Novel Electrochemical Studies of Ionic Liquids

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Room-temperature ionic liquids (ILs) have been proposed as alternative solvents for organic synthesis, separations, and electrochemical applications. Here, we report studies that probe the electrochemical and solvation properties of a tetraalkylammonium (methyltributylammonium bis(trifluoromethylsulfon)imide, M3BNIm) and an imidazolium (1-butyl-3-methylimidazolium hexafluorophosphate, $BMIPF_6$) based ionic liquid. It is demonstrated that despite impurities, the cathodic limit at a Pt electrode is enhanced for the tetraalkylammonium-based IL. Electrogenerated chemiluminescence of tris(2,2′-bipyrindinyl)ruthenium ($Ru(bpy)_3{}^{2+}$) was observed in both ionic liquids, and differences in the response were interpreted in terms of the solvent reactivity and polarity. As ILs have been proposed as alternatives to organic solvents in extraction processes, an understanding of the relative lipophilicity of the IL ions and the equilibrium potential difference established across the IL/water interface is of fundamental relevance. Here, electrochemical measurements at a conventionally polarized liquid−liquid interface (water/1,2-dichloroethane) were used to determine the relative lipophilicity of the IL constituent ions. From formal ion transfer potential values ($\Delta_o^w \phi_i^0$) obtained, the standard ionic partition coefficients could be estimated. The polarizability of the neat ionic liquid/water interface was investigated. From these studies, it can be seen that $BMIPF_6$ is hydrophilic while M3BNIm is moderately hydrophobic. The significance of the potential difference established across the IL/water interface is discussed.

Introduction

Ionic liquids (ILs) or room-temperature molten salts are of interest because of their unique chemical and physical properties. These include high thermal stability, negligible vapor pressure, low toxicity, low melting temperature, and good electrochemical stability.[1,2] For example, they have been proposed as "green" alternatives to volatile organic chemicals (VOCs) in extraction processes,[3−6] as the solvent/base electrolyte in solar cell applications,[7,8] as media for selective catalytic processes,[9−13] and as components in electrochemical capacitors.[14,15] A typical ionic liquid which is air and water stable is based on the combination of bulky substituted *N*-alkylpyridinium or *N*,*N*′-dialkyimidazolium cations with a variety of anions such as $AlCl_4{}^-$, $PF_6{}^-$, $BF_4{}^-$, $CF_3SO_3{}^-$, and $(CF_3SO_2)_2N^-$.

In comparison to other areas such as catalysis, extraction, and organic synthesis,[2,5,16] relatively few fundamental electrochemical studies of these ionic liquids have been reported. Most have considered the electrochemical potential window of the melt,[14,15,17−21] an exception being the water-soluble 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid where the electrochemistry of ferrocene, tetrathiafulvalene, lithium, copper, cadmium, and silver[22−25] dissolved in the melt was considered. Recently, Schroder et al.[26] reported studies concerning the effect of dissolved water on the redox properties of three redox couples in two hydrophobic imidazolium-based $PF_6{}^-$ and $BF_4{}^-$ melts. As ionic liquids have been proposed as alternative solvents in diverse electrochemical applications such as electroplating of base metals, rechargeable batteries, and electrochromic devices, it is of interest to increase the amount of fundamental data available to realize fully the potential of these solvents.

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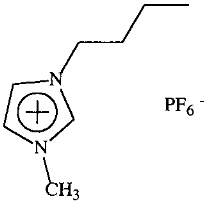
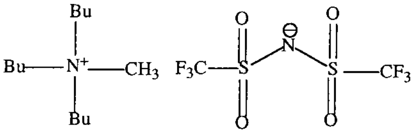
Here, we consider some novel approaches based on redox reactions at metallic electrodes, electrogenerated chemiluminescence (ECL), and liquid−liquid electrochemistry to further evaluate the electrochemical and solvation properties of two typical ionic liquids. Imidazolium melts are the most widely studied, and thus the 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF$_6$) was chosen as an example for study. MacFarlane et al.[20] and more recently Xu et al.[15] have demonstrated that quaternary ammonium cations can be combined with "soft" anions (e.g., bis(trifluoromethylsulfon)imide, known simply as "imide") to obtain ILs that are liquid at room temperature. Such cations are known to have good electrochemical stability, which accounts for the general use of their salts as base electrolytes in nonaqueous electrochemistry. Methyl tributylammonium imide (M3BNIm) was chosen as a typical example for study.



BMIPF$_6$



M3BNIm

To investigate these ILs as alternative solvent/base electrolyte systems for conventional electrochemical measurements at metallic electrodes, the redox behavior of tris(2,2′-bipyridinyl)ruthenium (Ru(bpy)$_3^{2+}$) was investigated in both liquids. As Ru(bpy)$_3^{2+}$ is one of the most commonly used reactants in ECL,[27] the possibility of observing ECL in an ionic liquid was also considered.

Ionic liquids such as BMIPF$_6$ and M3BNIm, which are immiscible with water, have been proposed as media for selective separation, for example, in two-phase catalytic reactions. However, unlike volatile organic solvents, ionic liquids are composed of ions, which can partition into the aqueous phase depending on their relative hydrophobicity/hydrophilicity. Contacting two immiscible phases results in a spontaneous distribution of the neutral and ionic species.[28] In contrast to conventional organic solvents used in solvent extraction, where the degree of miscibility is dependent on the mutual solubility of the neutral solvents, constituent IL ions can partition into the aqueous phase establishing an interfacial potential difference. In this sense, the characteristics of the immiscible interface between a hydrophobic ionic liquid and water can be understood with reference to electrochemical studies of the interface between two immiscible interfaces (known by the acronym ITIES; interface between two immiscible electrolyte solutions).[29] A typical ITIES is the interface formed between a hydrophilic electrolyte dissolved in water and a hydrophobic electrolyte dissolved in an organic solvent (e.g., 1,2-dichloroethane). The potential difference established is dependent on the relative hydrophilicity/hydrophobicity of the constituent anions and cations.[29−31] Generally, the distribution of a charged species between the organic and aqueous phase can be expressed by the Nernst equation for ITIES,[29]

$$\Delta_{\mathrm{o}}^{\mathrm{w}}\phi = \Delta_{\mathrm{o}}^{\mathrm{w}}\, \phi_i^0 + \frac{RT}{z_iF}\ln\left(\frac{a_{\mathrm{i}}^{\mathrm{o}}}{a_{\mathrm{i}}^{\mathrm{w}}}\right) = \Delta_{\mathrm{o}}^{\mathrm{w}}\, \phi_i^{0'} + \frac{RT}{z_iF}\ln\left(\frac{c_{\mathrm{i}}^{\mathrm{o}}}{c_{\mathrm{i}}^{\mathrm{w}}}\right) \quad (1)$$

where a_i, c_i, and z_i refer to the activity, concentration, and charge number of ion i in water (w) and the organic phase (o), respectively; $\Delta_{\mathrm{o}}^{\mathrm{w}}\phi$ represents the Galvani potential difference established across the interface, and $\Delta_{\mathrm{o}}^{\mathrm{w}}\,\phi_i^0$ is the standard transfer potential and $\Delta_{\mathrm{o}}^{\mathrm{w}}\,\phi_i^{0'}$ is the formal transfer potential of ion i. Other symbols have their usual meaning. The standard transfer potential is related to the standard Gibbs energy of transfer $\Delta G_{\mathrm{tr},i}^{0,\mathrm{o}\rightarrow\mathrm{w}}$ as follows: $\Delta_{\mathrm{o}}^{\mathrm{w}}\,\phi_i^0 = -\Delta G_{\mathrm{tr},i}^{0,\mathrm{o}\rightarrow\mathrm{w}}/z_iF = (\mu_i^{0,\mathrm{o}} - \mu_i^{0,\mathrm{w}})/z_iF$ where μ_i^0 is the standard chemical potential. $\Delta G_{\mathrm{tr},i}^{0,\mathrm{o}\rightarrow\mathrm{w}}$ can be considered as a measure of the lipophilicity of the ion.[32]

