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Charge-transfer processes at the interface between hydrophobic ionic liquid and water*

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Abstract: This article provides a brief review of theoretical and methodological concepts in the area of the charge-transfer processes at the interface between a hydrophobic ionic liquid (IL) and an electrolyte solution in water (W). Electrochemical methods of study of the W|IL interfaces are described, current experimental problems are indicated, and the most important experimental results are summarized. The relevance of electrochemistry at the W|IL interfaces to the extraction behavior of ILs is outlined.

Keywords: ionic liquids; liquid–liquid interfaces; two-phase liquid systems; ion transfer; electron transfer; standard Gibbs energy of ion transfer; polarized potential window.

INTRODUCTION

The electrochemistry of two-phase liquid systems has been developed over the past 30 years [1–5]. In those studies, one of the liquid phases has been the solution of a hydrophilic electrolyte in water (W), and the other one the solution of a hydrophobic electrolyte in a polar organic solvent that is immiscible with water, such as nitrobenzene (NB), 1,2-dichloroethane (DCE), and 2-nitrophenyl octyl ether (NPOE) [1–5]. The interface formed between these two liquid phases has been designated as the interface between two immiscible electrolyte solutions (ITIES) [1]. Now, we have another liquid medium, that is, the hydrophobic ionic liquid (IL), also known as the room-temperature molten salt or room-temperature ionic liquid (RTIL), which could replace the organic electrolyte solution. The advantages of the hydrophobic ILs for electrochemistry of two-phase liquid systems include negligible volatility, fairly good conductivity, and unique solvation properties. There are two main reasons that have driven the research in this new field. The first one is the uniqueness of the solvation environment of ILs and the properties of the W|IL interface, which can be considerably different from those of the conventional ITIES. The second one is the decisive importance of electrochemical aspects in understanding the extraction behavior of ILs [6–8], which do not seem to have received full attention yet.

The term "hydrophobic" is preferred to "lipophilic" to designate ILs suitable for use in electrochemical studies, because many ILs that are immiscible with W are also immiscible with a nonpolar organic solvent. The term "ionic liquid" also needs to be defined before use, as it can connote an electrolyte solution, and also a traditional molten salt such as NaCl at high temperatures. Nowadays, "ionic liquid" is widely used to refer to a salt made of a cation and an anion, of which at least one is a large

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organic ion, so that the melting point of IL is low, say below 100 °C [9]. An instructive discussion of terminology for this family of compounds is available [9,10]. In the two-phase W|IL systems, what the term IL connotes need not be strictly considered, because the IL phase also contains water once the partition equilibrium is established. In the systems so far reported, the solubility of water in IL ranges from a few ppm to not more than a few wt %, the latter value corresponds to the mole fraction close to one-third. Even in this rather wet IL phase, the solvation environment does not seem to be watery and remains considerably different from that of W. Therefore, we shall use the term IL to denote not only a pure IL, but also an IL saturated with W. A hydrophobic IL may then be defined as the IL that is immiscible with W, forming a two-phase liquid system at a given temperature.

In this article, we summarize the salient features of the two-phase W|IL systems from the electrochemical point of view, mainly focusing on the charge transfer across the W|IL interface.

CLASSIFICATION OF THE CHARGE-TRANSFER REACTIONS

Classification of the charge-transfer reactions at the W|IL interface is analogous to that used in electrochemistry at the conventional ITIES [1–5]. Essentially, two basic charge-transfer types are to be considered, that is, the simple transfer of an ion with the charge number z_i from W to IL and the reverse

$$\mathrm{M}_i^{z_i}\,(\mathrm{W}) = \mathrm{M}_i^{z_i}\,(\mathrm{IL}) \tag{1}$$

and the simple electron transfer between a redox couple O1/R1 in W and a redox couple O2/R2 in IL

$$\mathrm{O1(W) + R2(IL) = R1(W) + O2(IL)} \tag{2}$$

Each of these heterogeneous charge-transfer reactions can be coupled to a series of homogeneous chemical reactions in W or IL. In the case of an IL, the ion association of the transferred ion with the counterion $\mathrm{C}_i^{z_i}$ of the IL can be expected to occur. Alternatively, a ligand that forms a complex with the transferred ion can be added to the IL. Both chemical reactions can be described as

$$\mathrm{M}_i^{z_i}\,(\mathrm{IL}) + \mathrm{C}_i^{z_i}\,(\mathrm{IL}) = \mathrm{M}_i\mathrm{C}_j^{z_{ij}}\,(\mathrm{IL}) \tag{3}$$

where $z_{ij} = z_i + z_j$ with the corresponding equilibrium constant K_{ij}

$$K_{ij} = \frac{a_{ij}(\mathrm{IL})}{a_i(\mathrm{IL})a_j(\mathrm{IL})} \tag{4}$$

where a's are the activities of the species involved. The coupling of the simple ion transfer, eq. 1, with the ion association or the complex formation, eq. 3, is referred to as the assisted or facilitated ion transfer.

METHODOLOGY

Research on equilibrium galvanic cells comprising IL is of fundamental importance for two reasons. First, these measurements can provide thermodynamic information such as the standard ion- or electron-transfer potential or, eventually, the standard Gibbs energy of ion or electron transfer. The phase-boundary potential, $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi = \phi^{\mathrm{W}} - \phi^{\mathrm{IL}}$, where ϕ^{W} and ϕ^{IL} are the inner electric potentials of W and IL, respectively, is one of the most important physicochemical properties in the two-phase liquid systems. Its role can be envisaged by the analogy with the role of the phase-boundary potential in the liquid–liquid extraction utilizing an organic solvent [11,12]. Second, the formation of the stable phase-boundary potential associated with the equilibrium partition of an ion between W and IL is the precondition for the practical realization of an ion-selective type reference electrode in the galvanic cell used for the polarization measurements of a single W|IL interface. The cell for measuring the change in the equilibrium phase-boundary potential across the W|IL interface can be represented by Scheme I [7]

RE | SX or RY(W2) | SY (IL) | SX or RY (W1) | RE (I)

where SY is the IL composed of the cation S^+ and the anion Y^-, RX is a highly hydrophilic electrolyte composed of the cation R^+ and the anion X^- (e.g., LiCl), the single vertical bar represents the phase boundary, RE's are conventional aqueous reference electrodes (e.g., saturated calomel or silver-silver chloride electrodes), and W1 and W2 represent the aqueous phases in the contact with IL. Under certain conditions, which are discussed in the "Phase-boundary potential" section, the phase-boundary potentials at the W1|IL and W2|IL interfaces are controlled solely by the equilibrium partition of the common S^+ and Y^- ion. Figure 1 shows a convenient cell design, where the thickness of the IL layer supported on a glass frit is around 2 mm.

