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Theory of a reversible redox reaction in an ionic liquid that is coupled to an ion transfer across the aqueous electrolyte/ionic liquid interface

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Abstract A theory is provided for a reversible electro-oxidation of a neutral redox probe dissolved in room-temperature ionic liquid, which is sandwiched between an electrode surface and an aqueous solution as a thin film. If the peak potentials in cyclic voltammetry depend on the bulk concentration of electrolyte in water, the oxidation is most probably coupled to the transfer of anions from water into ionic liquid; but if the peak potentials are independent of the electrolyte concentration, the transfers of anions from water into ionic liquid and cations from ionic liquid into water are equally probable.

Keywords Liquid/liquid interface · Ionic liquid · Coupled electron and ion transfers

Introduction

Water-immiscible room-temperature ionic liquids (RTIL) have potential application in extraction and separation technology [1–5] and in electrochemistry [6–8]. The ion transfer across the RTIL/aqueous solution interface can be driven by electrochemical generation of charged species in the RTIL phase being sandwiched between a solid electrode surface and an aqueous electrolyte [9–15]. This can be realized by dissolving a redox probe in RTIL. Neither the probe nor the product of its electrode reaction should be soluble in water. To maintain electroneutrality, the electron transfer at the electrode/RTIL interface has to be coupled to an ion transfer at the RTIL/water interface [13–15]. Various electrode materials can be used, e.g., gold [9, 11], glassy carbon [12], ITO [13], graphite [14], or carbon paste using RTIL as a binder [15]. The RTIL is applied either as a thin layer [11–13] or a droplet [14] or the electrode material is impregnated with the RTIL [10]. The mechanisms of these electrode reactions were explained on the basis of the theory of electron transfer coupled to ion transfer across the organic liquid/aqueous solution interface. However, a difference between organic liquids and ionic liquids is that the partition of inorganic salts between water and majority of organic liquids is rather small [16], while it can be significant in the case of ionic liquids [13]. Furthermore, a supporting electrolyte may be added to organic liquids with the purpose to increase ionic conductivity of organic solutions, while no electrolyte is usually added to ionic liquids. Therefore, the concentration of a certain electrolyte in the ionic liquid depends only on its partition from water. In this paper, the influence of partition of an electrolyte between water and RTIL on the mechanism of electrode reaction is described.

The model

It is assumed that a stationary, planar, solid electrode is covered by a thin film of RTIL, which is absolutely immiscible with water so that neither anion nor cation of RTIL can be dissolved in water. In the film, an electro-

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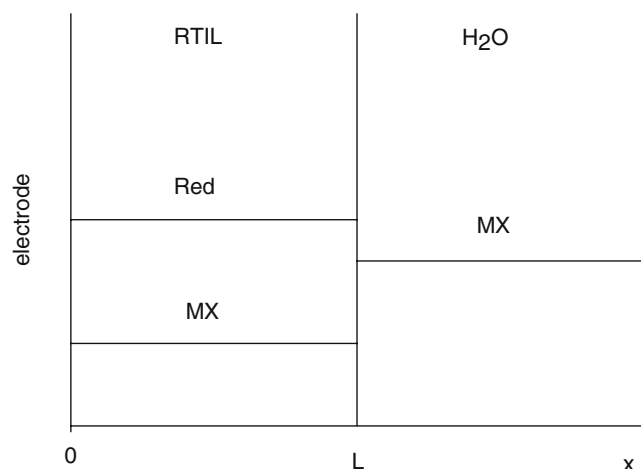
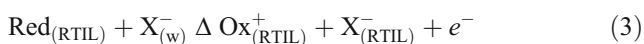**Scheme 1** An electrode covered by the film of RTIL and immersed into an aqueous electrolyte solution

active, neutral compound Red is dissolved. The electrode is immersed into an aqueous solution of the electrolyte MX. In equilibrium, a certain concentration of MX appears in the RTIL because of the partition of MX between water and RTIL (see Scheme 1):