Electrochemical measurements at ITIES have been shown to be a suitable technique for determining the partition coefficients of ionic species and also to construct ionic partition diagrams.[32,33] Here, the transfer of IL ions was studied at the polarized water/1,2-dichloroethane interface (w/1,2-DCE). In a related study, neat ILs were used in place of the organic solvent/hydrophobic base electrolyte normally used in ITIES measurements and the size of the available potential window at the water/IL interface was investigated.

Experimental Section

Methyl tributylammonium bis(trifluoromethylsulfon)imide ($(CF_3SO_2)_2N^-$) (M3BN$^+$Im$^-$) was obtained by metathesis from methyl tributylammonium chloride (Sachem, Austin, TX) and lithium bis(trifluoromethylsulfon)imide (3M Corp., St. Paul, MN) by the procedure described by McFarlane.[17] 1-Butyl-3-methylimidazolium hexafluorophosphate (BMI$^+$ PF$_6^-$) was prepared by metathesis of the corresponding imidazolium chloride (Sachem, Austin, TX) and HPF$_6$ as in a previous study.[34] The resulting ILs were washed well with water and treated with both alumina and activated carbon to remove impurities. All chemicals and solvents were of the highest commercially available quality and were used as received.

For the electrochemical measurements at metallic electrodes, an acetone solution of tris(2,2′-bipyrindinyl)ruthenium (Ru(bpy)$_3^{2+}$) perchlorate was added under stirring to the IL with the acetone subsequently removed by heating under vacuum. All ionic liquid solutions were dried under vacuum for at least 36 h at 100 °C. Prior to electrochemical measurements at metallic electrodes, the solutions were degassed and transferred to airtight cells. The success of water and dissolved oxygen removal could be easily gauged from cyclic voltammograms (CVs) at a Pt electrode, since both of those limit the electrochemical window, if present. Solutions were dried and degassed until the characteristic peaks disappeared.

CVs and chronoamperograms were recorded using a CHI 900 potentiostat (CH Instruments, Austin, TX). A three-electrode configuration was used where a Pt electrode (macro $d = 0.1$ cm, micro $d = 25$ and 2 μm), a Pt coil, and a silver wire served as working, counter, and quasi-reference electrodes, respectively. The preparation of ultramicroelectrodes used ($d = 25$[35] and 2 μm[36]) has been described previously.

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The ECL signal was measured with a photomultiplier tube (PMT) (type R928, Hamamatsu Corp., Middlesex, NJ) installed under the electrochemical cell in a black box as described previously.[37] A voltage of −750 V was applied to the PMT with a high-voltage power supply (Series 225, Bertan High Voltage Corp., Hicksville, NY). The ECL signal measured from the PMT as a photocurrent was transformed into a voltage signal by an electrometer (model 6517, Keithley, Cleveland, OH) and fed into the external input channel of an Autolab electrochemical workstation (Eco Chemie BV, The Netherlands). Cyclic voltammetric ECL and ECL transients were then recorded. A charge coupled device (CCD) camera (CH260, Photometrics Inc, Phoenix, AZ) cooled with liquid nitrogen to below −110 °C and interfaced with a personal computer was used to acquire the ECL spectra. The camera was focused with a 100 mm lens (Pentax) on the output of a grating spectrometer (Chemspec 100S, American Holographics Inc., Littleton, MA). The recorded spectra were calibrated with a Hg−Ar vapor lamp. The CCD camera and general configuration of the spectra acquisition have been described previously.[38] This entire setup was located in a dark room. The absorption and fluorescence spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer and Jobin-Ivon fluorimeter (Fluorolog), respectively.

For the ITIES measurements, cyclic voltammetry at the micropipet-supported liquid−liquid interface[39] was used to study the transfer of $M3BN^+$, Im^-, BMI^+, and PF_6^- ions at the polarized water/1,2-dichloroethane (1,2-DCE) interface. The preparation of the tip and experimental arrangement used were as previously described.[39] The tip was filled with the aqueous phase and dipped into the organic phase. A simple two-electrode arrangement was used, and the electrochemical cell can be written as follows:

$$\mathrm{Ag/AgCl/LiX_{(water)}//BTPPATPBF_{5\ (1,2\text{-}DCE)} + IL/Ag}$$

where $BTPPATPBF_5$ refers to the hydrophobic organic base electrolyte used (bis(triphenylphosphoranylidene) ammonium tetrakis pentafluoroborate), LiX refers to the aqueous base electrolyte (LiCl or Li_2SO_4), IL refers to the ionic liquid dissolved in the DCE phase, and // represents the polarizable interface under investigation. A silver/silver chloride electrode served as both counter and reference electrode for the aqueous phase, while an Ag quasi-reference electrode (QRE) was used in the organic phase. The cell potential scale was referenced to the absolute scale using the transfer of the tetramethylammonium cation (TMA^+) as an internal reference.[32] This involved adding TMACl to the aqueous phase after each measurement and correlating its transfer potential on the cell scale with its literature value on the absolute galvanic scale ($\Delta_o^w \phi_{TMA^+}^{0'} = 0.16$ V[40]). The potential was taken as that of the water phase with respect to the organic phase $\Delta_o^w\phi = (\phi^w - \phi^o)$.

In separate measurements, the 1,2-DCE phase was replaced by neat IL and the polarizability of the resulting aqueous/ionic liquid interface was investigated. The size of the available potential window is representative of the lipophilicity of the IL ions.

