface between the IV and V phases was formed at the tip of the micropipette and the nonpolarized interface between the III and IV phases was formed at the tip of the glass tube. The area of the polarized interface is estimated to be at least 3 orders of magnitude smaller than that of the nonpolarized. The potential applied to the Ag/AgCl electrode on the right-hand side with respect to the left is denoted as E . The current (I) corresponding to the flow of a positive charge from W to RTIL is taken to be positive. IR drop was not compensated for. The resistance calculated from conductivity of the RTIL and geometry outside the micropipette was ca. 10 $\text{M}\Omega$. As the current was in the sub-nA level, the IR drop was estimated to be 10 mV at most. The temperature during the CV measurements

was maintained at $56\pm1^\circ\text{C}$ by circulating water through the jacket of the cell.

Results and Discussion

Physicochemical properties of the water-saturated RTILs

The T_m values for various TFPB-based ionic liquids are listed in Table 1. T_m for $[\text{C}_n\text{mim}][\text{TFPB}]$ decreases from 134°C to 82°C with increasing n from 2 to 5. This decrease is ascribed to the weakened electrostatic interaction between cations and anions with increasing the size of the cations. On the other hand, T_m from $n = 5$ to 12 does not change drastically. This is likely to be due to the combination of several factors: the decrease in the electrostatic interaction, the increase in the van der Waals interaction, and the decrease in the symmetry of the structure of cations with increasing n . The chain-length dependence of T_m is similar to that for a series of $[\text{C}_n\text{mim}][\text{BF}_4]$.¹⁸

The substitution of the 1-methylimidazolium moiety of $\text{C}_{12}\text{mim}^+$ to other aromatic one resulted in almost the same T_m ; the T_m values of $[\text{C}_{12}\text{Py}][\text{TFPB}]$ (64°C) and of $[\text{C}_{12}\text{Iq}][\text{TFPB}]$ (72°C) were similar to that of $[\text{C}_{12}\text{mim}][\text{TFPB}]$ (72°C). Elongation of the alkyl chain of C_{12}Iq^+ to C_{18}Iq^+ decreased the T_m value from 72°C to 31°C . This decrease is in contrast to the dependence of $[\text{C}_n\text{mim}]\text{BF}_4$ on n , where the minimum value of T_m is at $n = 5$.¹⁸ The lower T_m of $[\text{C}_{18}\text{mim}][\text{TFPB}]$ than that of $[\text{C}_{12}\text{mim}][\text{TFPB}]$ may result from the structure of C_nIq^+ with the large and planar isoquinoline ring. The combination of TFPB^- and TOMA^+ , an aliphatic cation with low symmetry, also led to ionic liquids with low T_m of 36°C . Among the TFPB-based ionic liquids prepared, $[\text{C}_{18}\text{Iq}][\text{TFPB}]$ and $[\text{TOMA}][\text{TFPB}]$ were used for the measurements of the physicochemical properties and for the electrochemical measurements at the RTIL|W interface because of the low T_m values.

The physicochemical properties for $[\text{C}_{18}\text{Iq}][\text{TFPB}]$ and $[\text{TOMA}][\text{TFPB}]$ are listed in Table 2. The η values at 56°C , 0.557 and 0.470 Pa s for $[\text{C}_{18}\text{Iq}][\text{TFPB}]$ and $[\text{TOMA}][\text{TFPB}]$, respectively, are two or three orders of magnitude greater than those for molecular liquids with low molecular weights, and are significantly greater than that for tetrahexylammo-

nium bis(trifluoromethylsulfonyl)imide ([THxA][C₁C₁N]), one of hydrophobic RTILs, saturated with water, 0.130 Pa s at 50°C. Correspondingly, the κ values at 56°C, 87 and 130 $\mu\text{S cm}^{-1}$, are smaller than that for [THxA][C₁C₁N] saturated with water, 470 $\mu\text{S cm}^{-1}$ at 50°C. The $S_{\text{W/R}}$ values at 56°C, 0.31 and 0.20 wt%, are similar to that for [THxA][C₁C₁N] saturated with water at 25°C, 0.30 wt%. The $S_{\text{R/W}}$ values at 56°C, 4×10^{-6} and 1×10^{-6} M, is three orders of magnitude smaller than that for [C₈mim][C₁C₁N], 1.4×10^{-3} M (25°C)²¹ and comparable to that for [THxA][C₁C₁N], 7×10^{-6} M (25°C).⁶ The low solubility of [C₁₈Iq][TFPB] and [TOMA][TFPB] in W is highly desirable in view of environmental concerns in using RTIL-W two-phase systems in a large scale.