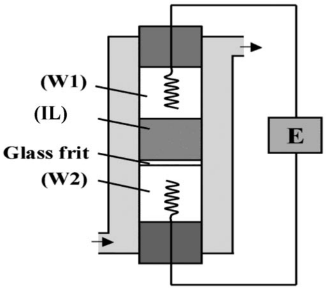

Fig. 1 Schematic illustration of the electrochemical cell for potentiometry of the W|IL interface: W1, IL, and W2 correspond to the phases shown in Scheme I in the text; E is the electrometer; arrows show the inlet and outlet of circulating water supplied from a thermostat. Adapted from [7].

The geometric shape of the IL phase has been often that of a planar liquid membrane, with two dimensions considerably larger than the third one [13–15]. Alternatively, the use of the micropipette-supported W|IL interface allows us to reduce the volume of both the IL and the aqueous phase [16]. By using a membrane cell, the polarization measurements can be accomplished in two configurations [15], which are represented by Schemes II and III

RE | SX or RY(W2) | SY (IL) | RX (W1) | RE (II)

RE | RX (W2) | SY (IL) | RX (W1) | RE (III)

The partition of the common ion S^+ or Y^- in cell II can ensure that the W2|IL interface remains nonpolarized even under the current flow conditions, and the change in the voltage E_{cell} applied across the cell affects only the phase-boundary potential $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi$ at the W1|IL interface (single-interface polarized membrane, SIPM)

$$E_{\mathrm{cell}} = \Delta_{\mathrm{IL}}^{\mathrm{W1}}\phi + IR - E_{\mathrm{ref}} \tag{5}$$

where I is the electric current flowing through the cell, R is the ohmic resistance, and E_{ref} includes the constant potential differences at all nonpolarized cell interfaces. On the other hand, in the cell III, both membrane interfaces are polarized when the electric current flows through the cell (two-interface polarized membrane, TIPM), and the change in the voltage E_{cell} applied across the cell affects the potential difference at both the W1|IL and W2|IL interfaces

$$E_{\mathrm{cell}} = \Delta_{\mathrm{IL}}^{\mathrm{W1}}\phi - \Delta_{\mathrm{IL}}^{\mathrm{W2}}\phi + IR - E_{\mathrm{ref}} \tag{6}$$

From a practical point of view, it is necessary to ensure the constant value of the reference potential E_{ref} and to consider the ohmic potential drop IR in eqs. 5 and 6. The polarization of REs can be avoided by using the four-electrode system [15] with two couples of the current-supplying (counter) and the potential measuring (reference) electrodes, which are connected to the phases W1 and W2. Under certain conditions (e.g., low electrical current or large-area reference electrodes), three- or two-electrode configurations are possible, where one or two reference electrodes, respectively, comprise the function of both the reference and counter electrodes. The polarization of the reference W2|IL interface in the SIPM configuration can be reduced by increasing the concentration of the common ion (S^+ or Y^-) in the reference aqueous phase W2. The ohmic potential drop in eqs. 5 and 6 is usually associated with the resistance of the IL phase, which can be reduced by increasing the ratio of the working area to the thickness of the IL layer [13–15]. In spite of this, the resistance remains quite large and has to be compensated instrumentally using, e.g., the positive feedback [14,15]. The scheme of the four-electrode membrane cell, where the IL is supported by a microporous filter, is shown in Fig. 2. An efficient method for suppressing both the polarization effects in E_{ref} and the ohmic potential drop is based on the use of the micropipette-supported W|IL interface (Fig. 3) [6,16,17]. Here, the tip of the micropipette is filled with an aqueous solution and dipped in the IL.

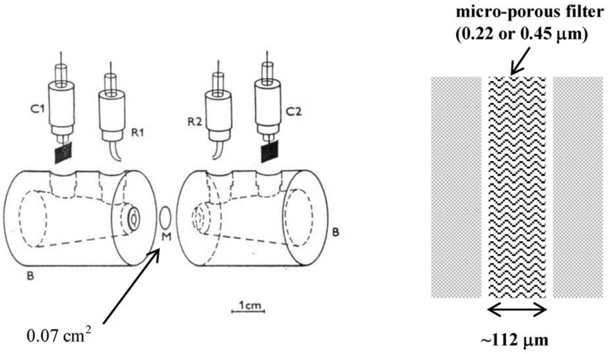

Fig. 2 Scheme of the four-electrode membrane cell (left) and of the IL membrane (M) supported by a microporous filter (right): R1 and R2 are the reference electrodes, C1 and C2 are the current-supplying (counter) electrodes, M is the membrane.

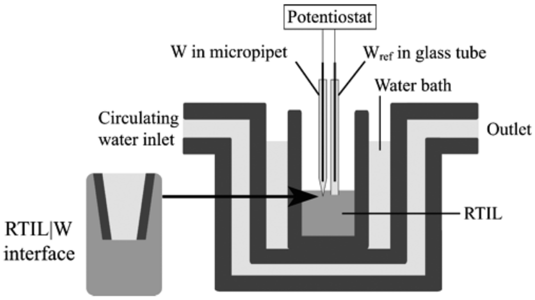

Fig. 3 Scheme of the cell for the polarization measurements at the micropipette-supported interface between water (W) and an RTIL. Reprinted with permission from [17]. © 2006 American Chemical Society.