Results and Discussion

(1) Electrochemistry at Metallic Electrodes. Typical CVs recorded at a 25 μm Pt microelectrode to determine the electrochemical windows of the neat ILs are given in Figure 1. As can be seen from the figure, there is little difference between the anodic limits with PF_6^- and Im^- anions. This is in agreement with previous reports by McEwen et al.[14,19] where a glassy carbon (GC) electrode was used. However, Xu et al.[15] recently reported that PF_6^- was more stable than Im^- by ca. 0.6 V also based on studies at a GC electrode. For the cathodic window limit, there is a difference of ca. 2 V between the reduction potentials for the imidazolium and tetraalkylammonium cations. The lower potential for reduction of 1,3-dialkylimidazolium has been attributed to H(2) acidity.[18] The additional cathodic (ca. −3 V vs QRE) and anodic (ca. +1.5 V vs QRE) waves apparent for M3BNIm indicate residual impurities at the mM level (ca. 0.4% impurity level). However, various purification treatments attempted (the neat melt was washed with water, extracted to 1,2-DCE, treated separately with alumina and Ag_2O to remove residual Cl^-, and refluxed in activated carbon for several hours; the ionic liquid solution was then filtered, rotovapped to remove 1,2-DCE, and dried under vacuum) had little effect on the height of these waves. The cathodic wave height was sensitive to the presence of dissolved oxygen and decreased with N_2 sparging, reaching the limiting minimum value shown in Figure 1. The sigmoidal shape suggests that the electrode reaction is coupled to homogeneous chemical reactions. These waves are most likely due to residual impurities in the metathesis reactants used in the preparation, and the success of their removal will depend on the purification of the starting materials used. The anodic impurity may be the reason for the apparent lower stability of the imide ion at a GC electrode observed by Xu et al.[15] If these impurities can be removed, the electrochemical window at a Pt electrode is almost 6 V. The reported electrochemical stability of the melt is dependent on the electrode used (graphite, tungsten, GC, or Pt).[15,21] To our knowledge, this is the largest potential window noted for an IL at a Pt electrode. Considering reports by Suarez and co-workers,[21] the window may be even greater at electrodes less reactive than Pt, such as tungsten or GC.

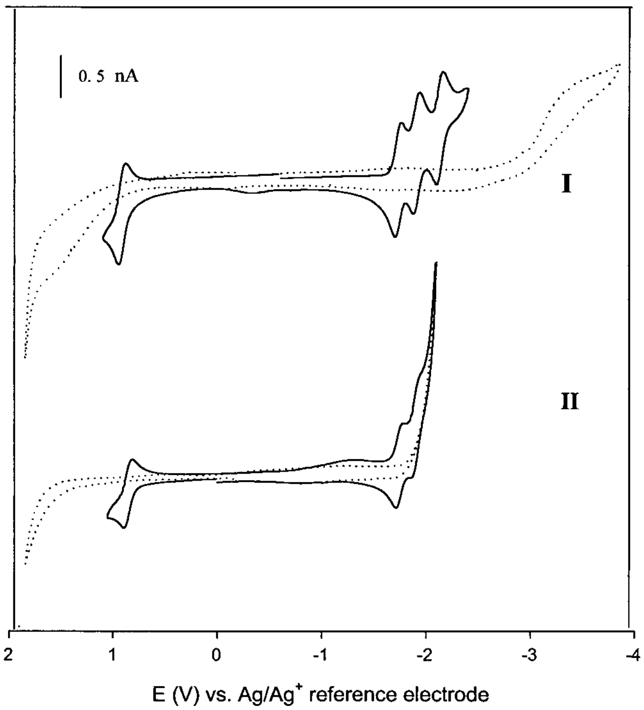

Figure 1. Cyclic voltammograms of neat ILs at a Pt microelectrode with and without added $Ru(bpy)_3^{2+}$ (diameter = 25 μm, scan rate = 100 mV s^{-1}): (I) M3BNIm and (II) $BMIPF_6$. $Ru(bpy)_3^{2+}$ concentrations: (I) 38 mM and (II) 13 mM.

CVs in the presence of dissolved $Ru(bpy)_3^{2+}$ are also given in Figure 1. The resulting voltammograms were peak shaped indicative of linear diffusion of the reactants to and from the electrode surface. Three reduction peaks

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Table 1. Diffusion Coefficients Determined for $Ru(bpy)_3^{2+}$ in Neat IL and the IL Viscosity Determined Using the Stokes−Einstein Relation

	$D_{Ru(bpy)_3^{2+}}$ ($cm^2\ s^{-1}$)	η (cP)[a]	c (mM)
M3BNIm	$1.18 \pm 0.12 \times 10^{-9}$	2710 ± 690	38
$BMIPF_6$	$4.8 \pm 0.5 \times 10^{-9}$	660 ± 175	13

[a] Estimated from $D_1\eta_1 = D_2\eta_2$ using $D = 2.3 \pm 0.6 \times 10^{-6}$ $cm^2\ s^{-1}$ and $\eta = 1.39$ cP for *N*,*N*-dimethylformamide (ref 43).

are apparent in the $M3BN^+$ IL, while the reduction of BMI^+ obscures the third reduction peak. This confirms the increased cathodic stability of M3BNIm. The difference in peak potentials for the oxidation and first reduction peaks ΔE_p ($= E^0_{ox} - E^0_{red}$) was 30 mV greater for the M3BNIm salt. ΔE_p can be taken as a measure of the solvent polarity and generally decreases as solvent polarity increases, which would suggest that the $BMImPF_6$ IL is more polar.[41] However, this effect can also be due to association between electrogenerated ions and the IL anion.

The $Ru(bpy)_3^{2+}$ voltammetric response was peak shaped, even with the 25 μm diameter electrode. Because of the high viscosity of the melts, diffusion coefficients of the redox species are low and mass transfer is controlled by linear diffusion for an electrode of this size. CVs are therefore peak shaped. A steady-state response was only observed with the smallest ultramicroelectrode used (diameter = 2 μm), where the mass transfer coefficient was sufficiently enhanced.[27] Chronoamperometric measurements carried out using the 2 μm ultramicroelectrode allow determination of the concentration (c) and diffusion coefficient (D) of $Ru(bpy)_3^{2+}$ in both ILs.[26,42] The potential was stepped from a zero current potential to a potential in the diffusion-limited plateau. The resulting chronoamperometric curves were plotted versus $t^{-1/2}$, and the diffusion-limiting current, i_d, was determined by extrapolating the linear portion to $t \rightarrow \infty$. It has been shown that for long times, the following relation holds:

$$i/i_d = 1 + 2r\pi^{-3/2}D^{-1/2}t^{-1/2}$$

Thus, D can be determined, with a precision of about 10%, from the slope of i/i_d versus $t^{-1/2}$.[42] The concentration can then be calculated from $i_d = 4rFDc$. Assuming that the Stokes−Einstein relation ($D_1\eta_1 = D_2\eta_2$) holds for ionic liquids, the viscosity (η) of the liquid can be estimated using values for the diffusion coefficient in a solvent of known viscosity.[43] Values obtained are also listed in Table 1. Both ILs are very viscous with the $M3BN^+$ especially so, and this may limit their application at room temperature. The viscosity values of $BMIPF_6$ calculated in this manner are 2−3 times higher than the values reported at room temperature previously.[44,45] This disagreement is perhaps due to ion pair interactions between the ions comprising the ionic liquid solvent and the doubly charged $Ru(bpy)_3^{2+}$. Several studies[45] have shown that $BMIPF_6$ should not be considered a random array of disordered ions (as a dissolved salt in an inert solvent might be) but is rather a three-dimensional network of ion pairs and aggregates. If a highly charged ion such as $Ru(bpy)_3^{2+\bullet}$ were ion paired in a larger network of ions, its effective molecular weight and radius would be higher than expected, which would decrease its diffusion coefficient, and result in an error in the viscosity estimate.