Polarized potential window of the interface between W and TFPB-based RTILs

CVs at the [C₁₈Iq][TFPB]/W and [TOMA][TFPB]/W interfaces are shown in Figure 2a and 2b, respectively. The width of the ppw was 0.8 V for both [C₁₈Iq][TFPB] and [TOMA][TFPB]. This is much greater than 0.45 V, the width of the widest ppw so far reported at the RTIL|W interfaces.⁴ In Figure 2c is shown a CV at the interface between water and an imide-based RTIL, [C₁₈Iq][C₂C₂N]. The ppw at the [C₁₈Iq][C₂C₂N]/W interface is 0.3 V. The negative end of the ppw for [C₁₈Iq][TFPB] is located at a potential similar to that for [C₁₈Iq][C₂C₂N], indicating that the negative end is limited by the transfer of Cl⁻ from W to RTIL. This was confirmed by the fact that the current at the negative end of the ppw was proportional to the concentration of Cl⁻ in W (results not shown).

The positive end of the potential window for [C₁₈Iq][TFPB] is 0.5 V more positive than that for [C₁₈Iq][C₂C₂N]. This positive shift is ascribed to the greater hydrophobicity of TFPB⁻ than that of C₂C₂N⁻. The CVs recorded with changing the concentration of LiCl in W revealed that the ion limiting the positive end for [C₁₈Iq][TFPB]/W interface is not TFPB⁻ but Li⁺, while the ion for the [C₁₈Iq][C₂C₂N]/W interface is C₂C₂N⁻. The hydrophobicity of TFPB⁻ is thus stronger than the hydrophilicity of Li⁺, i.e., the standard ion-transfer potential of TFPB⁻ at the RTIL|W interface, $\Delta_{\text{R}}^{\text{W}}\phi_{\text{TFPB}}^0$, is more positive than that of Li⁺, $\Delta_{\text{R}}^{\text{W}}\phi_{\text{Li}}^0$. The similar tendency is known in CVs at the interface between an aqueous solution of LiCl and 1,2-dichloroethane (DCE) containing TFPB-based salts; the transfer of Li⁺ across the interface was observed at the positive end of the ppw.²²

The difference in the ppw at $[C_{18}Iq][TFPB]/W$ interface and that of $[C_{18}Iq][C_2C_2N]/W$ interface, 0.5 V, roughly agrees with the difference in the standard ion-transfer potentials for the two ions at the DCE/W interface, 0.44 V (0.15 V for $C_2C_2N^{-4}$ and 0.59 V for Li^{+23}). The ppw at the $[TOMA][TFPB]/W$ interface was also limited not by the transfer of ions constituting **RTILs**, but by Li^{+} and Cl^{-} , as the same width of the ppw was observed for $[C_{18}Iq][TFPB]$ and $[TOMA][TFPB]$.

When the dissolution of ions constituting the **RTIL** determines the width of the ppw, the solubility of the **RTIL** in W can be estimated from the width of the ppw at the **RTIL**/W interface.^{2, 6} The solubility product of **RTIL** in W, K_s^W , is related to the difference in the standard ion-transfer potentials for the anion and the cation constituting the **RTIL**, $\Delta_R^W \phi_{A-}^0 - \Delta_R^W \phi_{C+}^0$, through:²

$$\Delta_R^W \phi_{A-}^0 - \Delta_R^W \phi_{C+}^0 = -\frac{RT}{F} \ln K_s^W \quad (1)$$

We estimated the solubility of $[C_{18}Iq][TFPB]$ or $[TOMA][TFPB]$ in W at 56°C to be less than 10^{-6} M, by assuming that the difference, $\Delta_R^W \phi_{TFPB}^0 - \Delta_R^W \phi_{C_{18}Iq}^0$, is greater than 0.8 V because the ppw is limited not by $C_{18}Iq^{+}$ and $TFPB^{-}$ but by Li^{+} and Cl^{-} . The estimated solubility is one order of magnitude smaller than that measured from UV absorbance. This difference is likely to be caused by micelle formation in water. The critical micelle concentration in aqueous solution of chloride salt of octadecyldimethylbenzylammonium cation, which has similar hydrophobicity and surface activity to $C_{18}Iq^{+}$, is 7.1×10^{-6} M at 25°C.²⁴

