Electrochemistry

— Headline—

Ionic Liquid|Water Interface: A New Electrified System for Electrochemistry

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A room-temperature ionic liquid (RTIL) consisting of hydrophobic cations and anions forms a two-phase system with water (W). The interface between the RTIL and W is inevitably electrified because of the dissolution of cations and anions constituting the RTIL into the W phase and the two-phase system should, hence, be considered as a new electrochemical system where the phase-boundary potential across the RTIL/W interface plays a key role in determining physicochemical properties of the two-phase system, notably the interfacial charge transfer and the structure of the electrical double layers at the interface. When the solubility of the RTIL in W is on the order of a few mmol dm$^{-3}$ or higher, the RTIL/W interface behaves as an electrochemically nonpolarized interface; the phase-boundary potential is determined by the composition of the two phases. At the opposite extreme where the solubility is a few tens μmol dm$^{-3}$ or lower, the interface can be taken as an electrochemically polarized interface, since the phase-boundary potential can be controlled by externally applying a voltage across the two terminals of the cell that comprises the RTIL/W interface. This electrochemical polarizability allows us to employ a variety of electrochemical techniques for studying the RTIL/W interface. Electrochemical view points as well as electrochemical techniques are powerful in clarifying the unique properties of this new electrified interface. Conversely, this two-phase system poses us intriguing problems, which can in turn widen the scope of electrochemistry.

Key Words: Ionic Liquid, Ionic Liquid-water Two-phase Systems, Electrified Interface

1 Introduction

In many branches of electrochemistry, room-temperature ionic liquids (RTILs), or room-temperature molten salts, have recently been studied intensively aiming at using RTILs as ion-conducting media for fuel cells, lithium ion batteries, double-layer capacitors, and solar cells.$^{1,9}$ For all these applications, an RTIL single phase is utilized as an ionic conductor. In designing RTILs for such purposes, lowering viscosity and elevating the decomposition voltage have been of primary interest. Even a trace amount of water in an RTIL can be harmful for many of such applications. There is yet another important, from the view point of electrochemistry, application of RTILs that are saturated with water, that is, the use of hydrophobic RTILs for a new liquid-liquid two-phase system. Some examples of hydrophobic RTILs are listed in Table 1. In such two-phase systems, the RTIL and water (W) phases are mutually saturated (See Table 1 for mutual solubility) and the physicochemical properties of the RTIL can be significantly different from those of pure RTILs.$^{10}$ Aside from their bulk properties, the interfacial properties, such as charge transfer across and the double layer structure at the RTIL/W interface are of particular interest. After air-stable and moisture-stable RTILs were introduced in the early 1990s,$^{11-13}$ such RTIL-W two-phase systems have been studied in the field of organic synthesis for phase-transfer catalysis and separation of reactants or products and catalysts.$^{14-16}$ Another immediate-ly conceivable application of RTIL-W two-phase systems is liquid-liquid extraction of charged as well as neutral compounds.$^{17,18}$ In these RTIL-W two-phase systems, the phase-boundary potential (PBP) plays a key role in determining the physicochemical properties of the interface between the RTIL and W phases.$^{19,20}$ The progress in electrochemistry of RTIL-W two-phase systems has started rather recently.$^{19,24}$ This paper describes first the main features of the PBP across the RTIL/W interface and then introduces some examples of the applications. Problems and challenges in this field will be mentioned for further developments of the electrochemistry of this new electrified interface.

2 Phase-boundary Potential Across RTIL/W Interface

When a hydrophobic RTIL is brought into contact with W, the RTIL dissolves in W to some extent and the latter is eventually saturated with the RTIL, while water dissolves in the RTIL phase, resulting in the mutual saturation of the two phases. At this partition equilibrium, there exists a PBP across the RTIL/W interface, Δ$^{s}$φ = \( \phi^{w} - \phi^{i} \), where \( \phi^{w} \) and \( \phi^{i} \) are the inner potentials of the W and RTIL phases, respectively. This PBP is brought about by the difference in the transfer Gibbs energies of the cation and anion of the RTIL. If the interfacial electron transfer between a redox couple in the RTIL and that in W takes place, the exchange of electrons across the interface can also participate in the determination of.
Table 1  Physicochemical Properties of Some Hydrophobic RTIL at 25°C.