Values for D, c, and η determined in this way are susceptible to the presence of adsorbed moisture from the air, and the currents tended to increase if the cell was not completely airtight. This was true even at very low water concentrations where the characteristic peaks for water decomposition were not apparent. The presence of adsorbed water decreases the viscosity and increases the diffusion rate in the melt, as has been noted previously.[26]

(2) Electrogenerated Chemiluminescence. For the ECL experiments, a larger Pt working electrode was used ($A = 0.78$ mm^2) to increase the amount of light generated to detectable limits. Typical CVs and corresponding ECL emission versus potential curves are given in Figure 2. The CV response is peak shaped as expected, with greater uncompensated resistive drop, iR_u, compared to the ultramicroelectrode. The increase in current after the third reduction peak apparent in Figure 2b may be due to fouling of the electrode by neutral $Ru(bpy)_3$.

In a classical ECL experiment, excited states are produced by electron transfer between oxidized and reduced species generated at an electrode by alternating potential steps or sweeps or at a pair of closely spaced electrodes.[27]

$$R^+ + R^- \rightarrow R^* + R \qquad (2)$$

$$R^* \rightarrow R + h\nu \qquad (3)$$

For R = $Ru(bpy)_3^{2+}$, the redox reaction occurs between $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^+$. For the case of the M3BNIm melt, ECL peaks at 0.085 and −1.85 V were apparent as the potential was repetitively scanned between the oxidation and first reduction peaks indicating that both the electrogenerated species are stable in the IL. When the potential was scanned to more negative potentials (< −1.85 V), the ECL signal decreased due to both diffusion limitation and reduction of $Ru(bpy)_3^+$ to neutral $Ru(bpy)_3$. The very low intensity of the ECL signal is due to the slow diffusion of the reacting species in the viscous melt. In contrast, for $BMIPF_6$, the absence of an ECL signal at reducing potentials indicates that the oxidized form, $Ru(bpy)_3^{3+}$, is not sufficiently stable on the time scale of the experiment and thus is not available to react with electrogenerated $Ru(bpy)_3^+$. On the other hand, $Ru(bpy)_3^+$ was sufficiently stable and an ECL peak is observed at 0.085 V. The intensity is also low, though in this case there was also evidence of a coreactant effect[27] as the ECL signal intensity increased when the potential was scanned into regions where BMI^+ is reduced. This indicates that the reduction products of the IL cation might also react with electrogenerated $Ru(bpy)_3^{3+}$ resulting in an increase in ECL intensity, which is much higher than that in M3BNIm as the reactive BMI^+ concentration is in excess of $Ru(bpy)_3^{2+}$. As the potential was scanned to more negative potentials, extra oxidation peaks were apparent in the middle of the window on scan reversal (e.g., the extra peak apparent at ca. −0.85 V) due to oxidation of the products of BMI^+ reduction. The CV response became distorted after scanning to very negative potentials (−2.75 V); however, the ECL signal at 0.085 V increased by several orders of magnitude (not shown). As can be seen from Figure 2a, light emission does not decay to zero upon scan reversal until the applied potential is ca. −0.5 V which is considerably more negative than the $Ru(bpy)_3^{3+}$ oxidation potential. This reason for this is unclear, but it may be caused by some residual process involving the +3 form and a species acting as a coreactant.

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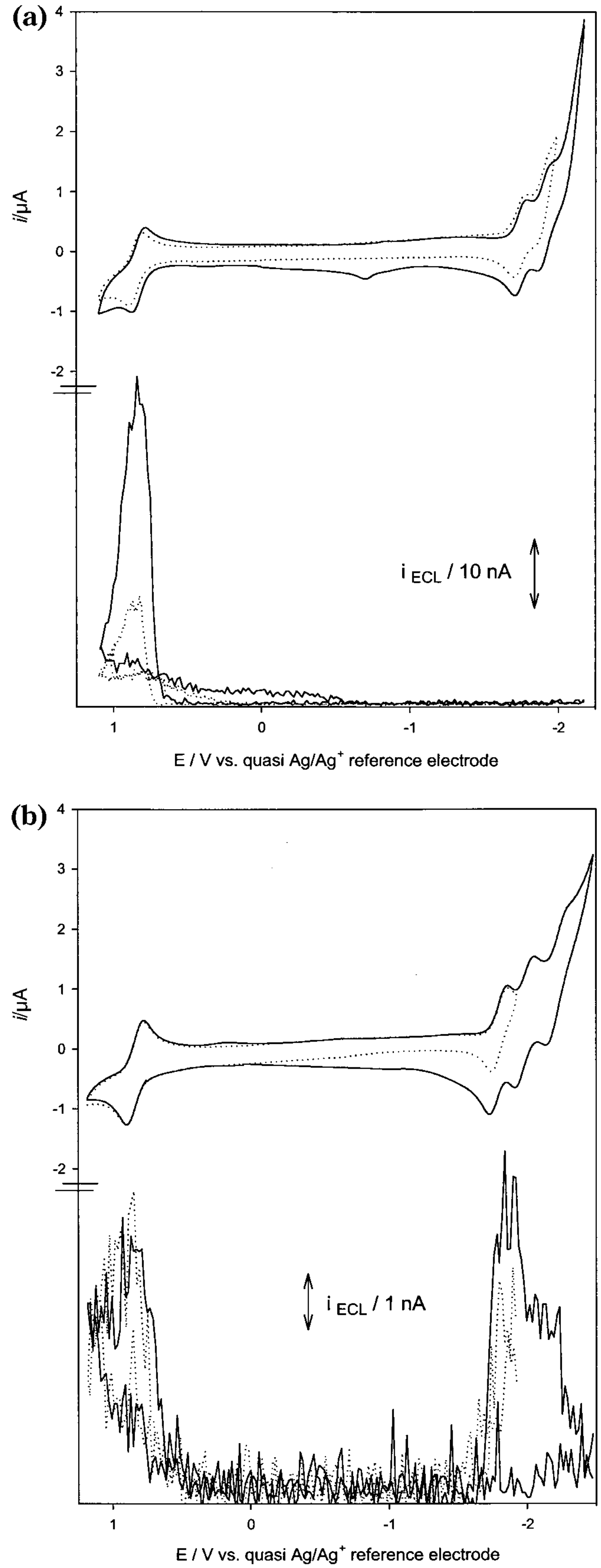

Figure 2. Cyclic voltammograms and ECL−voltage curves recorded simultaneously at a Pt electrode for Ru(bpy)$_3^{2+}$ dissolved in neat (a) BMIPF$_6$ and (b) M3BNIm (scan rate = 100 mV s^{-1}, $A = 0.78$ mm^2). Concentrations are as in Figure 1.

