

# Mutual Solubility of Hydrophobic Ionic Liquids and Water in Liquid-Liquid Two-phase Systems for Analytical Chemistry

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Liquid-liquid two-phase systems formed by a hydrophobic ionic liquid and water find several useful ways of application in analytical chemistry. One of the most important properties of such two-phase systems is the mutual solubility of the IL and water. Recent advancements on this subject have been reviewed. The solubility of ionic liquids in water is related to the standard Gibbs energies of the transfer of ions constituting the ionic liquid from the ionic liquid phase to water. Although this single ionic property cannot be measured thermodynamically and also varies from one ionic liquid to another, the standard Gibbs energy of the ion transfer from a polar aprotic solvent, such as nitrobenzene and 1,2-dichloroethane, to water is a convenient measure for it. The solubility of an ionic liquid in water and the electrochemical properties at the interface between the two phases are intimately related with each other.

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## 1 Introduction

Attempts to use ionic liquids (ILs), room-temperature molten salts, for analytical chemistry date back to 1966.<sup>1,2</sup> One may count the use of tetraalkylammonium halides with organic diluents for the extraction of metal ions in the 1960s and 1970s<sup>3,4</sup> among such attempts. The number of papers published in this area was limited to a few<sup>5-12</sup> before room-temperature ionic liquids with moderately hydrophobic anions were introduced in the 1990s;<sup>13,14</sup> since then, however, the research on ionic liquids has been burgeoning, particularly after the turn of the century. More than a dozen review articles dealing with the application of ILs to analytical chemistry have appeared in the last five years.<sup>15-30</sup>

Among many possibilities of applying ionic liquids, IL-water (W) two-phase systems that consist of an aqueous or a nonpolar molecular solvent and an ionic liquid are of considerable relevance with analytical chemistry and separation technology. A direct application of IL-W two-phase systems is the extraction of neutral compounds of relatively low molecular weights,<sup>31-47</sup> biopolymers<sup>44,48-51</sup> and ions.<sup>52-85</sup> Several reviews on extraction with ILs are available.<sup>26,86-91</sup> The possibility of using ILs as a

stationary phase in HPLC<sup>92-95</sup> and countercurrent chromatography<sup>96,97</sup> has been examined.

From an electroanalytical chemistry viewpoint, hydrophobic ILs are promising for modifying the electrode surface,<sup>98-106</sup> preparing membranes for ion-selective electrodes,<sup>107-111</sup> salt bridges,<sup>112-114</sup> and other potentiometric as well as voltammetric sensors.<sup>115</sup> A remarkable growth in the number of papers dealing with carbon paste and other carbon electrodes impregnated with ILs attests the strong interest to apply ILs for electroanalytical chemistry.<sup>116-161</sup> In these applications, understanding the solubility of ILs in a sample solution should be of decisive importance for the stability of the electrodes and their proper functioning, though is seldom addressed. Other fields of applications of ILs that require detailed knowledge about the properties of the two-phase systems include aqueous two-phase organic synthesis<sup>34,162-168</sup> and environmental science. Although the negligible volatility of ILs is one appealing point in the use of ILs in place of volatile organic solvents, the finite solubility of ILs in water has raised concern in wastewater treatments and other circumstances.<sup>169-187</sup>

Since ILs are salts having certain solubility in water, the interface between an IL and water is inevitably electrified. There are a number of systems in which the phase-boundary potential across the IL|W interface plays a crucial role in determining the physicochemical characteristics of the systems.<sup>188,189</sup>

Table 1 Mutual solubility of water and moderately hydrophobic ionic liquids at 25°C

IL	Solubility of water in IL			Solubility of IL in water			Ref.
	wt%	mol kg <sup>-1</sup>	$x_{\text{W}}^{\text{IL}}$ <sup>a</sup>	wt%	mol kg <sup>-1</sup>	$x_{\text{IL}}^{\text{W}}$ <sup>b</sup>	
[C <sub>2</sub> mim <sup>+</sup> ][C <sub>1</sub> C <sub>1</sub> N <sup>-</sup> ]	1.94	1.08	0.298	1.81	$4.60 \times 10^{-2}$	$8.38 \times 10^{-4}$	226
[C <sub>4</sub> mim <sup>+</sup> ][C <sub>1</sub> C <sub>1</sub> N <sup>-</sup> ]	1.48	$8.20 \times 10^{-1}$	0.257	0.716	$1.72 \times 10^{-2}$	$3.07 \times 10^{-4}$	226
[C <sub>6</sub> mim <sup>+</sup> ][C <sub>1</sub> C <sub>1</sub> N <sup>-</sup> ]	1.05	$5.83 \times 10^{-1}$	0.208	0.237	$5.30 \times 10^{-3}$	$9.56 \times 10^{-5}$	226
[C <sub>8</sub> mim <sup>+</sup> ][C <sub>1</sub> C <sub>1</sub> N <sup>-</sup> ]	0.87	$4.83 \times 10^{-1}$	0.187	$8.87 \times 10^{-2}$	$1.87 \times 10^{-3}$	$3.36 \times 10^{-5}$	226
	0.96	$5.3 \times 10^{-1}$	0.20	$7.1 \times 10^{-2}$	$1.5 \times 10^{-3}$	$2.7 \times 10^{-5}$	257
	0.9	$5 \times 10^{-1}$	0.2	$8.3 \times 10^{-2}$	$1.4 \times 10^{-3}$	$2.5 \times 10^{-5}$	200
	0.9	$5 \times 10^{-1}$	0.2	$8.5 \times 10^{-2}$	$1.8 \times 10^{-3}$	$3.2 \times 10^{-5}$	112
[C <sub>8</sub> mim <sup>+</sup> ][C <sub>2</sub> C <sub>2</sub> N <sup>-</sup> ]	0.6	$3 \times 10^{-1}$			$1.1 \times 10^{-3}$		200

