Ion transfer processes at ionic liquid based redox active drop deposited on an electrode surface

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Ion transfer across the boundary formed at an ionic liquid drop deposited on an electrode immersed in aqueous solution, generated by electrochemical redox reaction at the electrode–ionic liquid interface, is studied to obtain information about the ability of anions to be transferred into a room temperature ionic liquid.

Room temperature ionic liquids (RTILs)[1,2] are environmentally friendly media for various chemical processes and components of physicochemical systems.[2–5] Biphasic systems with an RTIL in direct contact with an aqueous phase are an example. These recyclable media are applied in synthesis, extraction or liquid–liquid separation.[3,4] Therefore physicochemical studies on the RTIL–aqueous solution interface are of great interest.

The ability of RTILs to extract ions or neutral molecules from an aqueous phase is characterised by their partition coefficients. Since the simple shake-flask experiments consume large amounts of the rather precious RTIL, small volume techniques such as microextraction are preferred. They are based on the single drop and membrane or porous hollow fiber protected RTIL.[6,7] A similar strategy can be applied in electrochemical studies of biphasic systems.
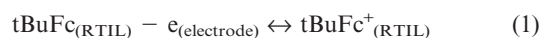
The ability of RTILs to acquire ions can be assessed from electrochemical experiments. Their role as electrochemical solvents is already well established.[8] However, only a few electrochemical studies of biphasic systems where the RTIL phase is in direct contact with the aqueous electrolyte have been reported.[9–13] They involve systems based on the polarised liquid–liquid interface which are difficult experimentally and suffer from having a very narrow, if any, potential window.[10–12,14] Droplet(s) or film of RTILs deposited on the electrode surface represent another option.[9,13,15] They have been used to assess RTILs' ability to extract the ionic redox probe from the aqueous phase[9] or to study the electrochemistry of surface confined microcrystals of a redox active compound.[13,15] Electrodes modified with droplet(s) or microphases of RTILs are easier to handle. More important, the methodology of ion transfer oriented biphasic system electrochemical studies involving droplet(s) or films of redox active oil is already well developed.[16,17]

Preliminary results of the study of ion transfer processes at an RTIL based redox active drop deposited on a planar electrode surface are reported here. For this purpose electrochemical properties of Au electrodes modified with a drop of redox probe, t-butylferrocene (tBuFc) solution in three RTILs were studied.

Two of them have a common cation and another pair have a common anion. The selected RTILs are: 1-decyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ($C_{10}mimN(Tf)_2$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_4mimN(Tf)_2$) and 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6). The electrodes were immersed in an aqueous salt solution.

The cyclic linear polarization of a Au electrode modified with 2 μl of 10 mM tBuFc in $C_{10}mimN(Tf)_2$ and immersed in an aqueous solution results in a symmetric voltammogram with a shape resembling that of a quasi reversible heterogeneous electron transfer (Fig. 1).

On the basis of the diffusion coefficient obtained from ultra-microelectrode voltammetry in a single RTIL drop one may conclude that the whole electrode surface remains electroactive. Reaction (1) has to be accompanied by ion transfer across the RTIL|aqueous solution interface in order to maintain local electroneutrality. The anion insertion into RTIL and the cation ejection from RTIL represent the two possibilities. Determining which of them dominates is crucial for understanding of the electrode reaction mechanism in biphasic systems.[16,17] It provides an indication of the ability of ions to cross the RTIL|aqueous solution interface. If reaction (1) is followed by the anion insertion (2):

$$tBuFc_{(RTIL)} - e_{(electrode)} \leftrightarrow tBuFc^+_{(RTIL)} \qquad (1)$$

$$tBuFc^+_{(RTIL)} + X^-_{(aq)} \rightarrow tBuFc^+_{(RTIL)} + X^-_{(RTIL)} \qquad (2)$$

the formal potential ($E_{Red/Ox}$) is described by a Nernstian type equation (3):[17,18]

$$E_{Red/Ox} = E^0_{tBuFc^+_{RTIL}/tBuFc_{RTIL}} + \Delta^{RTIL}_{aq}\varphi^0_{X^-} + \frac{RT}{F}\ln c_{X^-}$$
$$+ \frac{RT}{F}\ln\frac{c^*_{tBuFc}}{2} \qquad (3)$$