An interesting experimental approach to the polarization of the W|IL interface is based on the IL supported by an electronic conductor (e.g., Au, graphite), which is dipped in the aqueous phase [18]. In this case, the transfer of an ion from water to the IL is driven by the electron-transfer reaction of, e.g., ferrocene at the Au or PG|IL interface (Fig. 4), cf. also the recent review [19].

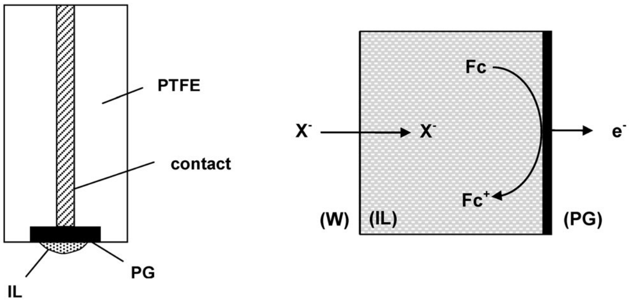

Fig. 4 Scheme of the experimental arrangement for the polarization measurements at the W|IL interface based on IL supported by the pyrolytic graphite (PG) or metal electrode (left) and the mechanism of the coupled charge-transfer reactions at the W|IL and PG–IL interfaces (right).

ELECTROCHEMICAL POLARIZABILITY OF THE W|IL INTERFACE

Hydrophobic ionic liquids

A typical cation so far most widely used for hydrophobic ILs is 1-alkyl-3-methylimidazolium ($C_n\mathrm{mim}^+$). By combining it with an inorganic or organic anion, ILs of a different hydrophobicity have been prepared. A commonly used anion having a considerable stability in aqueous environments is bis(trifluoromethylsulfonyl)imide ($C_1C_1N^-$) and the homologs, $C_nC_mN^-$, where the subscripts n and m denote the number of carbon atoms in the perfluoroalkylsulfonyl moieties. Use of ILs composed of PF_6^- and BF_4^- should be avoided, because of the hydrolysis problem in the presence of water [20–23].

Table 1 lists the mutual miscibility of some moderately hydrophobic ILs with water used in electrochemical studies of the two-phase W|IL systems [7,17,24–27]. These data indicate that the mutual miscibility becomes smaller with increasing hydrophobicity of ions constituting ILs. In fact, the effect of the hydrophobicity on the mutual solubility is asymmetric; the solubility of IL in W is greatly influenced by the change in the hydrophobicity of the ions in IL than the solubility of W in IL [28]. For environmental concerns and for a longer lifetime of the IL, a smaller solubility of the IL in W is desirable. On the other hand, for electrochemical applications, we need to consider the electrochemical polarizability of the W|IL interface. In fact, the solubility of the IL in W, the width of the polarized potential window (ppw), and the polarizability of the interface, are all interlinked [7,29]. Before discussing these mutual relationships, we first define the relevant physicochemical quantities, that is, the standard Gibbs energy of the transfer of an ion i from W to IL, $\Delta G_i^{\mathrm{W}\to\mathrm{IL},0}$, and the derived quantity, the standard ion transfer potential, $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0$, which for an univalent cation or anion is simply the positive or negative of the former, respectively, divided by the Faraday constant. $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0 = \pm\Delta G_i^{\mathrm{W}\to\mathrm{IL},0}/\mathrm{F}$.

Table 1 Mutual miscibility of water and moderately hydrophobic ILs at 25 °C.

	Solubility of W in IL			Solubility of IL in W			
IL	wt %	mol kg^{-1}	$x_{\mathrm{W}}^{\mathrm{IL}\,\mathrm{a}}$	wt %	mol kg^{-1}	$x_{\mathrm{IL}}^{\mathrm{W}\,\mathrm{b}}$	Ref.
$\mathrm{C_6mimC_1C_1N}$	1.05	0.583	0.208	0.237	5.3×10^{-3}	9.6×10^{-5}	24
$\mathrm{C_8mimC_1C_1N}$	0.96	0.530	0.200	0.071	1.5×10^{-3}	2.7×10^{-5}	25
$\mathrm{C_8mimC_2C_2N}$	0.60	0.300			1.1×10^{-3}		7
$\mathrm{C_8mimC_1C_4N}$	0.54				4.3×10^{-4}		26
$\mathrm{C_8mimC_4C_4N}$	0.37				2.4×10^{-4}		26
$\mathrm{THAC_1C_1N}$[c]	0.30	0.160			7.0×10^{-6}		27
$\mathrm{C_{18}IqTFPB}$[d]	0.31	0.170			4.0×10^{-5}		17
TOMATFPB[d]	0.20	0.110			1.0×10^{-5}		17

[a] Mole fraction of W in IL.

[b] Mole fraction of IL in W.

[c] 25 °C.

[d] 56 °C.

Standard ion-transfer potential and hydrophobicity scale of ions

The solubility of ILs would better be expressed in terms of the contributions of the IL constituting cation and anion to the hydrophobicity of the IL [6,7]. The relevant quantitative measure is $\Delta G_i^{\mathrm{W}\to\mathrm{IL},0}$. For example, the solubility of a 1:1 IL SY is related to the sum $\Delta G_{\mathrm{IL}}^{\mathrm{W}\to\mathrm{IL},0} = \Delta G_{\mathrm{S^+}}^{\mathrm{W}\to\mathrm{IL},0} + \Delta G_{\mathrm{Y^-}}^{\mathrm{W}\to\mathrm{IL},0}$. Since IL is a salt having a limited solubility in W, it is convenient to define the solubility product of IL in W, $K_{\mathrm{s}}^{\mathrm{W}} = a_{\mathrm{S^+}}^{\mathrm{W}}\, a_{\mathrm{Y^-}}^{\mathrm{W}}$, where a_i^{W} is the activity of i (i = S$^+$ or Y$^-$) in W. From the condition of the partition equilibrium, we have

$$RT \ln K_{\mathrm{s}}^{\mathrm{W}} = \Delta G_{\mathrm{S^+}}^{\mathrm{W}\to\mathrm{IL},0} + \Delta G_{\mathrm{Y^-}}^{\mathrm{W}\to\mathrm{IL},0} = F(\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{S^+}}^{0} - \Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{Y^-}}^{0}) \tag{7}$$