a. Mole fraction of water in IL. b. Mole fraction of IL in water.

Some fundamental features of IL-W two-phase systems have been elucidated using electrochemical approaches.<sup>190-217</sup> In this review, the current understanding of the mutual solubility of ILs and water is summarized, while stressing the importance of electrochemical aspects of the two-phase systems.

## 2 Mutual Solubility of Ionic Liquid and Water

At the earlier stage of studying IL-W two-phase systems, water-immiscible ILs composed of BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> were frequently employed. However, the acid catalyzed hydrolysis of BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> in aqueous solutions<sup>54,218-220</sup> tends to bring about less-reproducible experimental results, and makes any proper interpretation of the data difficult. Tri(pentafluoroethyl)trifluorophosphate is far more stable in aqueous environments, but still undergoes gradual decomposition.<sup>221</sup> Special care must be exercised when acquiring reliable data for ILs composed of these anions.<sup>222</sup> Recent physicochemical data reported in literature are mainly on ILs that are stable in aqueous media, such as those based on bis(trifluoromethylsulfonyl)imide.<sup>223-227</sup>

### 2.1 Mutual solubilities of moderately hydrophobic ILs and water

Table 1 lists the mutual solubility of water and some 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>n</sub>mim<sup>+</sup>][C<sub>1</sub>C<sub>1</sub>N<sup>-</sup>]) at 25°C, where C<sub>n</sub>mim stands for a 1-alkyl-3-methylimidazolium and the subscript n denotes the number of carbon atoms in the alkyl moiety. For the imide anion, we hereafter use the abbreviation [C<sub>n</sub>C<sub>m</sub>N<sup>-</sup>] to simply represent imides having possibly different perfluoroalkylsulfonyl moieties concisely, where the subscripts n and m denote the number of carbon atoms in the perfluoroalkylsulfonylimide moieties.

It is apparent from Table 1 that the longer is the alkyl chain, the smaller is the solubility of water in the ILs, and also that of ILs in water. The logarithm of the molality of water in the IL,  $m_{\text{W}}$ , and that of the IL in water,  $m_{\text{IL}}$ , are plotted as a function of the number of carbon atoms,  $n_{\text{c}}$ , in the alkyl chain in [C<sub>n</sub>mim<sup>+</sup>][C<sub>1</sub>C<sub>1</sub>N<sup>-</sup>] in Figs. 1a and 1b, where the ordinates are shown in units of energy per mole.

Figures 1a and 1b quantitatively confirm the trends that have been remarked;<sup>73,226-228</sup> that is, the linear variation of the logarithm of the solubility of both water and ILs with the alkyl chain length of [C<sub>n</sub>mim<sup>+</sup>]. The water content does vary with  $n_{\text{c}}$  (Fig. 1a), but its change is much smaller than that of  $m_{\text{IL}}$ . This seems to be in harmony with the spatial heterogeneity in the structure of ILs.<sup>229-231</sup> The aggregation of the alkyl moiety of [C<sub>n</sub>mim<sup>+</sup>] would promote the association of water molecules.<sup>232</sup>