Voltammetry of the transfer of moderately hydrophilic cations and moderately hydrophobic anions

Within the wide potential window at the **RTIL**/W interfaces, the transfer of moderately hydrophilic cations and moderately hydrophobic anions across the interface becomes measurable voltammetrically. As an example, the CVs for the transfer of tetraethylammonium cation (TEA^{+}) across the $[C_{18}Iq][TFPB]/W$ interface are shown in Figure 3. In the CVs, the positive current flows at the potentials more positive than 0.1 V, which is due to the transfer of TEA^{+} from W to **RTIL**. Comparing these CVs with the CV showing

the potential window at the $[C_{18}Iq][C_2C_2N]|W$ interface (Figure 2c), one may recognize that it is not possible to observe the transfer of TEA^+ and other more hydrophilic cations across the $[C_{18}Iq][C_2C_2N]|W$ interface.

The shape of the CVs in Figure 3 depends on the scan rate; at low scan rates ($< 20 \text{ mV s}^{-1}$) a plateau current was observed, while at high scan rates ($> 200 \text{ mV s}^{-1}$) peaks appeared in both forward and reverse scans. The dependence reflects the geometry inside the micropipette in the forward scan and outside the micropipette in the reverse scan. Previous studies of ion transfer across the DCE|W interface, where ions transferable across the interface were dissolved in water inside micropipettes, show that the shape of CVs in the forward scan depends on the tip diameter: peak current controlled by linear diffusion for the diameter of tens micrometers,²⁵ $13 \mu\text{m}$ ²⁶ and $8 \mu\text{m}$,²⁷ and steady-state current controlled by spherical diffusion for the diameter of $2 \mu\text{m}$ ²⁶ and 80 nm .²⁸ Such a dependence is reasonable because the geometry inside a micropipette with a large tip diameter can be regarded as cylindrical and that with a small tip diameter as conical. The inner diameter of the tip of micropipettes used in the present study, $2\text{-}3 \mu\text{m}$, is in-between those for the two cases and thus peaks appeared only at high scan rates in the forward scan, similar to the case at the DCE|W interface with $1 \mu\text{m}$ diameter.²⁸ In the reverse scan, no peak appeared in the case of DCE because of the spherical diffusion in DCE outside the pipettes.^{25, 28} In contrast, the high viscosity (see Table 2) of the TFPB-based RTILs makes the mass transfer being cylindrical rather than spherical at a high scan rate, leading to the peak current in the reverse scan at higher scan rates.

(This paragraph was Modified) The plot of $\ln\{I/(I_L - I)\}$ vs. E (where I_L is the limiting current appearing as plateau) of the forward scan of the CV at 20 mV s^{-1} is shown in the inset of Figure 3. The slope of the regression line for the plot was 32 V^{-1} . This value is slightly smaller than the theoretical value for the reversible transfer of a monovalent ion at 56°C , 35.3 V^{-1} . This deviation seems to be attributable to experimental factors such as the conical shape of the micropipette, IR drop and charging current. More quantitative analysis of the voltammograms for ion transfer across the liquid-liquid interface formed at the tip of a micropipette will be published elsewhere.²⁹

We evaluated the half-wave potentials ($E_{1/2}$) for ion transfer across the $[C_{18}Iq][TFPB]||W$ interface for several ions (Table 3) from CVs recorded at lower scan rates. For comparison, the standard ion-transfer potentials across oil(O) $||W$ interface of ion i , $\Delta_O^W \phi_i^0$, for 1,2-dichloroethane (DCE) and nitrobenzene (NB) are also shown in Table 3 and the correlation of $E_{1/2}$ with $\Delta_{DCE}^W \phi_i^0$ and $\Delta_{NB}^W \phi_i^0$ are shown in Figure 4. $E_{1/2}$ for the $[C_{18}Iq][TFPB]||W$ interface shows the same tendency as $\Delta_{DCE}^W \phi_i^0$ and $\Delta_{NB}^W \phi_i^0$; the $E_{1/2}$ values are more positive for more hydrophilic cations and more hydrophobic anions. For cations, we obtained linear regression lines between $E_{1/2}$ and $\Delta_O^W \phi_i^0$ with the slopes of 1.3 (DCE) and 1.6 (NB), respectively. The slope greater than unity for both regression lines suggests the lower polarity of $[C_{18}Iq][TFPB]$ than these organic solvents. It has been reported that the polarity of $[THxA][C_1C_1N]$ is in-between those of NB and DCE,⁴ and that of series of tetraalkylammonium bis(2-ethylhexyl)sulfosuccinates (BEHSS) is higher than that of DCE.⁶ Since $TFPB^-$ is much more hydrophobic than $C_1C_1N^-$ and $BEHSS^-$, it is likely that $[C_{18}Iq][TFPB]$ has lower polarity than $[THxA][C_1C_1N]$ and the BEHSS-based RTILs.