Given the values of $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0$ for various anions and cations, we would know the solubility of ILs formed by different combinations of cations and anions. However, $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0$ is a single ionic property and is not measurable. Moreover, each IL has its own solvation environment and, hence, the value of $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0$ varies from one IL to another [6,7]. It seems to be a formidable task to find a universal scale for the hydrophobicity of ions applicable in studying ILs. It is fortunate that many ILs show the polarity similar to those of the polar organic solvents [30–32]. More specifically, ILs of the family $\mathrm{C}_n\mathrm{mimC_1C_1N}$ (n = 2–10) have a remarkably similar polarity as expressed on the normalized solvent polarity scale, $E_{\mathrm{N}}^{\mathrm{T}} = 0.65 \pm 0.2$ [31]. Alkylbenzyldimethylammonium salts of $\mathrm{C_1C_1N^-}$ and $\mathrm{C_2C_2N^-}$, where alkyl is decyl, dodecyl, or hexadecyl, also have similar $E_{\mathrm{N}}^{\mathrm{T}}$ values [33]. Water saturation increases the $E_{\mathrm{N}}^{\mathrm{T}}$ values by ca. 0.02 [31,33]. Hence, it is not unreasonable to use as a quantitative measure of $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0$ the standard ion-transfer potential $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi_i^0$ for the ion transfer between W and a polar organic solvent O, which has been established for several solvents such as NB and DCE based on the so-called tetraphenylarsonium tetraphenylborate (TATB) assumption [34,35].

Figure 5 shows the values of $\Delta_{\mathrm{NB}}^{\mathrm{W}}\phi_i^0$ for the two-phase W-NB system. The solubility of a salt made of any combination of a cation and an anion can be deduced from the values of $\Delta_{\mathrm{NB}}^{\mathrm{W}}\phi_i^0$ in Fig. 5. A reasonable correlation between the solubility of hydrophobic ILs and the values of $\Delta_{\mathrm{NB}}^{\mathrm{W}}\phi_i^0$ for the IL-constituting ions has been demonstrated for a series of ILs [27,28,36,37].

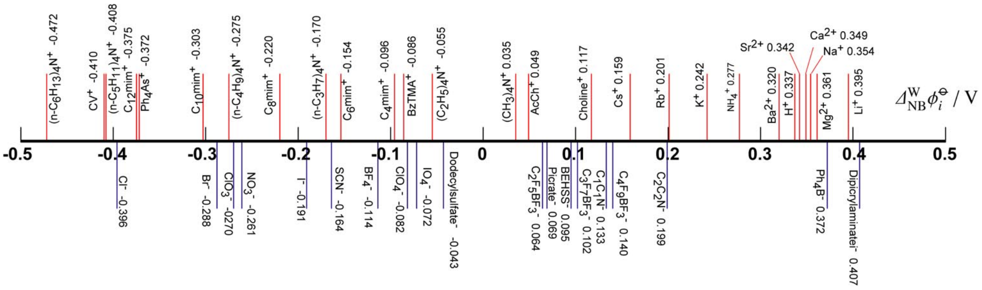

Fig. 5 A scale of the standard ion-transfer potentials for the two-phase NB-W system at 25 °C. The number by each line is the $\Delta^{\mathrm{W}}_{\mathrm{NB}}\phi^{0}_{i}$ value in V. Abbreviations: acetylcholine (AcCh$^+$), benzyltrimethylammonium (BzTMA$^+$), tetraphenylarsonium (Ph$_4$As$^+$), crystal violet (CV$^+$), tetraphenylborate (Ph$_4$B$^-$), tetraalkylammonium (Alkyl$_4$N$^+$); for others, see text. Adapted from [38].

Phase-boundary potential

When an IL SY is in partition equilibrium with W, a phase-boundary potential $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ develops across the W|IL interface. When the W phase does not contain ionic species other than the IL-constituting ions, $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ is determined by the sum of the standard ion-transfer potentials for S$^+$ and Y$^-$

$$\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi = \frac{(\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi^{0}_{\mathrm{S^+}} + \Delta^{\mathrm{W}}_{\mathrm{IL}}\phi^{0}_{\mathrm{Y^-}})}{2} \tag{8}$$

One can see that $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ can be positive or negative, depending on the relative magnitude and the sign of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi^{0}_{i}$. Unlike $K^{\mathrm{W}}_{\mathrm{S}}$, which is related to the difference between $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi^{0}_{\mathrm{S^+}}$ and $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi^{0}_{\mathrm{Y^-}}$, cf. eq. 7, the values of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ alike those of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi^{0}_{i}$ are not experimentally accessible. However, the existence of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ can be indirectly confirmed through a variety of experiments [8,38]. An approximate magnitude of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ can be deduced, e.g., from electrocapillary measurements [31], or it can be estimated from the $\Delta^{\mathrm{W}}_{\mathrm{NB}}\phi^{0}_{i}$ values in Fig. 5.

When the W phase contains either S$^+$ or Y$^-$, which are added to W as a salt of the hydrophilic counterions X$^-$ (e.g., F$^-$) or R$^+$ (e.g., Li$^+$), respectively, $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ varies according to the Nernst equation

$$\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi = \Delta^{\mathrm{W}}_{\mathrm{IL}}\phi^{0}_{\mathrm{S^+}} - \frac{RT}{F}\ln a^{\mathrm{W}}_{\mathrm{S^+}} \tag{9}$$

$$\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi = \Delta^{\mathrm{W}}_{\mathrm{IL}}\phi^{0}_{\mathrm{Y^-}} + \frac{RT}{F}\ln a^{\mathrm{W}}_{\mathrm{Y^-}} \tag{10}$$

It is therefore possible to change $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ by changing the concentration of the salt, RY, or SX added to W.