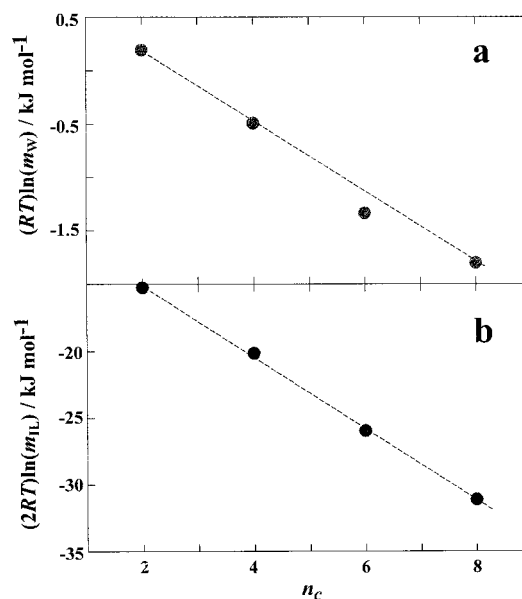


Fig. 1 Dependence of the solubility of water in [C<sub>n</sub>mim<sup>+</sup>][C<sub>1</sub>C<sub>1</sub>N<sup>-</sup>] (a) and [C<sub>n</sub>mim<sup>+</sup>][C<sub>1</sub>C<sub>1</sub>N<sup>-</sup>] in water (b) on the number of carbon atoms in alkyl moiety of [C<sub>n</sub>mim<sup>+</sup>] at 25°C.  $m_{\text{W}}$  and  $m_{\text{IL}}$  are the concentrations in molality.

Notable in Fig. 1a is the fact that the solubility of water in IL is as high as 1 mol kg<sup>-1</sup> in the case of [C<sub>2</sub>mim<sup>+</sup>][C<sub>1</sub>C<sub>1</sub>N<sup>-</sup>]. This corresponds to a mole fraction of about 0.3, which suggests that the IL phase may be seen as a concentrated aqueous solution of a salt (see below), although the number of water molecules is one in three or four [C<sub>2</sub>mim<sup>+</sup>][C<sub>1</sub>C<sub>1</sub>N<sup>-</sup>] pairs, and the latter should prevail in determining the physicochemical properties of the IL phase. The last entry in Table 1 shows that the replacement of the anion [C<sub>1</sub>C<sub>1</sub>N<sup>-</sup>] with a more hydrophobic [C<sub>2</sub>C<sub>2</sub>N<sup>-</sup>] significantly reduces the mutual solubility. These linear dependences of the solubility on  $n_{\text{c}}$  in Table 1 and Figs. 1a and 1b prompt us to find a way to quantify the hydrophobicity of IL-constituting cations and anions separately.

### 2.2 Solubility product and standard Gibbs energy of ion transfer

Another important reason for introducing the hydrophobicity of individual ionic species is the very nature of the liquid-liquid equilibrium of IL-W two-phase systems. From an analogy with treating the solubility of sparingly soluble salts in water, it is easily seen that the solubility product in W of the 1:1 IL

composed of the cation,  $C^+$ , and the anion,  $A^-$ ,  $K_s^W = a_{C^+}^W a_{A^-}^W$ , is related to the standard Gibbs energies of the transfer of  $C^+$  and  $A^-$  from IL to W,  $\Delta G_{C^+}^{IL \rightarrow W,0}$  and  $\Delta G_{A^-}^{IL \rightarrow W,0}$ , through

$$-RT \ln K_s^W = \Delta G_{C^+}^{IL \rightarrow W,0} + \Delta G_{A^-}^{IL \rightarrow W,0}, \quad (1)$$

where  $a_i^W$  is the activity of  $i$  ( $i = C^+$  or  $A^-$ ). The standard state in the IL phase for  $\Delta G_i^{IL \rightarrow W,0}$  is the IL saturated with water. Obviously, the standard Gibbs energy for the transfer of CA,  $\Delta G_{CA}^{IL \rightarrow W,0}$  is the sum of  $\Delta G_{C^+}^{IL \rightarrow W,0}$  and  $\Delta G_{A^-}^{IL \rightarrow W,0}$ . Once we know the values of  $\Delta G_i^{IL \rightarrow W,0}$  for various cations and anions, we can estimate the solubility of an IL from this equation.  $\Delta G_i^{IL \rightarrow W,0}$  is a single ionic property that cannot be measured thermodynamically. Moreover, the solubility of an IL depends on the IL, itself, which means that the replacement of the counterion species with another alters the solubility of the same ion in W, and changes the standard state in the IL phase for defining  $\Delta G_i^{IL \rightarrow W,0}$ . Although Eq. (1) is conceptually simple, it is not as practical as what it might seem.

### 2.3 Hydrophobicity scale of ions

For a systematic understanding of the properties of IL-W two-phase systems, the hydrophobicity of ILs and its constituent ions has been experimentally studied through the partition coefficients of ILs between octanol and water,<sup>227,233,234</sup> and reverse-phase high-performance liquid chromatography.<sup>235-238</sup> These approaches provide a relative magnitude of the hydrophobicity for a series of cations, or that of anions. However, it is not feasible in these methods to establish a unique scale that is commonly applicable to both cations and anions, and hence to predict the solubility of ILs from the  $\Delta G_i^{IL \rightarrow W,0}$  values of the IL-constituting cationic and anionic species. Moreover, in some applications, for example, the extraction of the ionic component and the surface or colloid chemistry of ionic liquids, it is necessary and important to have a measure of the absolute magnitude of the hydrophobicity. This is because  $\Delta G_i^{IL \rightarrow W,0}$  is intrinsically related to the phase-boundary potential between the IL and water,  $\Delta_{IL}^W \phi$ , formed by the partition of  $C^+$  and  $A^-$  in W through<sup>200,205</sup>