$$\left[\mathrm{MX}_{(\mathrm{RTIL})}\right]* = \left[\mathrm{MX}_{(\mathrm{w})}\right]* \times K_{\mathrm{tr,MX}}^{\mathrm{w}\rightarrow\mathrm{RTIL}} \tag{1}$$

$$K_{\mathrm{tr,MX}}^{\mathrm{w}\rightarrow\mathrm{RTIL}} = \exp\left(-\frac{F}{2RT}\left[\Delta_{w}^{\mathrm{RTIL}}\phi_{X^-}^{\theta} - \Delta_{w}^{\mathrm{RTIL}}\phi_{M^+}^{\theta}\right]\right) \tag{2}$$

where $[\mathrm{MX}_{(\mathrm{w})}]*$ is a bulk concentration of MX in water, and $\Delta_{w}^{\mathrm{RTIL}}\phi_{X^-}^{\theta}$ and $\Delta_{w}^{\mathrm{RTIL}}\phi_{M^+}^{\theta}$ are the standard Galvani potential differences of anion X^- and cation M^+ on the water/RTIL interface, respectively.

On anodic polarization of the electrode, the compound Red is oxidized while either anions or cations of the supporting electrolyte are transferred across the water/RTIL interface:

$$\mathrm{Red}_{(\mathrm{RTIL})} + \mathrm{X}_{(\mathrm{w})}^{-} \, \Delta \, \mathrm{Ox}_{(\mathrm{RTIL})}^{+} + \mathrm{X}_{(\mathrm{RTIL})}^{-} + e^{-} \tag{3}$$

$$\mathrm{Red}_{(\mathrm{RTIL})} + \mathrm{M}_{(\mathrm{RTIL})}^{+} \, \Delta \, \mathrm{Ox}_{(\mathrm{RTIL})}^{+} + \mathrm{M}_{(\mathrm{w})}^{+} + e^{-} \tag{4}$$

It is further assumed that there are no fluxes of Red and Ox^+ across the liquid/liquid interface.

The potential difference between the working electrode and the reference electrode in water is a sum of the potential drop at the electrode/RTIL interface and the total potential drop across the RTIL/water interface [17]:

$$E = E_{\mathrm{E/RTIL}} + \Delta_{w}^{\mathrm{RTIL}}\phi \tag{5}$$

If the electrode reaction is reversible, the first potential drop is:

$$E_{\mathrm{E/RTIL}} = E_{\mathrm{Red/Ox^+}}^{\theta} + \frac{RT}{F}\ln\frac{[\mathrm{Ox}^+]_{x=0}}{[\mathrm{Red}]_{x=0}} \tag{6}$$

For the transfer of anions, the second drop is:

$$\Delta_{w}^{\mathrm{RTIL}}\phi = \Delta_{w}^{\mathrm{RTIL}}\phi_{X^-}^{\theta} + \frac{RT}{F}\ln\frac{\left[\mathrm{X}_{(\mathrm{RTIL})}^{-}\right]_{x=L}}{\left[\mathrm{X}_{(\mathrm{w})}^{-}\right]_{x=L}} \tag{7}$$

while for the transfer of cations it is:

$$\Delta_{w}^{\mathrm{RTIL}}\phi = \Delta_{w}^{\mathrm{RTIL}}\phi_{M^+}^{\theta} + \frac{RT}{F}\ln\frac{\left[\mathrm{M}_{(\mathrm{w})}^{+}\right]_{x=L}}{\left[\mathrm{M}_{(\mathrm{RTIL})}^{+}\right]_{x=L}} \tag{8}$$

where L is the film thickness.