The plots in Figure 4 for anions deviate from the regression lines for cations to the negative direction of $E_{1/2}$ more than 0.2 V for NB and than 0.1 V for DCE. One of the reasons for the deviation is the shift of $E_{1/2}$ from the formal potentials for ion transfer, $E_i^{0'}$, which is equal to $\Delta_R^W \phi_i^{0'} + E_{ref}$, where E_{ref} is the contribution from the potential difference across the other interfaces than the polarized interface. The difference between $E_{1/2}$ and $E_i^{0'}$ depends on the mode of mass transfer in both phases and may generally be represented as,

$$E_{1/2} - E_i^{0'} = \frac{RT}{z_i F} \ln \left(\frac{D_i^W}{D_i^R} \right)^\alpha \quad (2)$$

where R is the gas constant, T temperature, z_i the charge on i in signed units of electronic charge, F the Faraday constant, D_i^W and D_i^R the diffusion coefficients of i in W and RTIL, respectively, and α a constant. The value of α is 0.5 for the semi-infinite linear mass transfer and is 1.0 for the spherical one. The shift in the present case is expected to be between that in the former case and that in the latter. The magnitude of the shift is not negligible because there is a great difference in D_i^W and D_i^R due to high viscosity of

[C₁₈Iq][TFPB]. The ratio of the diffusion coefficients, D_i^W/D_i^R , was assumed to be 1100, which was estimated from the Walden rule, $D_i^W\eta^W = D_i^R\eta^R$, and the η values at 56°C (560 mPa s for [C₁₈Iq][TFPB] and 0.496 mPa s for W). The magnitude of the shift should be somewhere between 0.1 (for the linear case) and 0.2 V (for the spherical case) and is positive for cations and negative for anions. The opposite shifts for cations and anions result in the deviation of the plots for anions from the regression lines for cations to the negative direction of $E_{1/2}$ shown in Figure 4. Other possible factors such as the difference in the environment around the ions in organic solvents and those in RTIL may also be important. We plan to examine the difference in environments surrounding ions more quantitatively after analyzing CVs using digital simulation taking account of the actual shape of the tip.²⁹

Conclusions

A wide polarized potential window at the range of 0.8 V is available at the interfaces between water and the TFPB-based RTILs. Within this wide ppw, it is possible to measure the transfer of a variety of hydrophilic and hydrophobic ions across the interface driven by the phase-boundary potential. Such a wide potential window available at the RTIL|W interfaces will enable us to measure partition properties of ionic species in the RTIL-W two-phase systems. Liquid-liquid extraction of hydrophilic metal cations from aqueous solutions using hydrophobic ligands as well as potentiometric and amperometric sensing of ions are immediate applications of this interface having the wide ppw. Another attractive feature of the RTILs prepared is the extremely low solubility in W despite the high polarity of the RTILs. This seems to be of great advantage, combined with nonvolatility, for the applications of RTIL-W two-phase systems.

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Table 1. Melting points for TFPB-based ionic liquids.

Cation	$T_m / ^\circ\text{C}$
C ₂ mim	134
C ₄ mim	104 (102-104 ^a , 109 ^b)
C ₅ mim	82
C ₆ mim	82
C ₇ mim	69
C ₈ mim	75
C ₁₀ mim	85
C ₁₂ mim	72
C ₁₂ Py	64
C ₁₂ Iq	72 (−20 ^c)
C ₁₈ Iq	31 (−25 ^c)
TOMA	36 (−36 ^c)

^a Reference 16.

^b Reference 17.

^c Glass transition points.

Table 2. Physicochemical properties (density (d), viscosity (η), conductivity (κ), solubility of the **RTILs** in water ($S_{R/W}$) and solubility of water in the **RTILs** ($S_{W/R}$)) for [C₁₈Iq][TFPB] and [TOMA][TFPB] saturated with water.