$$\Delta_{IL}^W \phi = \frac{\Delta_{IL}^W \phi_{C^+}^0 + \Delta_{IL}^W \phi_{A^-}^0}{2}, \quad (2)$$

where  $\Delta_{IL}^W \phi_i^0$  ( $i = C^+$  or  $A^-$ ) is the standard ion-transfer potential of ion  $i$  having the ionic charge with the signed unit of electronic charge,  $z_i$ , defined by

$$\Delta_{IL}^W \phi_i^0 = -\frac{1}{z_i F} \Delta G_i^{IL \rightarrow W,0}. \quad (3)$$

As a convenient measure of  $\Delta G_i^{IL \rightarrow W,0}$ , we proposed the standard Gibbs energy of ion transfer between nitrobenzene (NB) and water or 1,2-dichloroethane (DCE) and water,  $\Delta G_i^{Org \rightarrow W,0}$  ( $Org = NB$  or  $DCE$ ).<sup>189,201,206</sup> A rational background of this idea is a remarkable similarity in the polarity of various ILs to those of polar aprotic solvents.<sup>239,240</sup> To examine the usefulness of  $\Delta G_i^{Org \rightarrow W,0}$  and  $\Delta_{IL}^W \phi_i^0$ , Fig. 2a compares the solubility of the ILs listed in Table 1 with  $\Delta_{IL}^W \phi_i^0$  of  $[C_n\text{mim}^+]$  ions in NB-W (filled circles) and DCE-W (open circles) two-phase systems at 25 °C.<sup>189,241</sup>

In both cases, linear relationships exist between the solubility in the unit of voltage and the  $\Delta_{Org}^W \phi_i^0$  values. This linearity ensures that both  $\Delta_{NB}^W \phi_i^0$  and  $\Delta_{DCE}^W \phi_i^0$  can be used as a quantitative measure of  $\Delta_{IL}^W \phi_i^0$ . The parallelism of the two plots is an indication that NB and DCE provide similar solvation

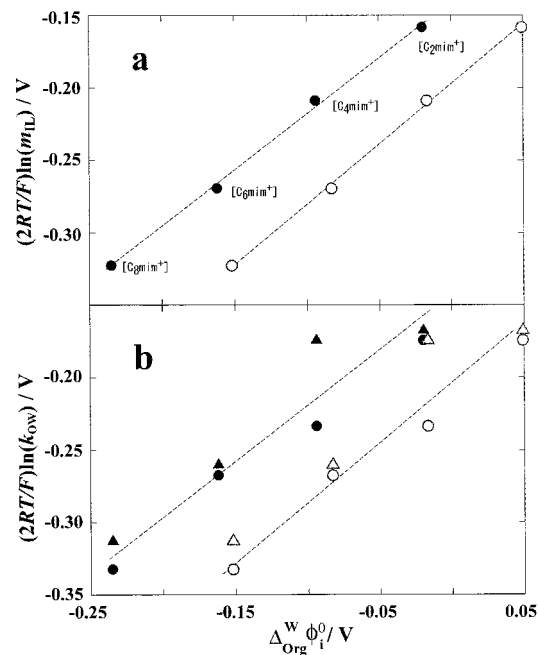


Fig. 2 Plots of the solubility of  $[C_n\text{mim}^+][C_1C_1N^-]$  in water (a) and the partition coefficient of  $[C_n\text{mim}^+][C_1C_1N^-]$  between 1-octanol and water,  $k_{OW}$ , (b) as a function of the standard ion transfer potential in nitrobenzene-water (filled circles) and 1,2-dichloroethane-water (open circles) two-phase systems. Cationic species shown by the plot in (a) apply to (b). A set of filled triangle and filled circles at a given value of  $\Delta_{Org}^W \phi_i^0$  shows the upper and lower estimates of  $k_{OW}$ .<sup>233</sup>

environments. The meaning of a horizontal shift in the two plots, about 80 mV between  $\Delta_{NB}^W \phi_i^0$  and  $\Delta_{DCE}^W \phi_i^0$ , will be discussed elsewhere.<sup>241</sup> The slope of 0.8 in both plots in Fig. 2a suggests that the ions slightly prefer their own ionic environments than NB or DCE in a partition to the aqueous phase. A similar comparison of the literature values of the octanol-water partition coefficients ( $K^{OW}$ ) for  $[C_n\text{mim}^+][C_1C_1N^-]$ <sup>233</sup> with  $\Delta_{IL}^W \phi_i^0$  is shown in Fig. 2b. Linear relationships are obvious in Fig. 2b, showing slopes similar to those in Fig. 2a. Thus, the octanol-water partition coefficient is also useful as a quantitative measure of the hydrophobicity of IL-constituting ions, though only the relative magnitude of the hydrophobicity is available, and the variety of ILs suitable for experimentally determining  $K^{OW}$  is limited.