Nernst equations for the reactions 3 and 4 are obtained by the combinations of Eqs. 5, 6, and 7 and Eqs. 5, 6, and 8, respectively:

$$[\mathrm{Ox}^+]_{x=0}\left[\mathrm{X}_{(\mathrm{RTIL})}^{-}\right]_{x=L}\exp\left(\frac{F}{RT}\Delta_{w}^{\mathrm{RTIL}}\phi_{X^-}^{\theta}\right) = [\mathrm{Red}]_{x=0}\cdot\left[\mathrm{X}_{(\mathrm{w})}^{-}\right]_{x=L}\cdot\exp(\varphi) \tag{9}$$

$$[\mathrm{Ox}^+]_{x=0}\left[\mathrm{M}_{(\mathrm{w})}^{+}\right]_{x=L} = [\mathrm{Red}]_{x=0}\left[\mathrm{M}_{(\mathrm{RTIL})}^{+}\right]_{x=L}\cdot\exp(\varphi)\cdot\exp\left(-\frac{F}{RT}\Delta_{w}^{\mathrm{RTIL}}\phi_{M^+}^{\theta}\right) \tag{10}$$

where $\varphi = \frac{F}{RT}\left(E - E_{\mathrm{Red/Ox^+}}^{\theta}\right)$.

Equations 9 and 10 were solved for cyclic voltammetry. Calculations were simplified by assuming that the transport of Red, Ox^+, X^-, and M^+ in the film can be neglected:

$$[\mathrm{Red}] = [\mathrm{Red}]* - \int\frac{I}{FSL}d\tau \tag{11}$$

$$[\mathrm{Ox}^+] = \int\frac{I}{FSL}d\tau \tag{12}$$

$$\left[\mathrm{X}_{(\mathrm{RTIL})}^{-}\right] = \left[\mathrm{X}_{(\mathrm{RTIL})}^{-}\right]* + \int\frac{I}{FSL}d\tau \tag{13}$$

$$\left[\mathrm{M}_{(\mathrm{RTIL})}^{+}\right] = \left[\mathrm{M}_{(\mathrm{RTIL})}^{+}\right]* - \int\frac{I}{FSL}d\tau \tag{14}$$

where $[\mathrm{Red}]*$, $\left[\mathrm{X}_{(\mathrm{RTIL})}^{-}\right]^{*}$, and $\left[\mathrm{M}_{(\mathrm{RTIL})}^{+}\right]^{*}$ are initial concentrations of Red, X^-, and M^+ in the film. Furthermore, it was assumed that the initial concentrations of anion X^- and cation M^+ in water were much higher than the
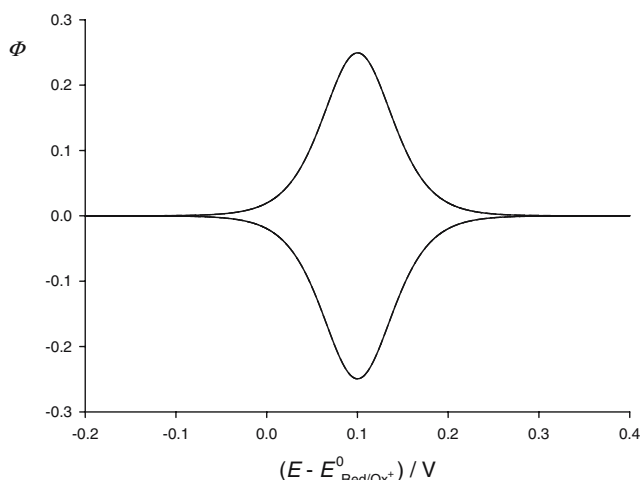
Fig. 1 Dimensionless cyclic voltammogram of the electrode reactions 3 and 4. $\Phi = I(FSL[\text{Red}]^*(F/RT)\nu)^{-1}$, $\Delta_w^{\text{RTIL}}\phi_{X^-}^\theta = \Delta_w^{\text{RTIL}}\phi_{M^+}^\theta = 0.1$ V, $[MX_{(w)}]^*/[\text{Red}]^*=100$

initial concentration of Red in the film, so that the diffusion of X^- and M^+ in water can be also neglected:

$$\left[X_{(w)}^-\right] = \left[X_{(w)}^-\right]^* \tag{15}$$

$$\left[M_{(w)}^+\right] = \left[M_{(w)}^+\right]^* \tag{16}$$

Under these conditions, the voltammetric responses were calculated by the numerical integration method described in the previous communication [18].