If the solubility of hydrophilic counterions in IL is not negligible, the net transfer of the salt from W to IL takes place and $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ develops as the mixed potential $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi_{\mathrm{mix}}$, which involves a contribution from the mass transport of ions in both phases, as is the case of the mixed potential in conventional ITIES systems [40,41]. The contribution of the distribution of hydrophilic ions to $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ becomes more pronounced with increasing magnitude of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$, that is, with departing of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ from 0, as can be envisaged in Fig. 5. This is one factor that limits the range of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ attainable through the partitioning of the potential determining ions to ca. ± 300 mV [39]. The other factor is the limited solubility of the salt, RY, or SX in W. Possibly, RY or SX added to W for the change of $\Delta^{\mathrm{W}}_{\mathrm{IL}}\phi$ significantly affects the bulk as well as the surface properties of the two-phase systems that are of primary interest.

In actual systems, when an IL is brought into contact with W, the IL-constituting ions start to transfer to W. The transfer continues until the partition equilibrium is established throughout the IL and W phases. During the course of this partitioning, the mass transport of the IL-constituting ions should be taken into account. The mode of the mass transport depends on the details of the solution composition and the diffusion coefficients of relevant ionic species. For the simplest case of the partitioning of S^+ and Y^- [29,42], the mixed potential difference takes the form

$$\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi = \Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{mix}} = \frac{RT}{F}\left(\frac{D_{\mathrm{S}^+}^{\mathrm{W}}}{D_{\mathrm{Y}^-}^{\mathrm{W}}}\right)^{1/4} + \frac{\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{S}^+}^{0} + \Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{Y}^-}^{0}}{2} \tag{11}$$

where D_i^{W} is the diffusion coefficient of the ion i in W. When $D_{\mathrm{S}^+}^{\mathrm{W}} \approx D_{\mathrm{Y}^-}^{\mathrm{W}}$, the mixed potential difference $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi$ is expressed by eq. 8. However, if the ionic strength in W is low, the diffusion potential in W may become significant, whose magnitude depends on the difference between the diffusion coefficients of S^+ and Y^- in W. In application of IL-salt bridges where the working principle is based on eq. 8 [7,43], care must be exercised in use of IL-salt bridges in low ionic strength solutions due to the effect of different diffusion coefficients of the IL-constitutent cations and anions in W [44].

Solubility product, polarized potential window, and electrochemical polarizability

In the voltammetric or other potential-controlled experiments at the W|IL interface, the range of the accessible potentials, i.e., the ppw, should have the width of at least 200 mV. From eq. 7, it is seen that $K_{\mathrm{s}}^{\mathrm{W}}$ is a direct measure of the width of ppw, provided that both ends of the ppw are determined by the dissolution of the IL-constituting ions. Since the voltammetric or polarographic current associated with the transfer of these ions increases exponentially well before $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi$ reaches the proxicimity of the corresponding standard ion-transfer potential $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0$, the width of the ppw is narrower by ca. 300 mV than the difference $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{Y}^-}^0 - \Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{S}^+}^0$. An approximate width of ppw for a moderately hydrophobic IL in contact with the aqueous solution containing only hydrophilic ions can be estimated from the $\Delta_{\mathrm{NB}}^{\mathrm{W}}\phi_i^0$ values shown in Fig. 5.

Generally, the increasing hydrophobicity of the IL-constituent ions results in a wider ppw. However, in the case of ILs composed of highly hydrophobic ions listed in Table 1, ppw may be determined not by the dissolution of the IL-constituting ions in W, but rather by the transfer of the hydrophilic ions from W to IL. Furthermore, the ppw can become narrower due to the facilitated transfer of the hydrophilic ions from W to IL through their ion pair formation with the IL-constituent ions [45]. A judicious choice of ions for both W and IL phases has allowed widening of ppw up to 1.1 V, albeit at an elevated temperature of 60 °C [46].

Figure 6 illustrates ppw available for a series of ILs based on perfluoroalkyltrifluoroborates [37]. It is apparent that aside from the width of ppw the ion-transfer resistance in the middle of ppw, $\mathrm{d}E/\mathrm{d}I$, can be a quantitative measure of the quality of the electrochemical polarizability. It can be shown for a moderately hydrophobic IL, $\mathrm{d}E/\mathrm{d}I$ is inversely proportional to the square root of $K_{\mathrm{s}}^{\mathrm{W}}$ [29].

For highly hydrophobic ILs, such as trioctylmethylammonium tetrakis[bis(3,5-trifluoromethyl)phenyl]borate (TOMATFPB), the dissolution of hydrophilic ions like Li^+ and Cl^- determines the width of ppw. The polarizability is then determined by the $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0$ values of the hydrophilic ions dissolved in W and by their concentrations.

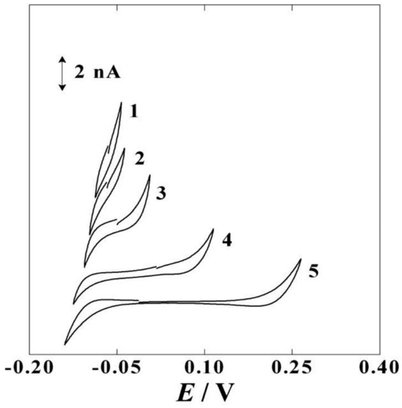

Fig. 6 Cyclic voltammograms (10 mV s^{-1}) at the interface between water and $C_8mimC_nF_{2n+1}BF_3$: $n = 2$ (1), 3 (2), 4 (3), and the interface between water and $THAC_nF_{2n+1}BF_3$: $n = 2$ (4), 6 (5). The aqueous phase contains 10 mM $MgCl_2$. Adapted from [37].