RTIL	FW ^a	d (g cm ⁻³)	η (Pa s)	κ (μ S cm ⁻¹)	$S_{R/W}$ (M)	$S_{W/R}$ (wt%)
[C ₁₈ Iq][TFPB]	1245.9	1.302 ^b	0.557 ^c	87 ^c	4 $\times$ 10 ⁻⁵ ^c	0.31 ^c (0.22 ^{c,d})
[TOMA][TFPB]	1231.9	1.228 ^b	0.470 ^c	130 ^c	1 $\times$ 10 ⁻⁵ ^c	0.20 ^c (0.14 ^{c,d})

^a Formula weight. ^b At 25°C. ^c At 56°C. ^d Molar ratio of water to **RTIL** in the **RTIL** phase.

Table 3. Half-wave potentials at the [C₁₈Iq][TFPB]/W interface at 56°C and the apparent standard ion-transfer potentials at the DCE/W interface and at the NB/W interface at 25°C.

Ion ^a	$E_{1/2}$ / V	$\Delta_{\text{DCE}}^{\text{W}} \phi_{\text{i}}^0$ / V	$\Delta_{\text{NB}}^{\text{W}} \phi_{\text{i}}^0$ / V
TMA ⁺	0.38	0.135 ^b	0.035 ^d
TEA ⁺	0.18	−0.011 ^b	−0.059 ^d
TPrA ⁺	0.01	−0.139 ^b	−0.170 ^e
Ch ⁺	0.44	0.202 ^b	0.117 ^f
Ach ⁺	0.40	0.112 ^b	0.049 ^f
C ₁ C ₁ N [−]	0.17	0.093 ^c	0.114 ^g
C ₂ C ₂ N [−]	0.27	0.154 ^c	0.187 ^g

^a TMA⁺: tetramethylammonium, TPrA⁺: tetrapropylammonium, Ch⁺: choline, Ach⁺: acetylcholine. ^b Calculated from mid-point potentials in reference 30 using the same way in reference 4. ^c Reference 4. ^d Reference 31. ^e Reference 32. ^f Reference 33 (at 22°C). ^g Measured using cyclic voltammetry.

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Figure captions

Figure 1. Scheme of the cell for cyclic voltammetry at the RTIL|W interfaces.

Figure 2. Cyclic voltammograms at the interfaces between water and (a)[C₁₈Iq][TFPB], (b)[TOMA][TFPB] and (c)[C₁₈Iq][C₂C₂N]. Scan rate: 200 mV/s. Temperature: 56°C. Inner diameters of the micropipette tip: 3 μm for (a) and (c) and 2 μm for (b).

Figure 3. Cyclic voltammograms at the interfaces between water and [C₁₈Iq][TFPB] in the presence of 10 mM TEA⁺ in W at 200(1), 100(2), 50(3), and 20(4) mV s⁻¹. (Inset) The log plot of the forward scan of the voltammogram at 20 mV s⁻¹ and the linear regression line of the plot. Temperature: 56°C. Inner diameter of the micropipette tip: 2 μm.

Figure 4. Correlation of the half-wave potentials for ion transfer across the [C₁₈Iq][TFPB]|W interface with the standard ion-transfer potentials across NB|W (solid circle for cations and solid square for anions) and DCE|W (open circle for cations and open circle for anions) interfaces. Solid and Dotted lines are linear fit to the plots of cations for NB|W and DCE|W interfaces, respectively.