<table>
<thead>
<tr>
<th>RTIL</th>
<th>Tm (°C)</th>
<th>η (mPa s)</th>
<th>d (g cm⁻³)</th>
<th>S_liq (mol dm⁻³)</th>
<th>S_w (wt %)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₅ mim⁺][C₂C₆N₃⁻]</td>
<td>-84°</td>
<td>0.093</td>
<td>1.32</td>
<td>1.8 × 10⁻³</td>
<td>0.9</td>
<td>28, 34, 60</td>
</tr>
<tr>
<td>[C₆ mim⁺][C₂C₆N₃⁻]</td>
<td>-</td>
<td>-</td>
<td>1.38</td>
<td>1.1 × 10⁻³</td>
<td>0.6</td>
<td>10, 38</td>
</tr>
<tr>
<td>[TBA⁺][BEHSS⁻]</td>
<td>-71°</td>
<td>0.373</td>
<td>0.993</td>
<td>3 × 10⁻²</td>
<td>8.9</td>
<td>60</td>
</tr>
<tr>
<td>[TPnA⁺][BEHSS⁻]</td>
<td>-71°</td>
<td>0.517</td>
<td>0.978</td>
<td>3 × 10⁻³</td>
<td>6.0</td>
<td>60</td>
</tr>
<tr>
<td>[THxA⁺][BEHSS⁻]</td>
<td>-74°</td>
<td>0.639</td>
<td>0.968</td>
<td>2 × 10⁻⁴</td>
<td>4.5</td>
<td>60</td>
</tr>
<tr>
<td>[THpA⁺][BEHSS⁻]</td>
<td>-80°</td>
<td>0.690</td>
<td>0.961</td>
<td>2 × 10⁻⁵</td>
<td>3.7</td>
<td>60</td>
</tr>
<tr>
<td>[THxA⁺][C₂C₆N₃⁻]</td>
<td>-8</td>
<td>0.388</td>
<td>1.186</td>
<td>7 × 10⁻⁶</td>
<td>0.3</td>
<td>60</td>
</tr>
<tr>
<td>[C₆ ClO₄⁻][TFPB⁻]</td>
<td>31</td>
<td>0.557</td>
<td>1.302</td>
<td>4 × 10⁻¹</td>
<td>0.31</td>
<td>45</td>
</tr>
<tr>
<td>[TOMA⁺][TFPB⁻]</td>
<td>36</td>
<td>0.470</td>
<td>1.228</td>
<td>1 × 10⁻²</td>
<td>0.20</td>
<td>45</td>
</tr>
</tbody>
</table>

*) glass transition point, **: 56°C.

The RTILs, as has been known in conventional liquid-liquid systems, are classified into two types: 1) Distribution potential across an RTIL/W interface

When an RTIL consists of a monovalent cationic and a monovalent anionic species, C⁺ and A⁻, Δ_H[,]\(\Phi\) is given by

\[
\Delta_{H,\phi}^W = -\frac{\Delta G_{C⁺ → W,0} - \Delta G_{A⁻ → W,0}}{2F} = \frac{\Delta_{H,\phi}^{C⁺,0} + \Delta_{H,\phi}^{A⁻,0}}{2},
\]

where \(\Delta G_{C⁺ → W,0}\) and \(\Delta G_{A⁻ → W,0}\) are the standard Gibbs energies of the transfer of C⁺ and A⁻ from RTIL to W, F is the Faraday constant, and \(\Delta_{H,\phi}^{C⁺,0}\) and \(\Delta_{H,\phi}^{A⁻,0}\) are the standard ion transfer potentials of C⁺ and A⁻, respectively, defined by

\[
\Delta_{H,\phi}^{C⁺,0} = -\frac{\Delta G_{C⁺ → W,0}}{zF}.
\]

Here \(z\) is the charge on the ion i with the signed unit of electronic charge (\(i = C⁺\) or \(A⁻\)). Equation (1) is formally the same as the distribution potential between the two immiscible phases formed by the distribution of a salt and tells us that the \(\Delta_{H,\phi}^\theta\) is fixed at a certain value determined by the properties of the cation and anion constituting the RTIL.

When other ions are present in the W phase, these ions may partition in the RTIL phase, depending on the hydrophobicity of these ions, and can affect \(\Delta_{H,\phi}^W\). If they are hydrophilic enough, the partition of these ions in the RTIL phase is negligible because of the hydrophobic environment of the RTIL phase and Eq.(1) is still valid.