CHARGE-TRANSFER PROCESSES

Simple ion transfer

Simple ion-transfer reactions at the nonpolarized and polarized W|IL interfaces have been studied using the potentiometric and voltammetric techniques, respectively. The experimental verification of the theory of the equilibrium-phase boundary potential ("Phase-boundary potential" section) was given using $C_8mimC_1C_1N$ and $C_8mimC_2C_2N$ as IL [7]. Potentiometric measurements were carried in the cell shown in Fig. 1, which can be described by Scheme IV

$$\mathrm{Ag|AgCl|C_8mimCl\ (W2)|C_8mimC_\mathit{n}C_\mathit{n}N\ (IL)|C_8mimCl\ or\ LiC_\mathit{n}C_\mathit{n}N\ +}$$
$$\mathrm{RCl\ (W1)|AgCl|\ Ag} \qquad \text{(IV)}$$

where $R^+ = Na^+$ or K^+. As illustrated in Fig. 7, the variation of the cell voltage E_{cell} with the mean activity of C_8mimCl or LiC_nC_nN in W1 is consistent with the theoretical prediction of the nernstian response [7]. After the correction for the effect of the C_8mimCl concentration on the potential of the reference Ag|AgCl electrode in the former case, the cell voltage in both cases was found to follow the Nernst equation, which predicts the slope of ±59 mV/decade for the cell voltage change (eqs. 9 and 10). The absence of the effect of NaCl or KCl added to the phase W1 confirmed that the observed response is associated with the relative magnitude of the ion-transfer potential differences following the sequence $\Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{X}^-}^0 << \Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_i^0 << \Delta_{\mathrm{IL}}^{\mathrm{W}}\phi_{\mathrm{R}^+}^0$, where $i = C_8mim^+$ or $C_nC_nN^-$, $R^+ = Li^+$, Na^+, or K^+ and $X^- = Cl^-$ [7]. The conclusion was made that the Nernstian behavior of the W|IL interface provides a key to understand the extraction properties of IL and also the electrochemistry using IL, as it has been proposed earlier [6].

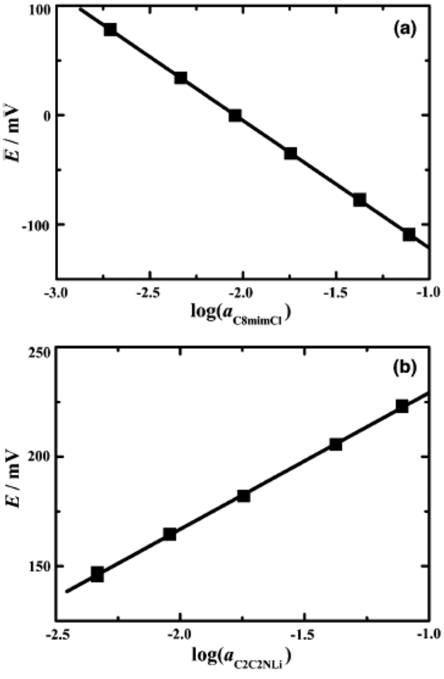

Fig. 7 Variation of the cell voltage (Scheme IV) with the mean activity of C_8mimCl (a) or LiC_2C_2N (b). Reprinted with permission from [7]. © 2003 Elsevier Science.

The realization of the polarized W|IL interface has been demonstrated for the first time by using tetrahexylammonium (THA^+) salts of $C_1C_1N^-$ and $C_2C_2N^-$ as IL [13], and shortly afterwards also using tetraoctylammonium 2,4,6-trinitrophenolate (TOATNP)* [14]. In both studies, a two-electrode cell was used for the polarization measurements (Fig. 1). In the former case, the cell can be described by Scheme V [13]

Ag|AgCl| LiCl + LiC_nC_nN (W2) | $THAC_nC_nN$ (IL) | LiCl +
MCl or $LiPF_6$ (W1)|AgCl| Ag (V)

where LiCl serves as the supporting electrolyte, and $M^+ = C_8mim^+$, tetrapropylammonium$^+$ ($TPrA^+$), or tetrabutylammonium$^+$ (TBA^+). Cyclic voltammogram of the transfer of the C_8mim^+ ion across the W1|RTIL interface is illustrated in Fig. 8. The peak current was found to be proportional to the square root of the sweep rate v (inset in Fig. 8), while the mid-potential that can be considered to be a measure of the standard ion-transfer potential was independent of v. These effects indicated that the charge transfer is reversible and controlled by the linear diffusion. Furthermore, the differences between the mid-point potentials for $TPrA^+$, TBA^+, and PF_6^- were found to be close to those obtained from polarization measurements at the conventional water–organic solvent interfaces [13]. The thermodynamic condition for the polarization measurements of the transfer of a moderately hydrophobic ion i can be formulated in analogy with the polarized ITIES [47] as $\Delta_{IL}^{W}\phi_{X^-}^{0}$, $\Delta_{IL}^{W}\phi_{S^+}^{0} << \Delta_{IL}^{W}\phi_{i}^{0} << \Delta_{IL}^{W}\phi_{R^+}^{0}$, $\Delta_{IL}^{W}\phi_{Y^-}^{0}$, where R^+ and X^- represent the ions of the aqueous supporting electrolyte.

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*Warning: preparation and use of this IL can be dangerous due to the possible explosion.

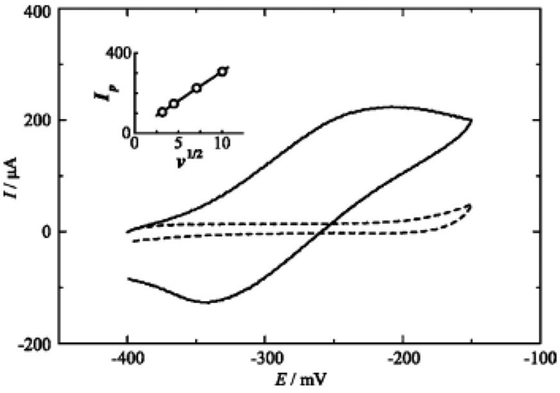

Fig. 8 Cyclic voltammograms (50 mV s^{-1}) at the interface between the aqueous solution of LiCl and $THAC_2C_2N$ used as IL in the presence (solid line) and absence (dashed line) of 2 mM C_8 mimCl in W1 (Scheme V) at 40 °C. Inset shows the dependence of the peak current in the forward sweep on the square root of the sweep rate. Reprinted with permission from [13]. © 2003 Elsevier Science.