where $E^0_{tBuFc^+_{RTIL}/tBuFc_{RTIL}}$ is the standard redox potential of the tBuFc/tBuFc$^+$ couple in RTIL, $\Delta^{RTIL}_{aq}\varphi^0_{X^-}$ is the standard transfer potential of X^- from water to RTIL, c_{X^-} and c^*_{tBuFc} are the initial concentrations of X^- and tBuFc in the aqueous and RTIL phase, respectively. Therefore the slope of $E_{Red/Ox}$ vs. log (c_{X^-}) can be regarded as a test of the anion's ability to enter the RTIL phase. Eventually its value of 0.059 V indicates that the electrode reaction follows the mechanism described by eqns. 1 and 2. The experimental $E_{Red/Ox}$ vs. log (c_{X^-}) dependence is linear for 10^{-4} mol dm$^{-3} \leqslant c_{X^-} \leqslant 10^{-1}$ mol dm^{-3}. Its slope (Table 1) ranges from a value not far from 0.059 V for the less hydrated
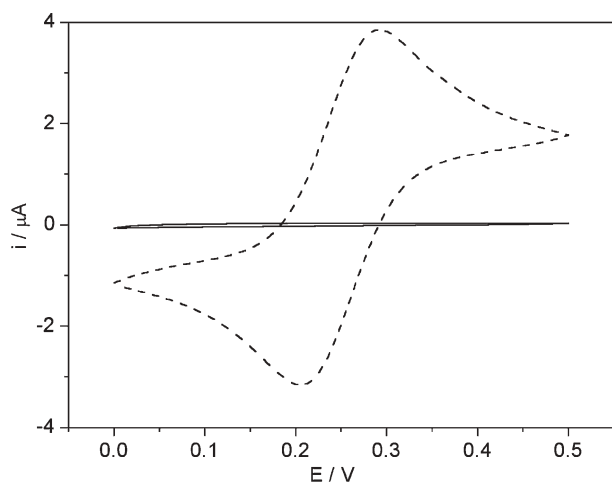
Fig. 1 Cyclic voltammograms (3rd scan, scan rate 0.01 V s^{-1}) obtained with a Au electrode covered with 2 μl 0.01 mol dm^{-3} tBuFc solution in $C_{10}mimN(Tf)_2$ immersed in 0.1 mol dm^{-3} aqueous KPF$_6$ (dashed) and with the same electrode in the absence of tBuFc (solid).

anions to close to zero for the most hydrated anions. This indicates the dominant role of insertion of large PF$_6^-$ or ClO$_4^-$ anions into the $C_{10}mimN(Tf)_2$ drop following electrooxidation of tBuFc. This process hardly occurs when more hydrophilic Cl$^-$ or F$^-$ anions are present in the aqueous phase. By analogy with the experiments with tBuFc droplets deposited on the electrode surface[19] one may conclude that the electrogenerated cation enters the aqueous phase (4):

$$tBuFc^+_{(RTIL)} \rightarrow tBuFc^+_{(aq)} \qquad (4)$$
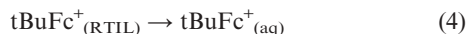
Since the concentration of nonelectroactive $C_{10}mim^+$ cations is almost three orders of magnitude larger than that of the redox probe, their ejection to the aqueous phase is more probable (5):

$$C_{10}mim^+_{(RTIL)} \rightarrow C_{10}mim^+_{(aq)} \qquad (5)$$

In the presence of large, multiatomic, less hydrated anions $E_{Red/Ox}$ values obtained from peak potentials of differential pulse voltammetry measured with a drop of tBuFc solution in $C_{10}mimN(Tf)_2$ depend on the anion present in the aqueous phase (Fig. 2). This indicates the effect of the anion on the ability of tBuFc molecules to be electrooxidized. This is not the case for a drop of RTIL with the less hydrophobic C_4mim^+ cation as component. The anion effect can be analysed using the relationship between $E_{Red/Ox}$ and $\Delta_{aq}^{RTIL} \varphi_{X^-}^0$ (see Fig. 3). The latter parameter is unavailable and we replace it with the standard transfer potential of X$^-$ from water to organic: nitrobenzene (NB)

Table 1 The slope of $E_{Red/Ox}$ vs. log (c_{X^-}) dependence obtained with a Au electrode covered with 2 μl 0.01 mol dm^{-3} tBuFc solution in $C_{10}mimN(Tf)_2$

Anion	$-\delta E_{Red/Ox}/\delta c$/V
F$^-$	0.006
Cl$^-$	0.004
BF$_4^-$	0.019
ClO$_4^-$	0.040
PF$_6^-$	0.051
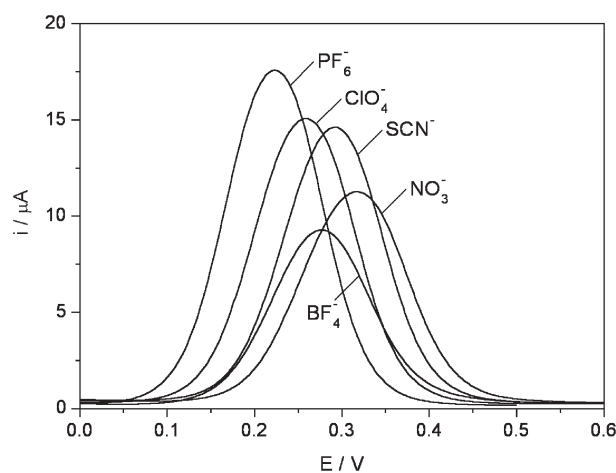
Fig. 2 The effect of selected anions on differential pulse voltammograms obtained with a Au electrode covered with 2 μl 0.01 mol dm^{-3} tBuFc solution in $C_{10}mimN(Tf)_2$ immersed in 0.1 mol dm^{-3} aqueous salt solution. Anions are marked on the figure.