It has been found that the identity of the anion constituting an IL strongly influences the miscibility of the IL with W,<sup>242</sup> but the effect of the anion has only been qualitatively assessed.<sup>225,233,234,242</sup> Figure 3 shows the effect of the change in the anionic species on the solubility of ILs composed of  $[C_8\text{mim}^+]$ . The solubility of W in the IL is plotted as a function of  $\Delta_{NB}^W \phi_i^0$  (filled circles) or  $\Delta_{DCE}^W \phi_i^0$  (open circles) in Fig. 3a. The unit of the ordinate is in V for ease of comparing with  $\Delta_{Org}^W \phi_i^0$ . The vertical bars on the left-hand side show the variance in the literature data for the solubility of  $[C_8\text{mim}^+][PF_6^-]$ .<sup>32,169,242,243</sup> By and large, the linearity also holds for the change in the solubility of W in the ILs with the change in the anionic species.

Figure 3b shows plots of the solubility of IL in W as a function of  $\Delta_{NB}^W \phi_i^0$  (filled symbols) or  $\Delta_{DCE}^W \phi_i^0$  (open symbols). The slopes of these linear relationships are both 0.7, which is only slightly smaller than those seen in Fig. 2. In other words, the identity of the anion affects the solubility of the ILs through  $\Delta G_i^{IL \rightarrow W,0}$ , as is the case of the cationic species on the solubility of ILs in W. The effect of the anions can be quantitatively estimated through

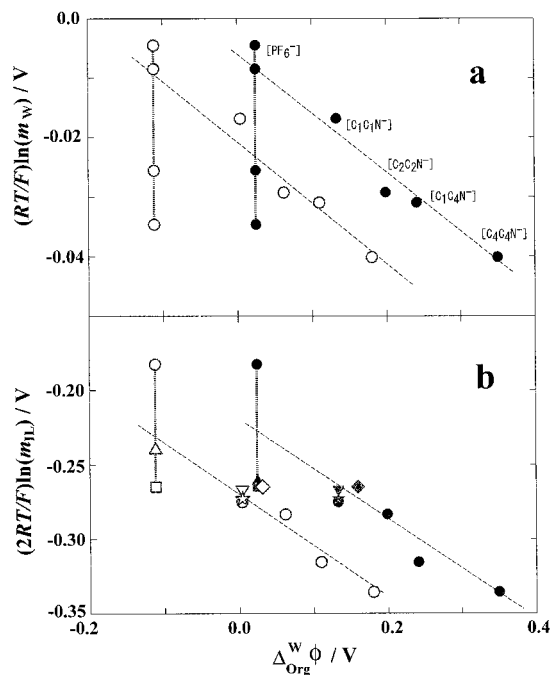


Fig. 3 Plots of the solubility of water in  $[C_8mim^+][C_n C_m N^-]$  (a) and  $[C_n C_m N^-]$  in W (b) as a function of the standard ion transfer potential, in nitrobenzene-water (filled circles) and 1,2-dichloroethane-water (open circles) two-phase systems. Anionic species shown by the plot in (a) apply to (b).

$\Delta_{NB}^W \phi_i^0$  or  $\Delta_{DCE}^W \phi_i^0$ , as are the cases of the effect of cationic species on the solubility. The significance of the anion identity in determining the mutual solubility is hence thermodynamically equivalent to that of the cation identity. Figures 3a and 3b thus demonstrate the usefulness of  $\Delta_{NB}^W \phi_i^0$  and  $\Delta_{DCE}^W \phi_i^0$  for predicting the mutual solubility of ILs and W.

### 3 Phase Behavior-Temperature Effect on the Mutual Solubility

The effect of temperature on the mutual solubility of ILs and W has been studied in the context of the phase behavior of highly concentrated electrolyte solutions, even before ILs became known as new “green” materials. The presence of upper and lower critical points has been confirmed for mixtures of tetraalkylammonium halides and water,<sup>244-247</sup> but at temperatures higher than room temperature. More recently, the phase behavior has been studied for ILs and water at lower temperatures using room-temperature ILs.<sup>227,232,248-250</sup> For hydrophobic ILs that are useful for applications of IL-W two-phase systems, the upper critical points seem to be located near or above 100°C.