An important implication of Eq. (1) is that \(\Delta_{H,\phi}^\theta\) does not depend on the type and concentration of electrolytes in W, provided that they are so hydrophobic that their partition in RTIL is negligible. In other words, hydrophobic RTILs can work as an ideal salt bridge since \(\Delta_{H,\phi}^\theta\) is maintained constant and insensitive to the type and concentrations of electrolytes in W (wide infra).

2.2 Hydrophobicity scale of ions

Since thermodynamic properties of individual ionic species are not measurable, neither \(\Delta_{H,\phi}^{C⁺,0}\) nor \(\Delta_{H,\phi}^{A⁻,0}\) is measurable. Moreover, unlike the transfer Gibbs energy of ions across two immiscible molecular solvents, both \(\Delta_{H,\phi}^{C⁺,0}\) and \(\Delta_{H,\phi}^{A⁻,0}\) are dependent on the particular RTIL species, \(\Delta_{H,\phi}^{C⁺,0}\) values for the same ionic species varies from one RTIL to another. It is therefore not possible to have a unique measure of \(\Delta G_{i → W,0}\) or \(\Delta_{H,\phi}^{C⁺,0}\) that is valid over different RTILs. Nevertheless, it is convenient to have a certain measure of the hydrophobicity or hydrophilicity of ions for estimating, even roughly, these values. In fact, different RTILs show very similar polarity whose magnitude is comparable to that of methanol.

This fact encourages us to find a hydrophobicity scale of ions that can be used for preparation of RTILs. For this purpose, the standard ion transfer potentials established for the nitrobenzene-water and 1,2-dichloroethane-water two-phase systems have been shown to be a handy measure of the hydrophobicity or hydrophilicity of ions used for RTILs.

Figure 1 shows the values of the standard ion transfer potential for the nitrobenzene-water-two-phase system, \(\Delta_{H,\phi}^{C⁺,0}\), for cations and anions as the locations on the abscissa of \(\Delta_{H,\phi}^{C⁺,0}\). First of all, it is seen that \(\Delta_{H,\phi}^{C⁺,0}\) values of the ions widely used for preparing hydrophobic RTILs are mostly located within ± 0.2 V and we can expect that the \(\Delta_{H,\phi}^\theta\) values of those RTILs would spread within \(\Delta_{H,\phi}^W\).
< 0.2 V. Second, ΔHφo values for most alkali metal ions and also Cl− ions are outside of this region. This is the basis of the approximation that validates Eq.(1) even in the presence of foreign ions in W: ΔHφ is likely to be located away from ΔHφo values of alkali metal ions.

Using Fig. 1, one can have an idea about the location of ΔHφ and also the width of the polarized potential window and the solubility of RTILs (vide infra).

2.3 Nerstian response of ΔHφ
Since any types of ionic species have finite solubility in an RTIL, a more general treatment of the partition equilibrium is preferable. A general equation for ΔHφ taking account of the partition of all ionic components in the system should have the same form as the expression of the PBP between the two immiscible electrolyte solutions.32,33 A simple yet important special case is that the W phase contains either C+ or A− whose amount exceeds the solubility of the RTIL in W. This excess of C+ or A− in W is achieved by dissolving a C+ salt of a hydrophilic anion or an A− salt of a hydrophobic cation, such as [C+]Cl− or [Na+]A−. The PBP is then given by,19

$$\Delta_{H}^{\Phi} = \frac{\Delta_{H}^{\Phi^0} + \Delta_{H}^{\Phi^0}}{2} \frac{RT}{F} \ln a_{C}^{\Phi^0} + \frac{RT}{F} \ln k_{w}^{H} \tag{3}$$

$$\Delta_{H}^{\Phi} = \frac{\Delta_{H}^{\Phi^0} + \Delta_{H}^{\Phi^0}}{2} \frac{RT}{F} \ln a_{C}^{\Phi^0} - \frac{RT}{F} \ln k_{w}^{H} \cdot \tag{4}$$

where $a_{C}^{\Phi^0}$ and $a_{C}^{\Phi^0}$ are the activities of C+ and A− in W and $k_{w}^{H}$ is the solubility product of [C+]A− in W, $k_{w}^{H} = a_{C}^{\Phi^0} a_{A}^{\Phi^0}$. In deriving Eqs.(3) and (4), we have assumed that the partition of Na+ and Cl− into the RTIL is negligible, that is, ΔHφ Na+ << ΔHφ C+ << ΔHφ Cl−.

