Polarized Potential Window Available at the Interface Between an Aqueous Electrolyte Solution and Tetraalkylammonium Imide Salts

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The polarized potential window (ppw) of 450 mV is available at the interface between water (W) and the room-temperature molten salt (RTMS) that consists of tetraoctylammonium cations and trifluoromethylsulfonylnonafluoro-butylsulfonylimide anions. The ppw at the interface between W and RTMS made of several combinations of hydrophobic cations and anions is correlated with the standard ion-transfer potentials of the ions at the 1,2-dichloroethane (DCE) interface. This correlation is useful not only to predict the width of the ppw but also to approximately estimate the point of zero charge at the RTMS/W interface.

1 Introduction

Recently, we reported two types of electrochemical interfaces between the room-temperature molten salt (RTMS), also called ionic liquid, and water (W), that is, nonpolarized and polarized RTMS/W interfaces.1,2 These new types of liquid/liquid interfaces are promising in many respects, especially as an environmentally benign alternative of volatile organic compounds that have been used extensively in solvent extraction and other systems involving liquid-liquid two-phase chemical processes.2,4 From an electrochemical viewpoint, the polarized RTMS/W interface is more attractive as it allows us to control the potential difference across the interface externally. In this respect, wider the polarized potential window (ppw), greater the possibility of studying a variety of electrochemical processes at the interface. The width of the potential window at the RTMS/W interface depends on the hydrophobicity of the ions constituting the RTMS as well as the hydrophilicity of the ions in the W phase. In our previous study, the polarized potential window of about 300 mV at 40°C was achieved for tetrahexylammonium bis(perfluoroethylsulfonylimide), [THA] [C6F5N], whose melting point is about 34°C, while the window narrows to 250 mV when the anion was replaced with bis(trifluoromethylsulfonylimide), [C6F5N]+, however at 25°C. Quinn et al. reported that the polarized potential window of about 50 mV was achieved at the interface between butyltrimethylammonium [C4H7N] and the aqueous phase containing LiCl.5 In the present study, we tried to widen the ppw using several combinations of hydrophobic tetraalkylammonium cations and perfluorosulfonylimide anions. We will show that the widest ppw of about 450 mV is available at 25°C and that the width of the available potential window is well correlated with the difference in the standard ion-transfer potentials between 1,2-dichloroethane (DCE) and W of the ions constituting the RTMS.

2 Experimental

2.1 Reagents

A bromide or iodide salt of either tetrahexylammonium ([THA]+), tetraheptylammonium ([Thpa]+), tetraoctylammonium ([TOA]+), or trietyltrimethylammonium ([TOMA]+) ions was mixed with a lithium salt of a perfluorooctylsulfonylimide, [C6F5N], in a methanol-water mixture, where the subscripts n and m denote the number of the fluorinated carbon atom of the perfluoroalkylsulfonylimide moiety in the imide ion. We used four lithium imides [n=1, m=1], [n=1, m=2], [n=2, m=2], and [n=1, m=4], which are generous gifts from Central Glass (Japan). Molten salts obtained were repeatedly washed with water to remove lithium bromide or lithium iodide. Molten salts we newly prepared, [THA] [C6F5N], [Thpa]+ [C6H13N], [TOA]+ [C8H17N], [TOA]+ [C6H13N], [TOMA]+ [C6H13N], and [TOMA]+ [C8H17N], were all in liquid state at room temperature after prepared as water-saturated RTMSs, though dry [TOA]+ [C6H13N] has the melting point at 31.2°C.6 Other reagents used for voltammetry of ion transfer across the DCEW interface were prepared or purified as described elsewhere.7

2.2 Voltammetry at RTMS/W interface

Cyclic voltammograms were recorded with a two-electrode cell described elsewhere.21 The composition of the reference side of the aqueous solution was 0.1 mol dm−3 Li[C6F5N] and 0.1 mol dm−3 LiCl. The other aqueous phase that formed a polarized interface was 0.1 mol dm−3 LiCl. The solution resistance was compensated for
by the positive feedback method.