ECL spectra (Figure 3a) were obtained from the annihilation reaction between the electrogenerated Ru(bpy)$_3^{3+}$ and Ru(bpy)$_3^+$ formed by stepping the potential between the oxidation and reduction potentials for Ru(bpy)$_3^{2+}$ in both melts with 100 ms steps. The fluorescence and absorption spectra obtained for Ru(bpy)$_3^{2+}$ in both melts are given in Figure 3b. The metal to ligand charge transfer (MLCT) absorption maxima ($\lambda = 450$ nm) in both solvents were consistent with previous reports[47,48] and did not depend on solvent polarity because the Ru(bpy)$_3^{2+}$ molecule has a highly symmetrical configuration. The ECL and photoluminescence (PL) maxima in BMIPF$_6$ (λ_{ECL} = 629 nm and λ_{PL} = 609 nm) are slightly red shifted compared to those in M3BNIm (λ_{ECL} = 620 nm and λ_{PL} = 600 nm), indicating that the former is more polar and stabilizes the excited state, and hence decreases the transition energy, with respect to the ground state.[48,49] Definition of the polarity of ionic liquids is complex as many different interactions may be involved, such as hydrogen bonding, π-interactions, or van der Waals forces.[13] From studies based on fluorescent and solvatochromic dyes,[18,50−52] the polarity reported for the 1,3-alkylimidizolium- and pyridinium-based ILs has typically been between that of acetonitrile and methanol. The polarity may be cation dependent.[51] However, it has been suggested that the apparent IL polarity may depend on the probe used.[13]

Examples of ECL intensity transients in both ILs are given in Figure 4. For the M3BNIm, light is observed for both the positive and negative pulses (Figure 4b). However, the intensity is higher in the positive pulse indicating that Ru(bpy)$_3^{3+}$ is less stable in comparison with Ru(bpy)$_3^+$. For the BMIPF$_6$ melt (Figure 4a), a similar response was noted though the difference between positive and negative pulses was not as great. Comparing Figures 4a and 2a, Ru(bpy)$_3^{3+}$ is sufficiently stable in BMIPF$_6$ to observe light on the transient time scale (1 s) but not for slower sweeps (>25 s). For both melts, the duration of each ECL transient was short (<0.4 s for M3BNIm and <0.2 s for BMIPF$_6$) and the decay is typically faster in the negative pulse direction. The decrease in ECL noted with repetitive pulses is likely to be due to the instability of Ru(bpy)$_3^{3+}$ or a buildup of Ru(bpy)$_3^0$ on the electrode surface. For the M3BNIm, the lag in ECL response with applied potential indicates an appreciable RC time constant. Note that in the transient measurements, the ECL response is in the μA range, while in the CVs, it is in the nA range.

These results show that ECL reactions can be investigated in ILs and the results give an indication of the reactivity of the ILs ions present at very high concentrations. The very high viscosity will however limit potential applications. Clearly, the electrochemical stability toward reduction at a Pt electrode is enhanced for the tetraalkylammonium-based melt despite the obvious impurities. If the impurities can be successfully removed, these melts may have potential application for electrochemical capacitors. While these new types of room-temperature molten salts are air and moisture stable, both O$_2$ and water still need to be removed or they will limit the electrochemical windows.

(3) Liquid−Liquid Electrochemistry. Standard transfer potential values $\Delta_o^w \phi_i^0$ ($= -\Delta G_{tr}^{0,o\rightarrow w}/z_iF$) for the

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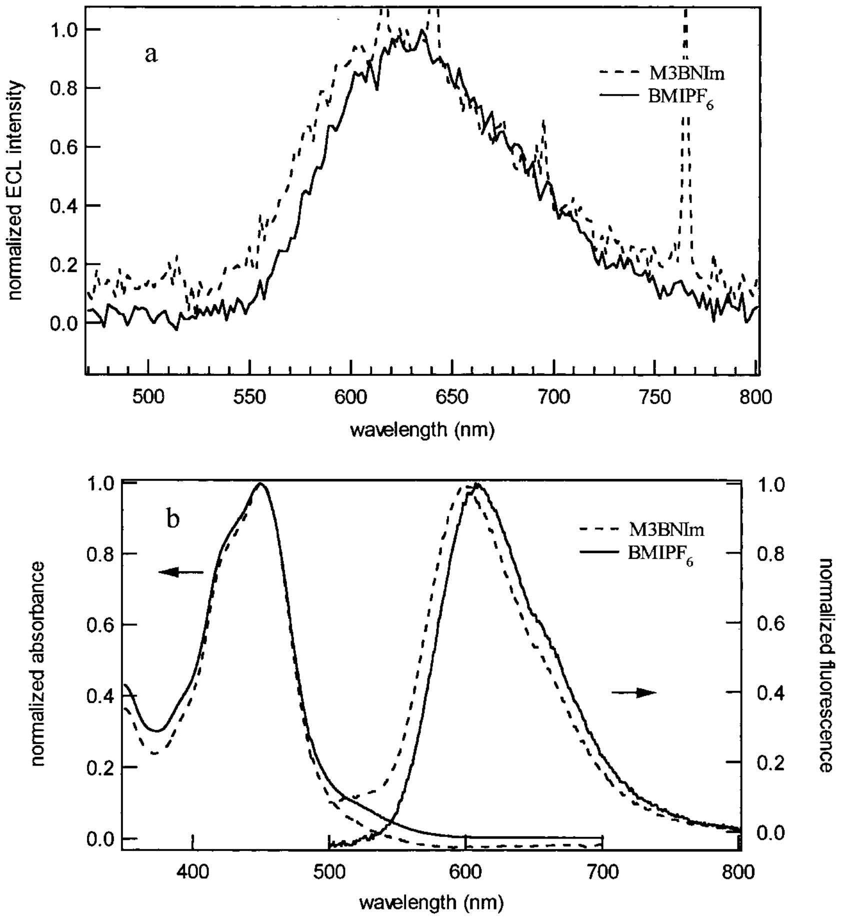

Figure 3. (a) ECL spectra for $Ru(bpy)_3^{2+}$ in M3BNIm (dashed line) and $BMIPF_6$ (solid line). (b) Fluorescence and absorption spectra for $Ru(bpy)_3^{2+}$ dissolved in neat M3BNIm (solid line) and $BMIPF_6$ (dashed line).

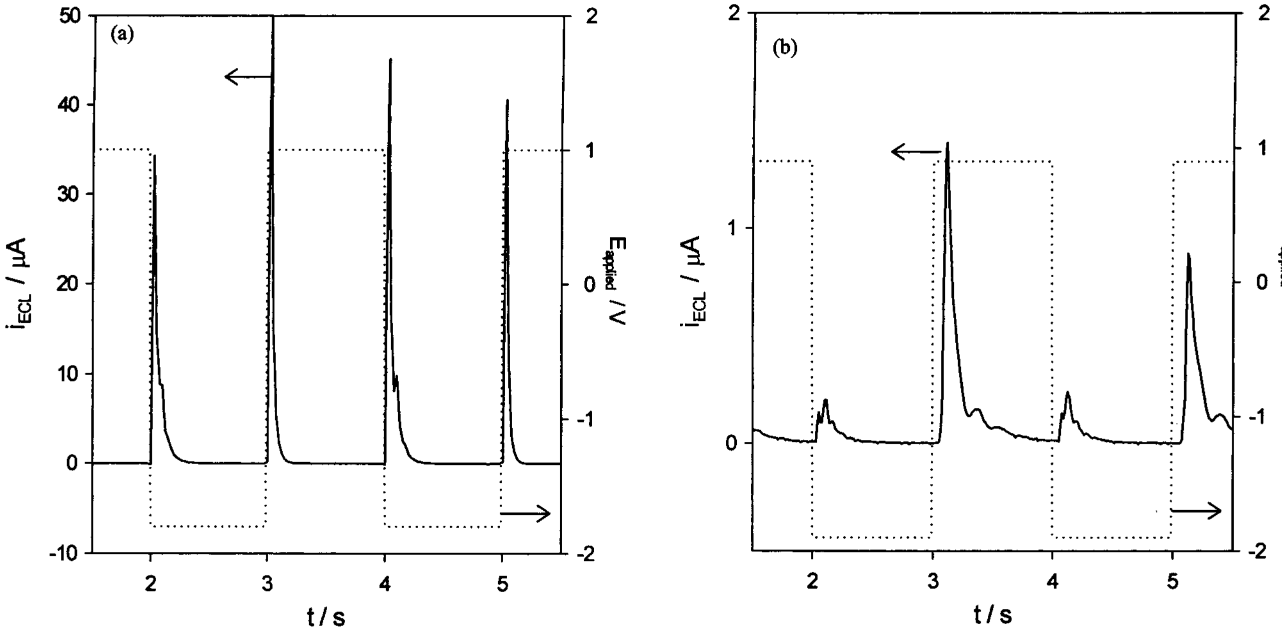

Figure 4. ECL transients of $Ru(bpy)_3^{2+}$ in (a) $BMIPF_6$ and (b) M3BNIm at a Pt electrode cycled at 0.5 Hz.