One can see that the PBP shows a nerstian response to both activities of C+ and A− in W. This is the basis of controlling ΔHφ by the concentrations of a salt in W. When the W phase contains more hydrophobic ionic species whose ΔHφ value is close to ΔHφ, the partition of this ion into the RTIL can be significant and the PBP is affected by the activity of this ion, in a way that is exactly the same as the nerstian response of ΔHφ to C+ and A− ions. The PBP is then understood in terms of the concept of mixed potential131 for the phase-boundary potential under the distribution of multiple ionic species.25

3 Electrochemical Polarizability
The solubility of a hydrophobic RTIL in W varies with the hydrophobicity of the ions constituting the RTIL and, quantitatively, they are related through13

$$\ln k_{w}^{H} = -\frac{\Delta G_{H}^{\Phi} - W_{H}}{R} + \frac{\Delta G_{\Lambda}^{\Phi} - W_{H}}{RT} = \frac{F}{R} (\Delta_{H}^{\Phi^0} - \Delta_{H}^{\Phi^0}) \lambda \tag{5}$$

From Eq.(1) and ΔHφo values in Fig. 1, one might expect that an RTIL composed of a tetrabutylammonium (TButA+) and dipicrylamine (DPA−) pair and another

![Fig. 1](image-url)

A scale of the formal and standard potentials for ion transfer across the nitrobenzene/water interface at 25 °C. The number by each ionic species indicates the value in V. Ph,B−: tetraphenylborate; AcCh+: acetylcholine; BzTMA+: benzyltrimethylammonium; Cmim+: 1-allyl-3-methylimidazolium. n designates the number of carbon atoms in the alkyl group; PhAs−: tetraphenylarsonium; CV−: crystal violet.

Data: in Ref., together with unpublished data from the authors’ group.
RTIL composed of a 1-butyl-3-methylimidazolium (C$_\text{mim}^+$) and bis(ethylhexyl)sulfosuccinate (BEHSS$^-$) pair have very similar values of $\Delta V\phi$, both of which are close to zero. However, Eq.(5) tells us that the solubility of [TPnA$^+$][DPA$^-$] is much smaller than that of [C$_\text{mim}^+$][BEHSS$^-$]. At the [TPnA$^+$][DPA$^-$]/W interface, even a trace amount of foreign ions can shift the value of $\Delta V\phi$, whereas the effect of such ions to $\Delta V\phi$ could be negligible at the [C$_\text{mim}^+$][BEHSS$^-$]/W interface because of its greater solubility in W.

From an electrochemical viewpoint, the difference in the solubility of [TPnA$^+$][DPA$^-$] and [C$_\text{mim}^+$][BEHSS$^-$] is reinterpreted in terms of the difference in the electrochemical polarizability of the interface. When the dissolution of the ions in W into the RTIL phase is negligible, it can be shown that the charge transfer resistance of the RTIL/W interface, $R_{ct}$, is inversely proportional to $\sqrt{K_0^w}$. Thus $K_0^w$ of the RTIL is a good measure of the electrochemical polarizability of the RTIL/W interface. For the interface that has a small value of $R_{ct}$, that is, a large $K_0^w$ like [C$_\text{mim}^+$][BEHSS$^-$], we cannot change $\Delta V\phi$ by externally applying the potential across the interface because of a large current across the interface; the interface is electrochemically nonpolarized, as illustrated in curve 5 in Fig. 2 for the interface between 1-methyl-3-octylimidazolium bis(pentafluoroethysulfonlylimide ([C$_\text{mim}^+$][C$_6$H$_4$N$^-$]). At the interface that has a large value of $R_{ct}$ like [TPnA$^+$][DPA$^-$], the current caused by the deviation of $\Delta V\phi$ by applying the voltage across the interface is small. Then, the interface practically behaves as an electrochemically polarized interface. In other words, the interface has a certain polarized potential window (ppw) (curves 1-4 in Fig. 2). Equation (5) shows that $K_0^w$ is also a quantitative measure of the ppw.

4 Applications of Nonpolarized RTIL/W Interface

4.1 RTIL salt bridge

The capability of RTILs as a conceptually new salt bridge has been demonstrated for 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_\text{mim}^+$][C$_6$H$_4$N$^-$]). The PBP is stable within $\pm$ 1 mV for the change in the concentration in W between 1 mmol dm$^{-3}$ and 0.5 mol dm$^{-3}$ for HCl, LiCl, NaCl, and KCl. The gelation of the RTIL phase with poly(vinylidene fluoride-co-hexafluoropropylene) did not affect the stability of the PBP. The shape of the interface, that is, the type of the contact of the salt bridge with a test solution, is immaterial, thanks to its thermodynamic basis of the generated PBP, not to the transport properties ions as is the case of KCl-type salt bridges. In many cases where KCl-type salt bridges have been used, the RTIL bridge is a better alternative of the century-old KCl-type.