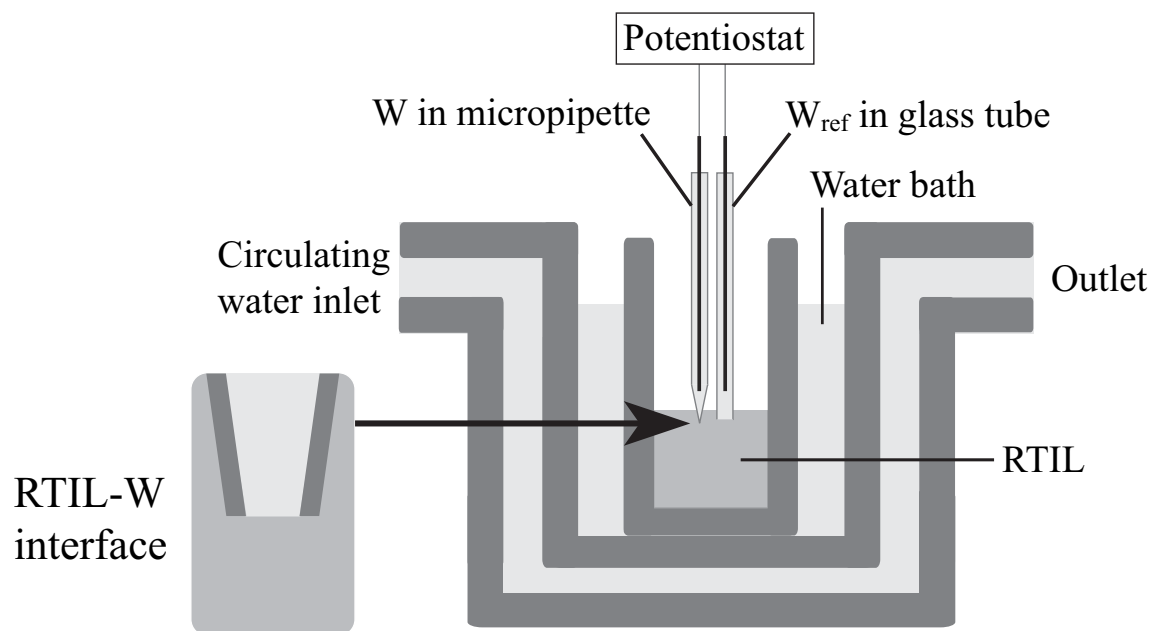


Fig.1 (Nishi et al.)

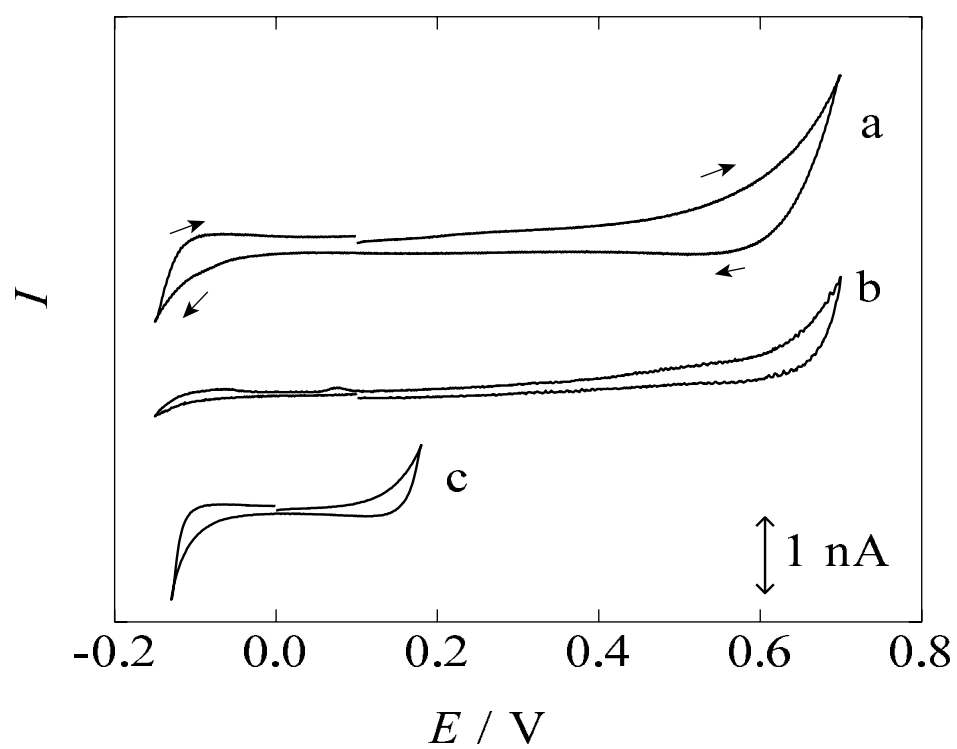


Fig.2 (Nishi et al.)