Quantitative modeling of the phase behavior of IL-W and IL-nonaqueous solvent two-phase systems has been studied. Two major approaches are those based on an electrolyte Non-Random Two-Liquid (eNRTL) model<sup>251</sup> and the Conductor-like Screening Model for Real Solvent (COSMO-RS).<sup>252</sup> Theoretical estimates of the activity coefficients of the relevant species at different temperatures and compositions of the systems can predict the solubility curves, which semiquantitatively reproduce experimental results.<sup>224,227,253-256</sup>

A characteristic feature of the solubility of hydrophobic ILs is a weak dependence of the solubility on the temperature for

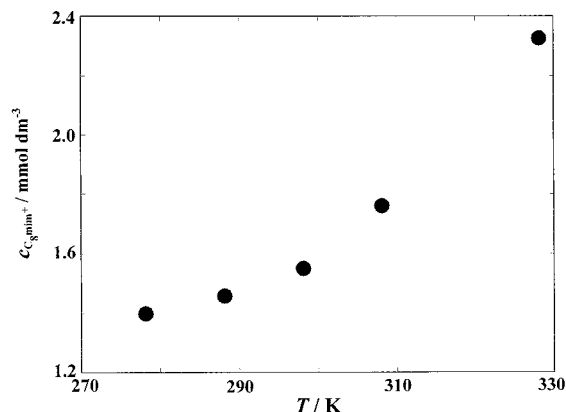


Fig. 4 Temperature dependence of the solubility of  $[C_8mim^+][C_1C_1N^-]$  in water.

$[C_1C_1N^-]$ -based ILs compared with that of water in ILs.<sup>224,225,228</sup> However, a closer look at the solubility of  $[C_8mim^+][C_1C_1N^-]$  in W reveals a considerable temperature dependence of the solubility,<sup>257</sup> as shown in Fig. 4. An increase in the solubility with temperature means that this two-phase system should have an upper critical solution temperature, as has been observed for several IL-W mixtures. From Eq. (1) and the Gibbs-Helmholtz equation, the molar solution enthalpy is estimated to be 13.9 kJ mol<sup>-1</sup> at 25°C.<sup>257</sup> The endothermic nature for the dissolution of  $[C_n m im^+][C_1 C_1 N^-]$  agrees on the order of magnitude with solution enthalpies of other moderately hydrophobic ILs by calorimetry<sup>258-260</sup> and the temperature dependence of the solubility.<sup>224,226</sup> The solution enthalpy from calorimetry measures the enthalpy change in the dissolution of the IL in its pure state to the aqueous solution, while the enthalpy obtained from the solubility of ILs in W corresponds to the dissolution of the water-saturated IL to W.

### 4 Solubility of Hydrophobic IL in W and Electrochemical Polarizability of Ionic Liquid-Water Interface

#### 4-1 Polarized potential window

It is well established that the Nernst equation holds for the partition of ionic species between IL and W,<sup>200</sup>

$$\Delta\phi = \Delta\phi_i^0 + \frac{RT}{z_i F} \ln \frac{a_i^{IL}}{a_i^W}, \quad (4)$$

where  $a_i^{IL}$  is the activity of  $i$  in the IL. Equation (4) means that the change in  $\Delta\phi$  can drive the ion transfer across the interface.<sup>197,201</sup>

Figure 5 shows cyclic voltammograms recorded at the interface between an aqueous solution of 0.1 mol dm<sup>-3</sup> LiCl and an IL composed of perfluoroalkyltrifluoroborate ( $[C_n F_{2n+1} BF_3^-]$ ) and  $[C_8mim^+]$  or tetrahexylammonium ( $[THA^+]$ ).<sup>261</sup> It is seen that with increasing the hydrophobicity the current-potential curves gradually become tilted and sprawled out to show a polarized potential window (ppw) where the current does not respond to the change in the applied potential. A rise in the current at the positive end of each voltammogram corresponds to the flow of  $[C_n F_{2n+1} BF_3^-]$  from IL to W. The inset of Fig. 5 shows a linear relationship between the width of the ppw and  $\Delta\phi_i^0$  values of  $[C_n F_{2n+1} BF_3^-]$ . In this case, the slope is unity, greater than those in Figs. 2 and 3, which fact suggests that