ions making up the ionic liquid at a conventional polarized liquid–liquid interface (water/1,2-DCE) give an indication of the relative lipophilicity of the melt while voltammograms at the immiscible IL/aqueous interface provide information about the polarizabilty of the interface. In contrast to the studies above at the Pt electrode, charge transfer across the immiscible interface is not a redox process and is simply a measure of the relative solvation properties of the transferring ionic species in each phase. Hydrophobic cations and anions are characterized by $\Delta_o^w \phi_i^{0'} \ll 0$ and $\Delta_o^w \phi_i^{0'} \gg 0$, respectively, and vice versa for hydrophilic ions.[29]

The micropipet-supported ITIES has an asymmetric diffusion regime as mass transfer inside the pipet is

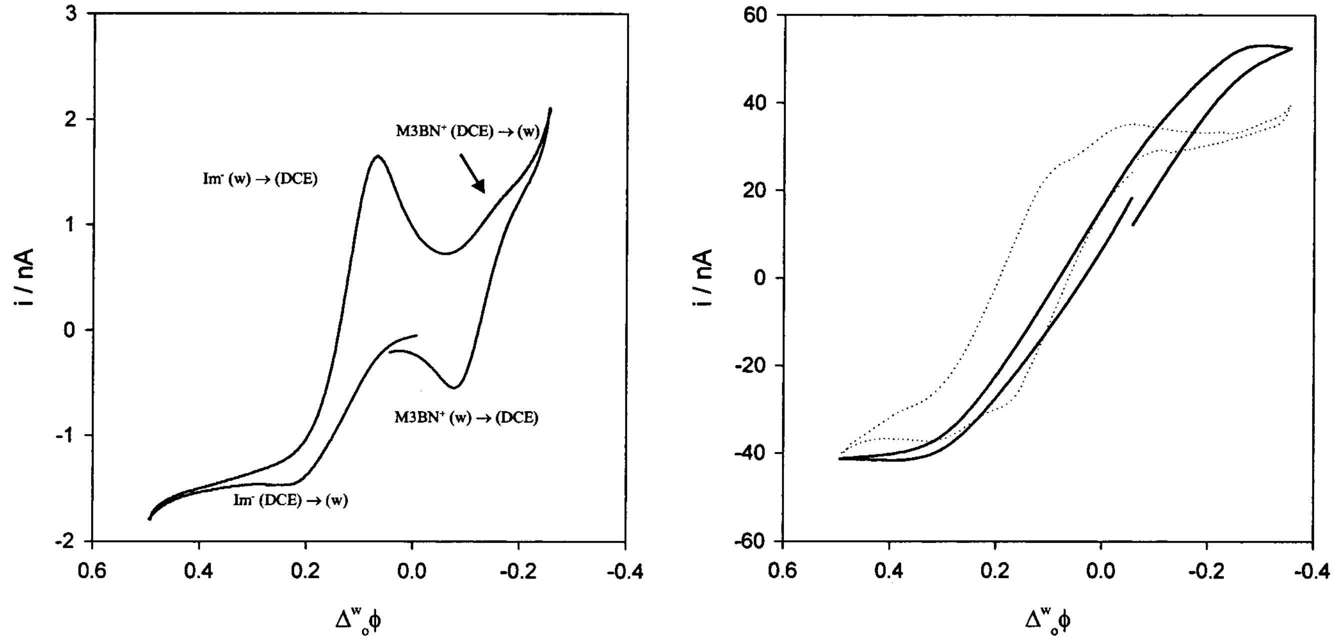

Figure 5. Cyclic voltammograms at the micropipet-supported water/1,2-DCE interface after the addition of the ILs to the DCE phase: (a) $M3BN^+$ Im^- and (b) BMI^+ PF_6^-. The dotted line in (b) gives the CV response after the addition of Li_2SO_4, a salting-out agent, to the aqueous phase. Scan rate = 100 mV s^{-1}; tip diameter, ca. 25 μm.

controlled by linear diffusion (aqueous phase) and by approximately spherical diffusion outside the pipet (organic phase).[39] This feature is useful in determining which species is transferring across the interface.[53] For example, as the applied potential is made more positive $\phi^w > \phi^o$, an anion may transfer from the organic to the aqueous phase or a cation may transfer in the opposite direction. At the micropipet interface set up here, the former results in a quasi-steady-state wave while the latter gives a peak-shaped CV response. At a symmetric interface (a conventional flat interface), it would not be possible to distinguish between these as the predicted response for both would be the same. For more details on the fundamentals of liquid/liquid junction electrochemistry, the reader is directed to recent reviews in refs 28 and 29.

CVs obtained for the transfer of M3BNIm and $BMIPF_6$ ions at the polarized water/1,2-DCE interface are given in Figures 5 and 6. In Figure 5a, the expected asymmetric CV response is clearly seen for $M3BN^+$ and Im^- transfers. Formal transfer potentials $\Delta_o^w \phi_i^{0'}$ were obtained from the half-wave potentials $E_{1/2}$ referenced against the transfer potential of TMA^+ to obtain $\Delta_o^w\phi_{1/2}$.[32] The standard ionic partition coefficient log $P_{DCE}^{0,i}$, where $P_{DCE}^{0,i} = c_i^o/c_i^w$, can be estimated from the following relation:[32]

$$\log P_{DCE}^{0,i} = -\Delta_o^w \phi_i^{0'} \frac{(zF)}{2.303RT} \tag{4}$$

Values of log $P_{DCE}^{0,i}$ are independent of the potential difference across the interface or the phase volume ratio and can be used as a simple prediction of the relative hydrophobicity/hydrophilicity of ions.

For the $BMIPF_6$ melt, $\Delta_o^w \phi_i^{0'}$ values could not be estimated because addition of the IL to the DCE phase resulted in a broad sigmoidal wave that was symmetric about equilibrium potential as can be seen in Figure 5b. Attempts to separate the transfer potentials by using a salting-out agent (Li_2SO_4) in the aqueous phase[54] gave slightly more definition in that two peaks can be observed in each scan direction (dotted line in Figure 5b). In this case, the IL partitions into the aqueous phase after contacting the aqueous and organic phases. Thus, as the applied potential is varied from the equilibrium potential ($I = 0$), current flows as the ions transfer to re-establish the partition equilibrium. The transfer potential of PF_6^- has been previously determined,[55] $\Delta_o^w \phi_{PF_6^-}^{0'} = -0.043$ V.