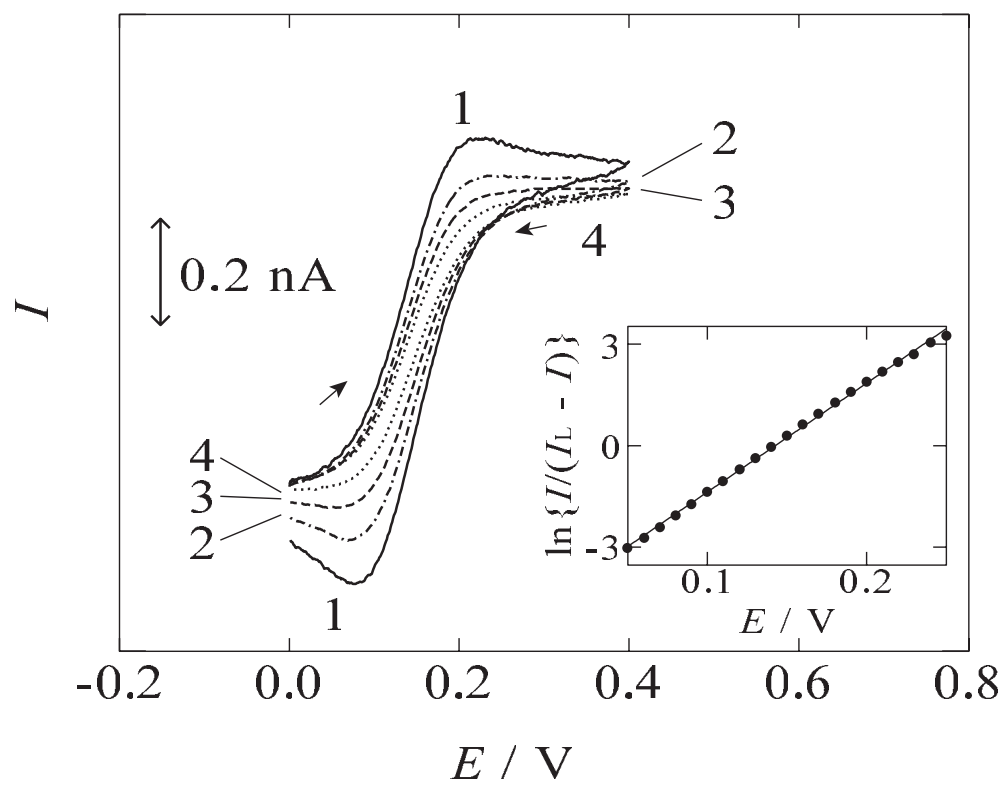


Fig.3 (Nishi et al.)

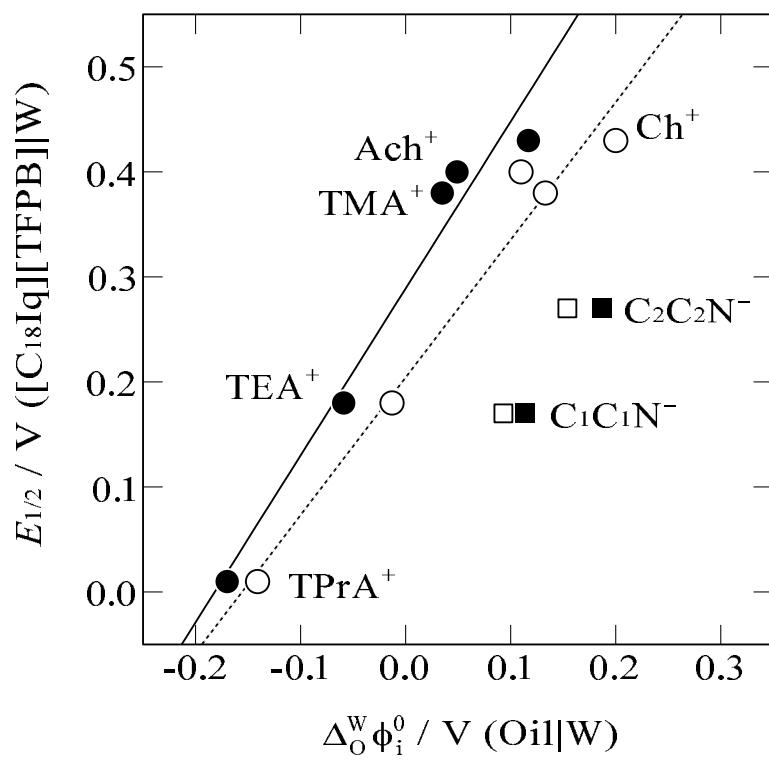


Fig.4 (Nishi et al.)