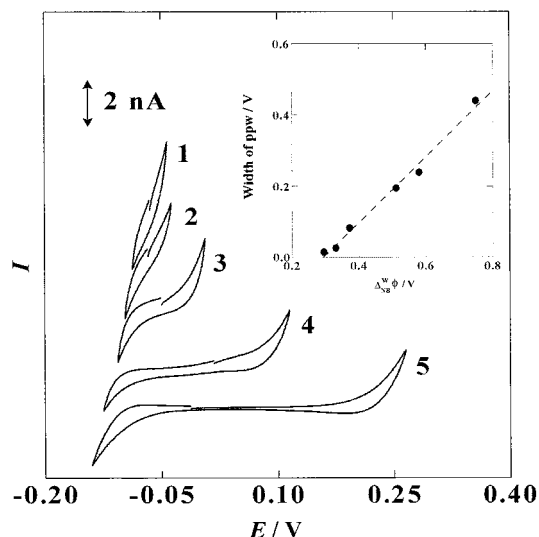


Fig. 5 Cyclic voltammograms at the interface between  $[C_8mim^+][C_nF_{2n+1}BF_3^-]$  ( $n = 2$  (1), 4 (2), and 3) and water and  $[THA^+][C_nF_{2n+1}BF_3^-]$  ( $n = 2$  (4), 6 (5)) at 25°C and water, where the aqueous phase contains 10 mmol  $dm^{-3}$   $MgCl_2$  and the scan rate is 10  $mV s^{-1}$ . The inset shows a plot of the width of ppw as a function of the standard ion transfer potential of  $[C_nF_{2n+1}BF_3^-]$  in nitrobenzene-water two-phase systems. Data are taken from Ref. 261.

solvation environments of the ILs are similar to that of NB.

In applications of IL-W two-phase systems in electroanalytical chemistry, the electrochemical polarizability, or the polarization resistance, should be known when designing electrochemical systems. At an IL/W interface, the electrochemical polarizability, defined as the slope,  $\frac{dE}{dI}|_{I \rightarrow 0}$ , is inversely proportional to  $\sqrt{K_3^W}$ ,<sup>217</sup> provided that both ends of the polarized potential window are limited by the transfer of the IL-constituting ions in W. For using an IL/W interface in IL-type salt bridges or IL-type reference electrodes, a low polarization resistance is preferable, for example,  $[C_8mim^+][C_nF_{2n+1}BF_3^-]$  in contact with water (curve 1 in Fig. 5). However, a necessary trade-off is the higher solubility of the IL in W.

On the other hand, the wider is ppw, the larger is the freedom of controlling  $\Delta\phi$  through an externally applied voltage across the interface. A wide ppw is preferred in voltammetry and other voltage-controlled techniques of electroanalytical chemistry using IL-W two-phase systems. The first voltammetric detection of ion transfer was made for tetrapropylammonium, tetrabutylammonium,  $[PF_6^-]$ , and  $[C_8mim^+]$  at the interface between  $[THA^+][C_2C_2N^-]$  and W, which has a ppw of 300 mV.<sup>201</sup> The widening of ppw to 850 mV was achieved at 56°C using a very hydrophobic anion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ( $[TFPB^-]$ ) in combination with *N*-octadecylisquinolinium ( $[C_{18}Iq^+]$ ). The widest ppw so far reported is 1.1 V at the interface between the highly hydrophobic IL, tetraheptylammonium ( $[THpA^+]$ )  $[TFPB^-]$  and 0.01 mol  $dm^{-3}$   $MgSO_4$  in W at 60°C.<sup>215</sup> The mutual solubility of highly hydrophobic ILs and W given in Table 2 is much smaller than those for moderately hydrophobic ILs (Table 1). Such a low degree of mutual solubility is beneficial in view of the contamination of sample solutions and the longer lifetime of the IL phase or the IL membrane.

For a comparison, Table 3 lists the mutual solubility of water and some polar aprotic solvents that have been used for studying the liquid-liquid equilibria and for ion sensors. One can see that

Table 2 Mutual solubility of water and highly hydrophobic ionic liquids

IL	Solubility of water in IL		Solubility of IL in water	Ref.
	wt%	mol $kg^{-1}$	mol $kg^{-1}$	
$[THA^+][C_1C_1N^-]$ <sup>a</sup>	0.3	$1.6 \times 10^{-1}$	$7 \times 10^{-6}$	210
$[C_{18}Iq^+][TFPB^-]$ <sup>b</sup>	0.31	$1.7 \times 10^{-1}$	$4 \times 10^{-5}$	212
$[TOMA^+][TFPB^-]$ <sup>b</sup>	0.20	$1.1 \times 10^{-1}$	$1 \times 10^{-5}$	212

a. 25°C.

b. 56°C.

Table 3 Mutual solubility of polar aprotic solvents and water at 25°C

Solvent	Solubility of W in O		Solubility of O in W		Ref.
	wt%	Molality	wt%	Molality	
DCE <sup>a</sup>	0.15	$8.4 \times 10^{-2}$	0.81	$8.3 \times 10^{-2}$	262
NB <sup>b</sup>	0.26	$1.5 \times 10^{-1}$	0.20	$1.6 \times 10^{-2}$	263
Octanol		2.3 (mol $dm^{-3}$ )	$4.5 \times 10^{-3}$	$3.4 \times 10^{-4}$	264, 265
NPOE <sup>c</sup>		$4.6 \times 10^{-2}$		$2.0 \times 10^{-6}$	266, 267
FNDPE <sup>d</sup>	—	—		$1.5 \times 10^{-4}$	268

a. 1,2-Dichloroethane, 20°C.