The use of ILs composed of the very hydrophobic anion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($TFPB^-$), and the very hydrophobic cations like *N*-octadecylisoquinolinium ($C_{18}Iq^+$) or trioctylmethylammonium ($TOMA^+$) has allowed extending ppw to ca. 0.8 V at 56 °C [17], as compared with ppw of ca. 0.2 V [6], 0.3 V at 40 °C [13], or 0.4 V at 25 °C [14] attained with $TBMAC_1C_1N$ ($TBMA^+$ = tributylmethylammonium), $THAC_2C_2N$, or TOATNP, respectively. This extension has enabled voltammetric measurements of a series of the moderately hydrophobic ions including tetramethylammonium (TMA^+), tetraethylammonium (TEA^+), $TPrA^+$, choline, acetylcholine, $C_1C_1N^-$, and $C_2C_2N^-$ [17]. A linear correlation was established between the reversible half-wave potential for the transfer of these ions across the W|IL and the standard ion-transfer potential for the same ions obtained from the polarization measurements at the W|NB or W|DCE interface [17].

Cyclic voltammetry was used to study the transfer of a series of cations and anions including TMA^+, TEA^+, $TPrA^+$, TBA^+, tetrapentylammonium (TPA^+), across an IL membrane composed of tridodecylmethylammonium cation ($TDMA^+$) and tetrakis(pentafluorophenyl)borate anion ($TPFPB^-$), and supported by a thin (~112 μm) microporous filter [15]. Reversible partition of $TPFPB^-$ allowed fixing the potential difference at the W2|IL interface in the SIPM cell (Scheme II) and polarizing the other membrane interface in a defined way. It was shown that width of ppw in this case attains the value of ca. 0.7 V at the ambient temperature of 25 ± 2 °C. Ion-transfer voltammograms measured using the TIPM cell (Scheme III) are illustrated in Fig. 9. TATB hypothesis [34,35] was used to estimate the standard Gibbs energies of ion transfer from water to IL and to establish the scale of the absolute potential differences. A single linear Gibbs energy relationship for the ion transfer from water to IL and *o*-dichlorobenzene (Fig. 10) suggested that the interactions affecting the ion Gibbs energy in IL are similar to those in a polar organic solvent equilibrated with water.

A number of ion transfer reactions at the W|IL interface were studied also using the experimental approach schematically depicted in Fig. 4 with ILs including $C_8mimC_nC_nN$ [18], 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate [48,49], $C_{10}mimC_1C_1N$ [50–52], $C_4mimC_1C_1N$, and C_4mimPF_6 [50]. Since the achievements in this area have been recently reviewed [19], we shall limit ourselves to a few general comments. First, the coupling mechanism of the charge transfer has been a matter of the considerable concern in all these studies. Second, in an agreement with the theoretical prediction [53], the peak potential of the current response was found to be a function of the concentration of the aqueous ion (mostly anion). Third, the peak potential correlates with the standard ion-transfer potential for the coupled ion (mostly anion) transfer, though the correlation is nonlinear.

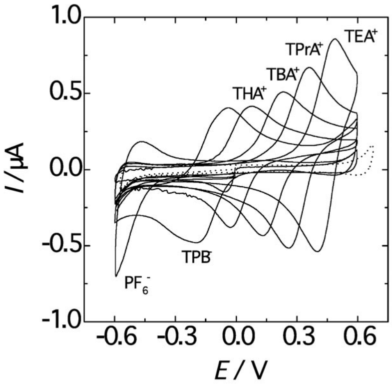

Fig. 9 Ion-transfer voltammograms (10 mV s^{-1}) measured using the TIPM cell, Scheme III, in the absence (dotted line) and presence (full line) of various cations and anions (0.1 mM) in the phase W1; ohmic drop compensation 400 kΩ. Adapted from [15].

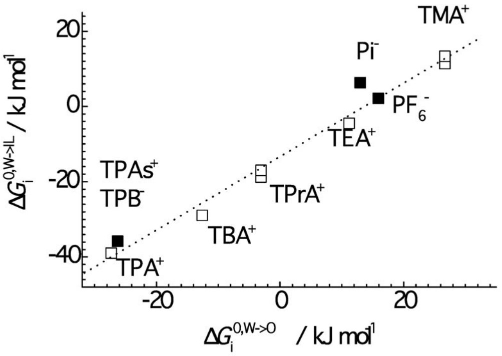

Fig. 10 Correlation of the standard Gibbs energies $\Delta G_i^{0,W\to IL}$ and $\Delta G_i^{0,W\to O}$ of cation (□) and anion (■) transfer to IL and *o*-dichlorobenzene, respectively; the dotted line has the slope of 0.98. Adapted from [15].

The spontaneous accumulation of the redox active ions, e.g., $Fe(CN)_6^{3-}$, into IL supported by a graphite or ITO electrode was reported [54,55], which seems to offer some analytical applications by modifying the electrochemical activity of the classical electrodes. Nevertheless, as it was noted [19], a high viscosity of IL suppresses the amperometric signal associated with the electrochemical reaction of the redox active ion, and the composite films based on IL have to be considered [52].

Facilitated ion transfer

Cyclic voltammetry has been used for the first time to study the transfer of alkali metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+) facilitated by the complex formation with dibenzo-18-crown-6 (DB18C6) at the polarizable W|IL interface supported by a micropipette (Fig. 3) using C_{18}Iq TFPB as IL [56]. Ion-transfer voltammograms measured under the conditions of the excess metal ion concentration over that of the ligand are shown in Fig. 11. The analysis of these voltammograms allowed determining the stoichiometry and the stability constants of the complexes in IL, indicating the relative enhancement of the selectivity of DB18C6 to K^+. The conclusion was made that such modification of the selectivity confirms the unique solvation environment for ions in IL compared to molecular solvents [56].