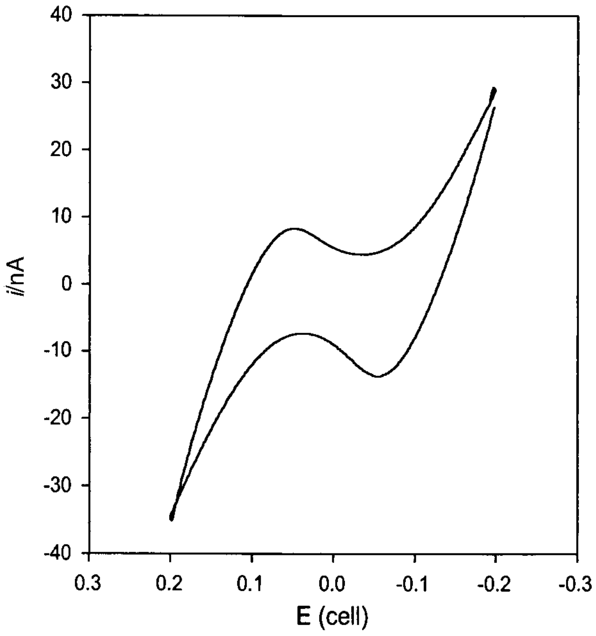

Figure 6. Cyclic voltammogram illustrating the available potential window at the neat M3BNIm/water interface. Scan rate = 100 mV s^{-1}.

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Table 2. Experimental Results Obtained by Cyclic Voltammetry for the Transfer of IL Ions Across the Water/1,2-DCE Interface[a]

	$\Delta_{\mathrm{o}}^{\mathrm{w}}\,\phi_i^{0'}$	$\Delta G_{\mathrm{tr}}^{0',\mathrm{o}\rightarrow\mathrm{w}}$	$\log P_{\mathrm{DCE}}^{0,i}$
$\mathrm{M3BN}^+$	−105	10.1	1.77
Im^-	96	9.2	1.62
$\mathrm{PF_6}^-$ [b]	−44	−4.2	−0.74
$\mathrm{BF_4}^-$ [c]	−176	−17	−3.0

[a] $\Delta_{\mathrm{o}}^{\mathrm{w}}\,\phi_i^{0'}$ is the formal transfer potential of ion i (mV), $\Delta G_{\mathrm{tr}}^{0',\mathrm{o}\rightarrow\mathrm{w}}$ is its formal Gibbs transfer energy (kJ mol^{-1}), and $\log P_{\mathrm{DCE}}^{0,i}$ is its standard partition coefficient. [b] Value taken from ref 55. [c] From ref 40.

The $\log P_{\mathrm{DCE}}^{0,i}$ values given in Table 2 clearly show that the $\mathrm{PF_6}^-$ ion is orders of magnitude more hydrophilic than either the Im^- or the $\mathrm{M3BN}^+$ ions. The hydrophilicity of the imidazolium ion can be assumed to be comparable to that of $\mathrm{PF_6}^-$ as the salt would not partition to the aqueous phase if the cation was significantly more lipophilic than the anion.

The polarizability of the neat melt/aqueous phase was also investigated. A polarizable interface is characterized by the existence of a potential region where there is negligible charge transfer ($I \cong 0$). The size of the potential window is indicative of the hydrophobicity/hydrophilicity of aqueous and organic electrolyte ions.[29] The CV response for the M3BNIm/LiCl(w) interface is given in Figure 6. The available window where ions do not transfer is very limited and is capacitive (<50 mV and with a high background current). The $\mathrm{BMIPF_6}$/LiCl(w) interface was not polarizable as changes in the applied potential from the equilibrium potential resulted in current overload (1 μA scale) (CV not shown). This is consistent with the above predictions based on the IL lipophilicity. These results indicate that M3BNIm is relatively hydrophobic while the $\mathrm{BMIPF_6}$ is quite hydrophilic. The BMI^+ and $\mathrm{PF_6}^-$ ions can partition readily across both the water/1,2-DCE and water/$\mathrm{BMIPF_6}$ interfaces. In these cases, the equilibrium potential difference across the interfaces may be established by the salt distribution potential,[56]

$$\Delta_{\mathrm{o}}^{\mathrm{w}}\phi = \frac{\Delta_{\mathrm{o}}^{\mathrm{w}}\,\phi_{\mathrm{PF_6}^-}^{0'} + \Delta_{\mathrm{o}}^{\mathrm{w}}\,\phi_{\mathrm{Im}^-}^{0'}}{2} \qquad (5)$$

$$\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi = \frac{\Delta_{\mathrm{IL}}^{\mathrm{w}}\,\phi_{\mathrm{PF_6}^-}^{0'} + \Delta_{\mathrm{IL}}^{\mathrm{w}}\,\phi_{\mathrm{Im}^-}^{0'}}{2}$$

where $\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi$ refers to $\phi^{\mathrm{w}} - \phi^{\mathrm{IL}}$. In biphasic separation studies, the equilibrium potential difference across the IL/aqueous interface will be determined by the distribution of all the ions in both phases and depends on the lipophilicity of the ions, their charge, initial concentration, and the IL/water volume ratio.[28,30,31] If, as a first approximation, ion pairing can be ignored, the distribution equilibrium can be described in terms of the standard ion transfer potential as a measure of hydrophobicity (or extractability) of an individual ion. The distribution ratio of each ion can be estimated using the Nernst equation:[57]

$$D_i \equiv \frac{c_i^{\mathrm{IL}}}{c_i^{\mathrm{w}}} = \exp\left[\frac{z_i F}{RT}(\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi - \Delta_{\mathrm{IL}}^{\mathrm{w}}\,\phi_i^0)\right] \qquad (6)$$

Partitioning of neutral species between two phases is independent of the interfacial potential and the aqueous pH and is simply related to the Gibbs free energy of transfer.[32]

$$\log P_{\mathrm{N}} = \log\left(\frac{c_{\mathrm{N}}^{\mathrm{IL}}}{c_{\mathrm{N}}^{\mathrm{w}}}\right) = -\frac{\Delta G_{\mathrm{tr,N}}^{0',\mathrm{w}\rightarrow\mathrm{IL}}}{2.303RT} \qquad (7)$$

Thus, hydrophobic neutral complexants such as the crown ethers will remain in the IL liquid phase irrespective of the aqueous pH and distribution of the other ions in the system as has been experimentally observed.[5] Crown ethers have a facilitating effect on aqueous metal ion transfer and decrease the energy requirement for their transfer due to

$$\mathrm{M}^+_{(\mathrm{IL})} + \mathrm{L}_{(\mathrm{IL})} \overset{k_{\mathrm{a}}}{\rightleftharpoons} \mathrm{M}^+\mathrm{L}_{(\mathrm{IL})}$$

For large association constants, K_{a}, and where $c_{\mathrm{L}}^{\mathrm{IL}} \gg c_{\mathrm{M}^+}^{\mathrm{w}}$, we can rewrite eq 1 as follows:[29]

$$\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi = \Delta_{\mathrm{IL}}^{\mathrm{w}}\,\phi_{\mathrm{M}^+}^{0'} + \frac{RT}{F}\ln\frac{c_{\mathrm{M}^+}^{\mathrm{IL}}}{c_{\mathrm{M}^+}^{\mathrm{w}}} - \frac{RT}{F}\ln(K_{\mathrm{a}}c_{\mathrm{L}}^{\mathrm{IL}}) \qquad (8)$$

The net effect is simply that metal ions can transfer at lower $\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi$.