b. Nitrobenzene.

c. 2-Nitrophenyl octyl ether.

d. 2-Fluoro-2'-nitrodiphenyl ether.

the degree of the solubility of the highly hydrophobic ILs in water is much smaller than those of typical polar aprotic solvents used for ion-transfer voltammetry, and is comparable to those of NPOE, which has been employed for ion-selective electrodes of the liquid-membrane type. This highlights the possibility of using these highly hydrophobic ILs in place of NPOE or FNDPE for ISE and other electroanalytical methods. Generally, highly hydrophobic ILs have higher melting points, but recently ILs that are liquid at room temperature have been successfully utilized in voltammetry and potentiometry.<sup>111,115</sup>

#### 4-2 Specific interaction between IL-constituent ions and hydrophilic counterions in W

The above argument about the width of the ppw assumes that the width of the ppw is determined by the hydrophobicity of the IL-constituent ions. However, when the ions constituting the IL are highly hydrophobic, hydrophilic ions in the W phase may be transferred upon applying a potential drop across the interface before the oppositely charged hydrophobic ions are expelled out of the IL phase. In fact, in the case of ILs composed of  $[TFPB^-]$ , hydrophilic cations, such as  $Li^+$ ,  $Na^+$ , or  $Mg^{2+}$  flow into the IL phase to limit the ppw. At the other end of the ppw, hydrophilic ions such as  $Cl^-$  and  $SO_4^{2-}$  may determine the width of the window.<sup>214</sup>

Interestingly, the transfer of hydrophilic ions to the IL phase can be facilitated by IL-constituting ions of opposite charge. Three voltammograms in the upper part of Fig. 6 recorded at the interface between  $[C_{14}Iq^+][C_2C_2N^-]$  and W show a narrowing of the ppw with increasing concentration of  $LiCl$  from 0.01, 0.1, to 1.0 mol  $dm^{-3}$ . However, the voltammogram in the lower part in Fig. 6, recorded when  $[THpA^+][C_2C_2N^-]$  was used as the IL, has a much wider ppw of about 350 mV. This clearly indicates that the transfer of  $Cl^-$  is facilitated by  $[C_{14}Iq^+]$  ions in the IL phase.

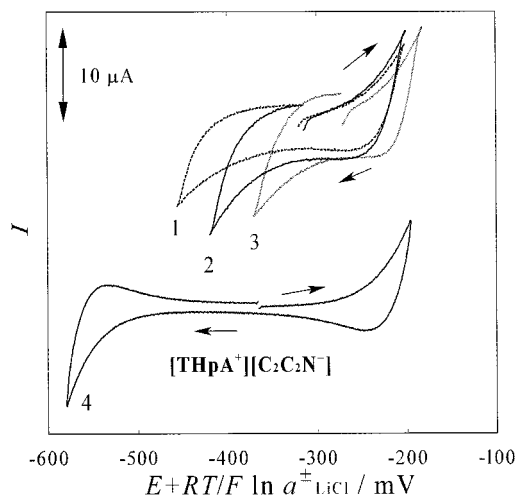


Fig. 6 Cyclic voltammograms at the interface between  $[C_{14}Iq^+][C_2C_2N^-]$  and aqueous LiCl solutions of 0.01 (broken line 1), 0.1 (solid line 2) and 1.0 mol  $dm^{-3}$  (dotted line 3), and at the interface between  $[THpA^+][C_2C_2N^-]$  and a 0.1 mol  $dm^{-3}$  aqueous solution of LiCl (solid line 4). The scan rate was 100  $mV s^{-1}$  and the interfacial area was about 0.03  $cm^2$ . Adapted from Ref. 214 with permission.

In other words, the degree of the ion-pair between  $[C_{14}Iq^+]$  and  $Cl^-$  is much stronger than that between  $[THpA^+]$  and  $Cl^-$ , suggesting the ion-pair formation of  $[C_{14}Iq^+]$  and  $Cl^-$  in the IL phase. The specific interaction between  $[C_{14}Iq^+]$  and  $Cl^-$  also exists at the interface between  $[C_{14}Iq^+][C_2C_2N^-]$  and W, which alters the structure of the electrical double layer in the vicinity of the interface.<sup>214</sup> In actual IL-W two-phase systems, the partition problems can be much more complicated than what is expected for simple IL-W two-phase systems.

## 5 Conclusion

In choosing a proper IL for a particular application of IL-W two-phase systems, considering the mutual solubility between the IL and W is important not only for the durability of the IL phase and possible contamination of the W phase with the IL, but also for tuning the electrochemical properties of the IL-W interface. Actual IL-W systems may be complicated by the participation of foreign ionic components to partition processes. Highly in need is the compilation of reliable data concerning the solubility and partition of ionic components between IL and W.

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