2.3 Voltammetry at DCE/W interface

Cyclic voltammograms were recorded with a four-electrode cell described elsewhere.11 The supporting electrolyte in DCE was tetratetramylammonium tetrabutylammonium chloride at the concentration of 20 mmol dm$^{-3}$. The reference side of the aqueous solution contained 5 mmol dm$^{-3}$ tetratetramylammonium chloride and 10 mmol dm$^{-3}$ MgCl$_2$. The other aqueous phase contained 0.1 mol dm$^{-3}$ LiCl in addition to 1 mmol dm$^{-3}$ Li[C$_2$C$_2$N]. Other salts of the ion whose interfacial transfer was to be studied. The solution resistance was compensated for by the positive feedback method. The transfer of the ions studied was d.c. reversible within the scan rate between 10 and 500 mV s$^{-1}$. The mid-point potentials of cyclic voltammograms obtained were evaluated with the standard deviation of about 3 mV and were referred to that of tetraethylammonium ion transfer.

3 Results and Discussion

Voltammograms obtained at the interfaces between W and [TOcA]$^+$ [C$_2$C$_2$N]$^-$ (Fig. 1, curve 1) and [THA]$^+$ [C$_2$C$_2$N]$^-$ (Fig. 1, curve 2) at the scan rate of 100 mV s$^{-1}$ show that the widths of the ppw are more than 450 mV and 350 mV, respectively.

Comparing with the ppw we reported previously at the interfaces between W and [THA]$^+$ [C$_2$C$_2$N]$^-$ (reproduced as curve 3, recorded at 40°C) and [THA]$^+$ [C$_2$C$_2$N]$^-$ (reproduced as curve 4),2 one can see the effect of using more hydrophobic ions for the RTMS on widening ppw. Table 1 summarizes the width of the ppw for several RTMS/W interfaces we obtained voltammetrically.

As the hydrophobicity of [C$_2$C$_2$N]$^-$ increases by elongating the perfluorooalkyl moieties, the ppw was widened, accordingly. This means that the current rise at the positive end of the ppw is caused by the transfer of [C$_2$C$_m$ N]$^-$ from the RTMS to the W phase. Similarly, the negative end of the ppw was widened by 100 mV by changing the cation from [THA]$^+$ to [THpA]$^+$. However, further increase in the size from [THpA]$^+$ to [TOA]$^+$ did not alter the width of the ppw. This indicates that the negative end of the ppw is limited not by the transfer of [THpA]$^+$ or [TOA]$^+$, but by that transfer of Cl$^-$ ion from W to RTMS. A similar bound of the ppw by the transfer of hydrophilic anions has been observed at the interface between W and the RTMS composed of tetraoctylammonium picrate.9

It is convenient if we have a quantitative measure of the hydrophobicity of the ions constituting the RTMSs. A simple method of evaluating the hydrophobicity of ions is to use the standard ion-transfer potential between an organic phase and water. Aside from 1-octanol that has been used in quantitative structure-activity relationships, DCE has been proposed to be an alternative that offers a voltammetric means of establishing a hydrophobicity scale with great ease.9-11 From cyclic voltammograms for the transfer of ions that are used for preparing RTMSs, we evaluated the apparent standard ion transfer potential of several relevant anions (Table 2). For converting the mid-point potential relativised to that of tetraethylammonium ion to the apparent values of the standard ion transfer potentials, $\Delta W_{DCE}^{o}$ was made by adding 19 mV for the standard ion transfer potential of tetraethylammonium ion from DCE to W$^{12}$ and subtracting 7 mV for the difference in the diffusion coefficient of the ion in DCE and W. Here, the adjective “apparent” connotes that the values obtained in the present study are not corrected for the possible ion-pair formation in DCE and are evaluated at the finite concentrations of the supporting electrolytes in both DCE and W.