The challenge in this direction is to optimize the component of the RTIL, taking account of the solubility, durability, and toxicity of the RTIL. The polarizability of the RTIL/W interface and the possible interference of the PBP with foreign components should be given careful thoughts in designing RTIL salt bridges.

4.2 Control of $\Delta V\phi$ of nonpolarized RTIL/W interface

The nernstian response of the RTIL/W interface described in Eqs.(3) and (4) has been demonstrated by potentiometry and voltammetry of a thin-RTIL-layer-coated electrode. The deviation from the nernstian response at higher concentrations of electrolytes in the W phase is presumably caused by the dissolution of the ions in W into the RTIL phase. A quantitative explanation needs the knowledge of the activities of dissolved ions in the RTIL, which are not known, and a subject of further studies.

The nernstian response to the potential determining ions has been utilized in studying the electrocapillarity of the RTIL/W interface, the interfacial electron transfer, and zeta potential of RTIL emulsion particles. In these applications, the range of $\Delta V\phi$ that has been achieved is about 300 mV, which is limited by the experimentally accessible concentration range of the potential-determining ions in W, a few mol dm$^{-3}$.

5 Polarized RTIL/W Interface

There have been several attempts to polarize the RTIL/W interface. To obtain a voltammogram that is amenable to quantitative analysis for evaluating a half-wave potential and other characteristic parameters, the ppw of at least 200 mV is required. Referring to Figs. 1 and 2, we can see that this corresponds to the difference of about 500 mV in $\Delta V\phi$ values of the cation and the anion constituting the RTIL.

For studying a particular charge transfer process, not only the width of the ppw but also the location of the ppw is to be optimized, so that the targeted charge transfer takes place within the ppw. The extension of the ppw to the positive direction of $\Delta V\phi$ has been achieved using tetraakis[3,5-bis(trifluoromethyl)phenyl]...
borate (TFPB⁻) as the anion of the RTIL.⁴⁵ By using this RTIL, voltammetry of the ion transfer of moderately hydrophilic cations, such as tetramethylammonium (TMA⁺) and acetylcholine (AcCh⁺) and of moderately hydrophobic anions, such as C₆H₄N⁻, was made possible, but at 56°C due to high viscosities. Voltammograms for the transfer of tetrapropylammonium, tetraethylammonium, C₆H₄N⁻, and C₂H₄N⁻ ions across the interface between N-octadecylisoquinolinium TFPB ([C₆H₄][TFPB⁻]) and water are displayed in Fig. 3.⁴⁶ It is seen that the transfer of these moderately hydrophilic cations and moderately hydrophobic anions are voltammetrically detected within the ppw using a micro liquid-liquid interface formed at the tip of a glass capillary filled with a corresponding aqueous solution.

The use of a micro liquid-liquid interface is virtually imperative in these measurements because of a large solution resistance of the RTIL phase. Care must be taken in interpreting voltammograms obtained, since the quasi-steady-state appearance reflects the shape of the capillary tip.⁴³, ⁴⁷, ⁴⁸ The half-wave potential and the limiting current is a function of the detailed shape of the capillary tip.

The width of the ppw of [C₆H₄][TFPB⁻]|W interface is determined by the transfer of Cl⁻ and Li⁺ ions, which are added in W as a supporting electrolyte, at the negative and positive ends, respectively.⁴⁹ For a wider ppw, an appropriate selection should be made not only for the RTIL but for the aqueous electrolytes. RTILs having a similar ppw and yet a lower melting point are to be sought for in order to use a polarized RTIL/W interface for practical applications, such as an electrochemical detector of ions in chromatography and electrophoresis, a membrane for ion-selective electrodes, and electrochemical extraction of metal ions.