From eq 6, it can be readily understood that the equilibrium potential difference must be greater than the formal ion transfer potential for its extraction from the aqueous to the IL phase. As the IL ions are present at high concentration (>2 M), equilibrium partitioning of the cation, anion, or salt may control $\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi$ and thus the extraction of aqueous phase ions.[28]

A recent report by Wadhawan et al.,[58] where apparent unusual partitioning of $\mathrm{Fe(CN)_6}^{4-/3-}$ from the aqueous phase to a thin layer of IL was observed, can be readily understood with reference to the interfacial potential difference across the IL/water interface. In this case, a thin layer of 1-methyl-3-(2,6-(*S*)-dimethyloctene-2-yl)-imidazolium tetrafluoroborate ($\mathrm{MDIMBF_4}$) was spread on a pyrolytic graphite electrode and contacted with aqueous solutions containing $\mathrm{NaBF_4}$. This is analogous to a nonpolarized ITIES, $\mathrm{C_1BF_4}//\mathrm{C_2BF_4}$, where $\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi$ is determined by the partitioning of the common ion $\mathrm{BF_4}^-$.[29] From the $\log P_{\mathrm{DCE}}^{0,i}$ value given in Table 2, this anion can be classified as hydrophilic and is expected to partition readily to the aqueous phase. As a first approximation, ignoring volume differences and ion pairing, $\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi$ can be written as follows:

$$\Delta_{\mathrm{IL}}^{\mathrm{w}}\phi = \Delta_{\mathrm{IL}}^{\mathrm{w}}\,\phi_{\mathrm{BF_4}^-}^{0'} - \frac{RT}{F}\ln\frac{c_{\mathrm{BF_4}^-}^{\mathrm{IL}}}{c_{\mathrm{BF_4}^-}^{\mathrm{w}}} \qquad (9)$$

This potential can in turn induce the partitioning of the other ions in the system.[28,30] Since the anion is hydrophilic, it can be assumed that $\Delta_{\mathrm{IL}}^{\mathrm{w}}\,\phi_{\mathrm{BF_4}^-}^{0'} < 0$, and because $c_{\mathrm{BF_4}^-}^{\mathrm{IL}} > c_{\mathrm{BF_4}^-}^{\mathrm{w}}$, the equilibrium potential established is <0, that is, $\phi^{\mathrm{w}} < \phi^{\mathrm{IL}}$. Thus, aqueous anions will have a tendency to transfer to the IL phase, and cations in the opposite direction. The reported partitioning of $\mathrm{Fe(CN)_6}^{3-}$ from water to IL and the absence of partitioning of aqueous phase $\mathrm{Ru(NH_3)_6}^{3+/2+}$ is consistent with this expectation.

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Increasing the concentration of $c^{w}_{BF_4^-}$ increases $\Delta^{w}_{o}\phi$ and thus decreases the driving force for anion transfer from water to the IL phase. The marked decrease in $Fe(CN)_6{}^{3-}$ partitioning to the IL phase as $c^{w}_{BF_4^-}$ increased from 0.2 to 1 M noted experimentally is thus also consistent. As $z = -4$ and -3 for $Fe(CN)_6{}^{4-}$ and $Fe(CN)_6{}^{3-}$, respectively, the former is predicted to be more hydrophilic, that is, $\Delta^{w}_{IL}\,\phi^{0'}_{Fe(CN)_6{}^{4-}} < \Delta^{w}_{IL}\,\phi^{0'}_{Fe(CN)_6{}^{3-}}$. In addition, the proposed interaction of $Fe(CN)_6{}^{3-}$ with C(2) of the imidazolium cation would induce a facilitating effect resulting in anion transfer at less negative potentials. This interaction is absent for the $Fe(CN)_6{}^{4-}$ anion. Thus, $\Delta^{w}_{IL}\phi$ established from eq 9 may be insufficient to drive $Fe(CN)_6{}^{4-}$ transfer and the anion cannot partition to the IL phase. This study is conceptually similar to studies by Anson and coworkers[59−61] where partitioning ions were used to provide the driving force for electron and ion transfer studies at the interface between a thin layer of nitrobenzene spread on pyrolytic graphite and water.

The effect of $\Delta^{w}_{IL}\phi$ on the extraction of metal ions has not been considered to date, and this may be the key to understanding the significant differences noted between ionic liquids versus traditional organic solvents.[5,6] The estimation of equilibrium potential difference requires knowledge of $\Delta^{w}_{IL}\,\phi^{0'}_{i}$ for all of the ions in both phases, their charge, initial concentration, phase volume ratio, association and complexation constants (more detailed information is given in refs 28, 30, 31, and 57). Standard transfer potentials for ion transfer across the IL/water interface have not been determined and would constitute a formidable task as each ionic liquid would have its own set of values. However, as outlined above, studies at a conventional ITIES, such as the water/1,2-DCE interface, can provide very useful indicators of lipophilicity of the IL ions, and these in turn can be used to estimate the behavior of the IL when contacted with water.

The cation $M3BN^+$ was not combined with Im^- in either of the previous reports where the properties of alkylammonium-based ILs were studied. M3BNIm was liquid at room temperature, and from preliminary differential scanning calorimetry (DSC) thermograms recorded (not shown), M3BNIm shows no indication of a phase change over the temperature range considered (5−250 °C). As noted previously,[20] the symmetry of the cation plays an important role in the depression of the melting temperature of quaternary ammonium imides. Methyl-triethylammonium imide (M3EtNIm) had a much higher melting point (93 °C). Hexyl-tributylammonium imide was reported to melt at 26 °C, while the melting point of the symmetric tetrabutylammonium melt was similar to that of M3EtNIm (96 °C).[15,20] M3BNIm deviates from predictions of MacFarlane et al.[20] who conclude that to obtain a room-temperature ionic liquid quaternary onium imide, a sufficient degree of asymmetry for melting point depression is provided by having one longer carbon chain of carbon number in the region 6−8, with the remaining shorter alkyl chains being identical. This criterion is not satisfied in this case, and from these reports, M3BNIm should have a melting point intermediate between 26 and 96 °C. More study is required to understand this unusual property of M3BNIm.

Conclusions

The alkylammonium cation has an increased cathodic stability at a Pt electrode compared with the 1,3-disubstituted alkylimidazolium cation, which may be up to 2 V greater if residual impurities can be successfully removed. ECL was observed in both melts, and differences in the response give an indication of the reactivity and polarity of the ionic liquids studied.

The relative lipophilicity of IL ions can be ascertained from charge-transfer studies at a conventional polarized liquid−liquid interface. As ionic liquids have been proposed as alternatives to organic solvents for extraction processes, an understanding of the relative lipophilicity of the IL ions and the equilibrium potential difference established across the IL/water interface is of fundamental relevance. This has not been taken into account to date and should be important in the design of “task specific ILs”[4] for extraction.

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