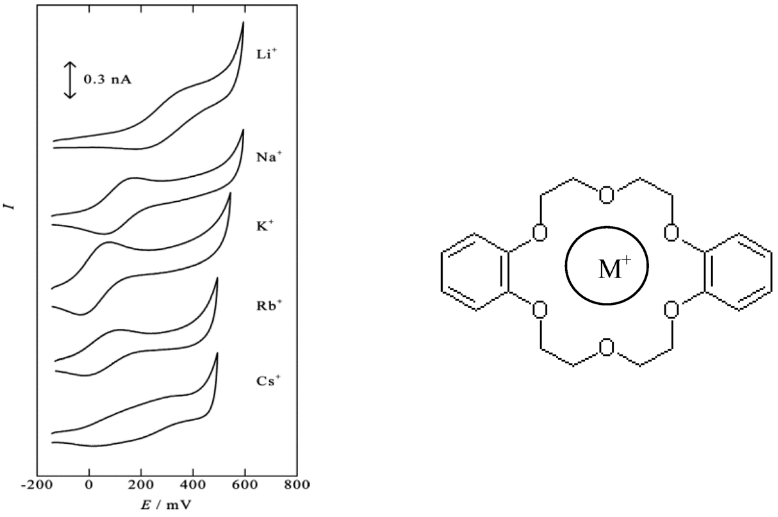

Fig. 11 Cyclic voltammograms (10 mV s^{-1}) for the transfer of M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+ facilitated by DB18C6 when the concentration of the alkali metal cation in the aqueous phase is 0.1 mol dm^{-3} and the concentration of DB18C6 in C_{18}IqTFPB used as IL is 20 mmol dm^{-3} (left), and the structure of the 1:1 complex in IL (right). Reprinted with permission from [56]. © 2006 American Chemical Society.

Electron transfer

First measurement of the electron transfer has been carried out using C_8mimC_1C_1N as IL containing 1,1'-dimethylferrocene (DMFc) as an electron donor and the aqueous phase containing $Fe(CN)_6^{3-}$ as an electron acceptor [57]. Electron-transfer kinetics was investigated by scanning electrochemical microscopy with the aim to uncover the differences between the electron-transfer kinetics at the W|IL and W|DCE interfaces. The most remarkable finding was the observation that the rate constant of the bimolecular electron-transfer reaction between DMFc and $Fe(CN)_6^{3-}$ decreased by factor of ca. 50 with increasing mole fraction of DCE in IL, while the diffusion coefficient of DMFc increased by about the same factor. A conclusion was made that some interfacial factor (e.g., the thickness or polarity of the phase boundary) makes the electron-transfer rate in the W|IL system faster than at the W|DCE interface [57].

RELEVANCE TO EXTRACTION BEHAVIOR OF IONIC LIQUIDS

In contrast to the extraction from water to an organic solvent, the extraction to IL always involves the multi-ion partition between the two liquid phases, even in case that the extracted species are electrically neutral. When an electrolyte is extracted, the number of ions involved is at least four. As a result of the multi-ion partition, the phase-boundary potential is established, the nature of which in general is that of the mixed or corrosion potential ("Phase-boundary potential" section). Actually, the phase-boundary potential results from the balance of the electrical currents I_i associated with the individual ion-transfer processes [40]

$$I = \sum_i I_i = 0 \tag{12}$$

The theoretical analysis based on eq. 12 shows that under certain conditions the phase-boundary potential can result from the balance of the opposite electric currents of a single ion leading to the Nernst potential ("Phase-boundary potential" section) [40].

The results of the numerous studies of ion-transfer processes at the nonpolarized and polarized W|IL interfaces summarized above can be used to rationalize the extraction behavior of ILs. In order to illustrate this point, we shall consider the unique example of the extraction of the Sr^{2+} ion from water to $C_5mimC_1C_1N$ facilitated by the complex formation of Sr^{2+} with *cis-syn-cis*-dicyclohexyl-18-crown-6 (CE) in the aqueous phase in the presence of various aqueous anions X^- ($X^- = Cl^-$, NO_3^- or SO_4^{2-}) [58]. By using the sophisticated EXAFS technique, the authors [58] analyzed the structure of the coordination sphere of the extracted Sr^{2+} ion in IL and came to a conclusion that the mechanism of the extraction process is the ion exchange

$$Sr(CE)^{2+}\ (W) + 2C_5mim^+\ (IL) = Sr(CE)^{2+}\ (IL) + C_5mim^+\ (W) \tag{13}$$

rather than the co-extraction of the aqueous anion

$$Sr(CE)^{2+}\ (W) + n\ X^-\ (W) = Sr(CE)^{2+} \cdot n\ X^-\ (IL) \tag{14}$$

From the electrochemical point of view, the preferred mechanism (eq. 13) is a trivial consequence of the relative magnitude of the standard ion-transfer potentials for $Sr(CE)^{2+}$, C_5mim^+, $C_1C_1N^-$, and X^-. Actually, as it follows from the potentiometric and voltammetric measurements (“Facilitated ion transfer” and “Electron transfer” sections), the standard ion transfer potential for X^- is much more negative than the standard ion-transfer potential for the remaining three ions. Hence, the positive current due to the transfer of $Sr(CE)^{2+}$ to IL can in no case be balanced by the negative current due to the co-extraction of X^-, and must be balanced by the negative current due to the counter-extraction of C_5mim^+.

CONCLUSIONS

By far the most advantageous property of ILs compared with NB, DCE, or NPOE, is the ultralow vapor pressure [59]. This dramatically changes the scene of electrochemical experiments with the two-phase liquid–liquid systems, because of no necessity to use a fume hood or other ventilation systems. This property of ILs is highly preferrable also in various practical applications. From the point of view of environmental protection, the fact that the hydrophobic ILs have certain solubility in W should be properly addressed, as in the case of organic solvents. The high viscosity of ILs poses interesting problems associated with the very slow diffusion of ions in the IL phase, which in fact considerably shifts our notion about the criterion of steady-state currents in voltammetry at micro IL|W interfaces [16,17,56,60]. The ultraslow relaxation of the electrical double layer at the IL|W interface after the modulation of the potential across the interface [61] may impose fundamental difficulties in the interpretation of voltammograms. It is noteworthy that IL can be immiscible not only with water, but also with an organic solvent [62], and even with another IL [63,64]. In all these systems, the electrochemical or electrical properties of ILs should be important and the approaches and concepts introduced above in principle should be also applicable.

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