6 Structure of RTIL/W Interface

It has been shown above that the PBP at an RTIL/W interface can be altered in the range of 300 mV and 1000 mV in nonpolarized and polarized interfaces, respectively. The distribution of such magnitudes of the PBP across the interface is intriguing. Electrocapillarity measurements at a RTIL/W interface provide a thermodynamic basis to deduce the structure of the electrical double layers. An electrocapillary curve of nonpolarized RTIL/W interface has been reported for [C₄mim⁺][C₆H₄N⁻] | W interface, from which the specific adsorption of C₄mim⁺ ions and its dependence on the PBP have been demonstrated.⁵⁰

Figure 4 shows electrocapillary curves for the interface between tetrahexylammonium bis(trifluoromethylsulfonyl)imide ([THA⁺][C₆H₄N⁻]) and an aqueous LiCl solution at three different concentrations of LiCl.⁵¹ The electrocapillary maximum appeared within the ppw and shifted to the negative direction with increasing concentrations of LiCl. Simultaneously, the interfacial tension increases with increasing concentration of LiCl. These features strongly suggest that neither Li⁺ nor Cl⁻ is specifically adsorbed at the interface around the point of zero charge. Further analysis of the surface excess of Li⁺ confirmed the absence of appreciable specific adsorption within the ppw.⁵² The double layer structure is thus well described by the Gouy’s model.⁵³ It might seem that this is unsurprising. However, this is not always the case at RTIL/W interfaces. The presence of specific interactions between the ions at the RTIL surface with the ions in the W phase has been suggested in other RTILs.⁵⁴

The double layer structure in the RTIL side of the interface has not been elucidated. The high salt concentration of about 1.5 to 2 mol dm⁻³, with an insignificant amount of water under the mutual saturation, suggests a rapid decay of the potential drop in the RTIL side of the interface. The possibility of the stratification of charged layers in the RTIL phase, which has been suggested in

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**Fig. 3** Cyclic voltammograms at the interface between [C₆H₄][TFPB⁻] and W containing 90 mmol dm⁻³ LiCl and 10 mmol dm⁻³ [TPrA⁺][Cl⁻] (curve 1) or [TEA⁺][Cl⁻] (curve 2), or 100 mmol dm⁻³ LiCl and 10 mmol dm⁻³ [Li⁺][C₆H₄N⁻] (curve 3) or [Li⁺][C₂H₄N⁻] (curve 4). Sweep rate: 20 mV s⁻¹. Inner diameter of the capillaries: 2 μm. Adapted from ref.⁴⁶

**Fig. 4** Electrocapillary curves at the interface between [THA⁺][C₆H₄N⁻] and W. The vertical bar at each point shows the standard deviation (error). The concentrations of LiCl in W phase are 1.0 mol dm⁻³ (curve 1), 0.1 (curve 2), and 0.01 (curve 3). Solid lines are to guide the eye. Adapted from ref.⁵¹ (Copyright, American Chemical Society).
concentrated aqueous electrolyte solutions\textsuperscript{53,54} and also at the RTIL/air interface\textsuperscript{55,56} is very likely in the RTIL side of the interface. Probing such characteristic features of the electrical double layer in the RTIL side is a challenge and would provide a clue to understand slower charge transfer kinetics in the RTIL phase\textsuperscript{57,58}.

The molecular details of the orientation of ions constituting an RTIL are of considerable interest in view of specific interactions of ions in W and those in the RTIL at the interface. Sum frequency generation has been successfully employed for studying the surface of 1-butyl-3-methylimidazolium BF\textsubscript{4} containing varying amount of water in contact with air.\textsuperscript{59} The dependence of the orientation of RTIL constituting ions at the RTIL/W interface on the PBP has been probed by surface second-harmonic generation.\textsuperscript{60} Further applications of such spectroscopic approaches in combination with molecular dynamics simulations will be illuminating for understanding interface-specific interactions of ions, or interfacial ion pair formation,\textsuperscript{61} that can determine the structure of the inner part of the double layer at the RTIL/W interface.

7 Conclusions

In using hydrophobic RTILs for a partition or a chemical reaction in liquid-liquid two-phase systems, the RTIL phase behaves in a manner similar to a molecular solvent immiscible with water yet having a high polarity, like nitrobenzene. However, there is a clear distinction between RTIL/W and organic solvent/W interfaces. The uniqueness of RTIL/W two-phase systems resides in the phase-boundary potential which stems from the very fact that RTILs are electrolytes. The main features of this electrified interface have been highlighted above. The concepts established in the foregoing studies of the electrochemistry of liquid-liquid interfaces\textsuperscript{62,63} are helpful and conveniently used. Understanding and exploiting the properties intrinsic to the RTILs have not, however, been fully developed and are expected to be achieved in a few years to come based on a combination of macroscopic knowledge with insight of molecular details of RTIL/W as well as RTIL/nonpolar organic solvent interfaces.

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