Results and discussion

A dimensionless cyclic voltammogram of reversible electrode reaction 3 is shown in Fig. 1. It was calculated for $\left[X_{(w)}^-\right]^*/[\text{Red}]^* = 100$ and $\Delta_w^{\text{RTIL}}\phi_{X^-}^\theta = \Delta_w^{\text{RTIL}}\phi_{M^+}^\theta = 0.1$ V, which meant that $K_{\text{tr,MX}}^{\text{w}\to\text{RTIL}} = 1$ and $\left[X_{(\text{RTIL})}^-\right]^*/[\text{Red}]^* = 100$. The peak potential of voltammogram is $E_P - E_{\text{Red/Ox}^+}^\theta = 0.1$ V. This can be explained by the theory of electrode reactions coupled to ion transfer across the liquid/liquid interface [18]. It predicts that, if $\left[X_{(\text{org})}^-\right]^*/[\text{Red}]^*\rangle 20$, the peak potential is given by the equation:

$$E_P = E_{\text{Red/Ox}^+}^\theta + \Delta_w^{\text{org}}\phi_{X^-}^\theta - \frac{RT}{F}\ln\left[X_{(w)}^-\right]^* + \frac{RT}{F}\ln\left[X_{(\text{org})}^-\right]^* \tag{17}$$

In the case of organic liquids, the concentrations $\left[X_{(w)}^-\right]^*$ and $\left[X_{(\text{org})}^-\right]^*$ are independent variables; but in RTIL they are connected by Eq. 1. Considering that in Fig. 1 $\left[X_{(\text{RTIL})}^-\right]^* = \left[X_{(w)}^-\right]^*$, the peak potential is defined by the equation:

$$E_P - E_{\text{Red/Ox}^+}^\theta = \Delta_w^{\text{RTIL}}\phi_{X^-}^\theta \tag{18}$$

The current–potential curve shown in Fig. 1 is also the response of reversible electrode reaction 4. This is because the assumed Gibbs free energies of transfer of anion X^- and cation M^+ from water into RTIL are 9.65 and −9.65 kJ/mol, respectively. Therefore, the Gibbs energy required to transfer M^+ from RTIL to water is equal to the energy of transfer of X^- from water into RTIL. For $\left[M_{(\text{org})}^+\right]^*/[\text{Red}]^*\rangle 20$, the peak potential of reaction 4 is given by the equation:

$$E_P = E_{\text{Red/Ox}^+}^\theta + \Delta_w^{\text{org}}\phi_{M^+}^\theta - \frac{RT}{F}\ln\left[M_{(\text{org})}^+\right]^* + \frac{RT}{F}\ln\left[M_{(w)}^+\right]^* \tag{19}$$

If $\left[M_{(\text{RTIL})}^+\right]^* = \left[M_{(w)}^+\right]^*$, as in Fig. 1, the peak potential is:

$$E_P - E_{\text{Red/Ox}^+}^\theta = \Delta_w^{\text{RTIL}}\phi_{M^+}^\theta \tag{20}$$

Cyclic voltammograms of electrode reactions 3 and 4 are also identical if $\left[X_{(w)}^-\right]^*/[\text{Red}]^* = \left[M_{(w)}^+\right]^*/[\text{Red}]^* = 100$, $\Delta_w^{\text{RTIL}}\phi_{X^-}^\theta = 0.1$ V, and $\Delta_w^{\text{RTIL}}\phi_{M^+}^\theta = 0.2$ V, which means that $K_{\text{tr,MX}}^{\text{w}\to\text{RTIL}} = 7.008$ and $\left[X_{(\text{RTIL})}^-\right]^*/[\text{Red}]^* = \left[M_{(\text{RTIL})}^+\right]^*/[\text{Red}]^* = 700.8$. The peak potential is $E_P - E_{\text{Red/Ox}^+}^\theta = 0.150$V. Considering Eqs. 1 and 17, the peak potential of reaction 3 is:

$$E_P - E_{\text{Red/Ox}^+}^\theta = \Delta_w^{\text{RTIL}}\phi_{X^-}^\theta + \frac{RT}{F}\ln K_{\text{tr,MX}}^{\text{w}\to\text{RTIL}} \tag{21}$$