phase[20] as a measure of the anion hydrophobic–hydrophilic properties. For the most hydrophobic $C_{10}mimN(Tf)_2$ drop $E_{Red/Ox}$ vs. $\Delta_{aq}^{NB} \varphi_{X^-}^0$ dependence is not linear (Fig. 3). Its slope changes from slightly below unity for the most hydrophobic (PF$_6^-$ or ClO$_4^-$) to close to zero for the most hydrophilic (Cl$^-$ or F$^-$) anions, indicating the role of anion hydrophobicity in its effective transfer to $C_{10}mimN(Tf)_2$. The correlation of the partition of an organic molecule between hydrophobic RTIL and the aqueous phase with its hydrophobicity has been reported recently.[21] Here, the observed effect (Fig. 3) correlates well with the change of the slope of $E_{Red/Ox}$ vs. log (c_{X^-}) dependence (Table 1), suggesting the possible order of $\Delta_{aq}^{RTIL} \varphi_{X^-}^0$ as PF$_6^-$ > ClO$_4^-$ > SCN$^-$ > BF$_4^-$ > NO$_3^-$. On the other hand the lack of anion dependence of $E_{Red/Ox}$ obtained with droplets of C_4mim^+ based RTIL indicates that reaction (1) is followed by cation ejection. This is probably because the Gibbs energy of C_4mim^+ cation transfer is smaller than the analogous parameter for any of the anions studied. Moreover,
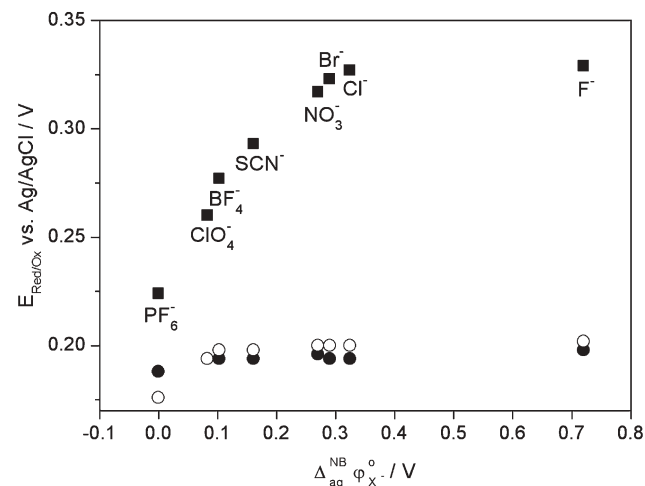
Fig. 3 The plot of redox potential, $E_{Red/Ox}$ obtained with a Au electrode covered with 2 μl 0.01 mol dm^{-3} tBuFc solution in $C_4mimN(Tf)_2$ (○), C_4mimPF_6 (●) and $C_{10}mimN(Tf)_2$ (■) vs. standard transfer potential of anion transfer from aqueous solution to nitrobenzene, $\Delta_{aq}^{NB} \varphi_{X^-}^0$.

tBuFc dissolved in an RTIL drop composed of the more hydrophilic C_4mim^+ cation is much easier to electrooxidise than in $C_{10}mimN(Tf)_2$, indicating more favorable ejection of the C_4mim^+ cation. This effect being in the range of 0.05–0.2 V also indicates the importance of the cation for the studied process.

Summarizing, to our knowledge for the first time anion insertion from an RTIL to aqueous solution coupled to the electrochemical redox reaction has been detected. It has to be mentioned that very recently RTIL cation ejection to aqueous solution generated by electrooxidation of decamethylferrocene dissolved in a thin film of RTIL deposited on a gold electrode covered with a self-assembled monolayer was reported.[22] The approach presented in our paper allows us to estimate the ability of an ion to be transferred to the RTIL phase, important for RTILs' biphasic applications, e.g. liquid–liquid separations. This method is much simpler and faster than that based on solubility data because it does not require synthesis of any new compound. One can also consider electrogenerated extraction of organic anions[23] using this approach. The use of an electroreducing reagent together with an appropriate ligand within the RTIL phase may allow for extraction of transition metal cations.[24] For this application the RTIL phase can be immobilized within a composite carbon ceramic matrix.[25]

$C_4mimN(Tf)_2$, C_4mimPF_6 and $C_{10}mimN(Tf)_2$ were prepared by reaction of 1-methylimidazole and the appropriate alkyl bromide[26] followed by anion exchange with HPF_6 or metathesis with $LiN(Tf)_2$ in water.[27] The Au electrode was modified by deposition of 2 μl (unless otherwise stated) of 10 mM tBuFc in RTIL or pure RTIL. The drop of RTIL is visible on the electrode surface. After that the electrode was transferred and immersed in an electrochemical cell with the aqueous electrolyte solution. The experiments in the absence of aqueous phase were performed in a cell similar to that described in the literature.[28]

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