The values of $\Delta W_{DCE}^{o}$ of [C$_2$C$_m$N]$^-$ ions studied are considerably more positive; these ions are more hydrophobic than PF$_6^-$ that has been most commonly used for hydrophobic RTMSs. In fact, there are few ions that possess $\Delta W_{DCE}^{o}$ values in this range, which fact highlights the uniqueness of the [C$_2$C$_m$N]$^-$ ions.

The difference in $\Delta W_{DCE}^{o}$ between [C$_2$C$_2$N]$^-$ and

### Table 1 Width of the potential window for RTMS in contact with 0.1 mol dm$^{-3}$ LiCl at 25°C.

<table>
<thead>
<tr>
<th>Anions</th>
<th>Width of ppw / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$_2$C$_2$N]$^-$</td>
<td>0.25 (0.35)</td>
</tr>
<tr>
<td>[C$_2$C$_m$N]$^-$</td>
<td>0.35 (0.50)</td>
</tr>
<tr>
<td>[C$_2$C$_2$N]$^-$</td>
<td>0.30 (0.45)</td>
</tr>
</tbody>
</table>

### Table 2 Half-wave potentials and apparent standard ion transfer potentials of anions at DCE/W interface at 25°C.

<table>
<thead>
<tr>
<th>Anions</th>
<th>$E_{1/2}^{o}$ - $E_{1/2}^{o,TET}$ / V</th>
<th>$\Delta W_{DCE}^{o}$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$_2$C$_2$N]$^-$</td>
<td>0.081 (0.939)</td>
<td></td>
</tr>
<tr>
<td>[C$_2$C$_m$N]$^-$</td>
<td>0.113 (1.25)</td>
<td></td>
</tr>
<tr>
<td>[C$_2$C$_2$N]$^-$</td>
<td>0.142 (1.54)</td>
<td></td>
</tr>
<tr>
<td>[C$_2$C$_2$N]$^-$</td>
<td>0.193 (0.205)</td>
<td></td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>-0.012 (0.00)</td>
<td></td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>-0.103 (-0.091)</td>
<td></td>
</tr>
<tr>
<td>Pic$^-$</td>
<td>0.027 (0.039)</td>
<td></td>
</tr>
</tbody>
</table>

*) Pic$^-$ is picrate ion.
[C$_2$C$_5$N]$^-$, 61 mV, and that between [C$_6$C$_7$N]$^-$ and [C$_6$C$_8$N]$^-$, 51 mV, coincide well with the difference in the width of the ppw observed above (Table 1). This parallelism strongly supports the idea that, first, the extension of the ppw to the positive direction is due to the increasing hydrophobicity of the anions, and second, the hydrophobic environment inside the RTMSs is not very much different from that of the DCE phase.

In the case of hydrophobic RTMSs that consists of PF$_6^-$ ions in combination with relatively hydrophobic cations, such as 1-octyl-3-methylimidazolium ions, the center of the ppw is located at a potential where the phase boundary potential, $\Delta^\text{ppw}\phi$, is considerably negative; the inner potential of the RTMS phase is more positive with respect to that of the W phase. In contrast, $\Delta^\text{ppw}\phi$ at the center of the ppw can be made more positive by using [C$_6$C$_5$N]$^-$ ions, so that the ppw includes the potential of zero charge. This provides us with more freedom in designing the RTMSW two-phase systems, particularly for those where interfacial processes such as adsorption are important.

4 Conclusion

The combination of tetraalkylammonium ions with [C$_6$C$_5$N]$^-$, in particular those with asymmetric ones, gives a RTMS having a wide ppw. The standard ion-transfer potentials between the DCE and W of the ions constituting the RTMS and of ions dissolved in W can conveniently be used to predict the width of the ppw and also the solubility of the RTMS in W.

Acknowledgement

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References