For reaction 4, the peak potential is defined by Eqs. 1 and 18:

$$E_P - E_{\text{Red/Ox}^+}^\theta = \Delta_w^{\text{RTIL}}\phi_{M^+}^\theta - \frac{RT}{F}\ln K_{\text{tr,MX}}^{\text{w}\to\text{RTIL}} \tag{22}$$

Considering Eq. 2, the peak potential of reactions 3 and 4 is given by the equation:

$$E_P - E_{\text{Red/Ox}^+}^\theta = \left(\Delta_w^{\text{RTIL}}\phi_{X^-}^\theta + \Delta_w^{\text{RTIL}}\phi_{M^+}^\theta\right)\big/2 \tag{23}$$

Equation 23 applies if $\left[X_{(\text{RTIL})}^-\right]^*/[\text{Red}]^* = \left[M_{(\text{RTIL})}^+\right]^*/[\text{Red}]^*\rangle 20$.
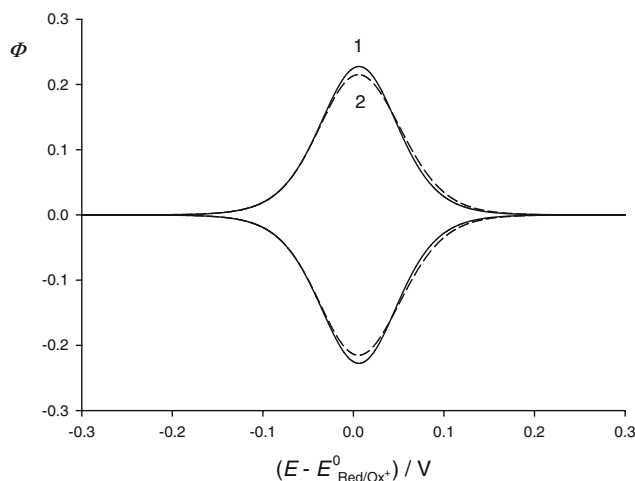

Fig. 2 Dimensionless cyclic voltammograms of (1) the electrode reaction 3 and (2) the electrode reaction 4. $\Delta_w^{\text{RTIL}}\phi_{X^-}^\theta = 0.1$ V, $\Delta_w^{\text{RTIL}}\phi_{M^+}^\theta = -0.1$ V, $[MX_{(w)}]^*/[\text{Red}]^*=100$

Figure 2 shows CV responses for lower solubility of MX in RTIL $\left(\Delta_w^{RTIL}\phi_{X^-}^\theta = 0.1 \text{ V}, \Delta_w^{RTIL}\phi_{M^+}^\theta = -0.1 \text{ V}, K_{tr,MX}^{w \to RTIL} = \right.$ $2.036 \cdot 10^{-2}, [MX_{(w)}]^*/, [Red]^* = 100 \text{ and } [MX_{(RTIL)}]^*/[Red]^* = 2.036)$. The peak potentials of reactions 3 and 4 are $E_P - E_{Red/Ox^+}^\theta = 0.0062 \text{ V}$ and $E_P - E_{Red/Ox^+}^\theta = 0.0057 \text{ V}$, respectively, which confirms that Eq. 23 does not apply if the condition $[MX_{(RTIL)}]^* \rangle 20 \cdot [Red]^*$ is not satisfied. The peak current of reaction 3 is higher ($\Phi_p = 0.2276$) than peak current of reaction 4 ($\Phi_p = 0.2151$). These differences increase with the decreasing solubility of MX in RTIL. This is shown in Fig. 3a,b for $K_{tr,MX}^{w \to RTIL} = 2.9 \cdot 10^{-3}$ and $4.146 \cdot 10^{-4}$, respectively. The peak potentials of reaction 4 are lower ($E_P - E_{Red/Ox^+}^\theta = -0.078 \text{ V}$ in Fig. 3a and -0.181 V in Fig. 3b) than the peak potentials of reactions 3 ($E_P - E_{Red/Ox^+}^\theta = -0.018 \text{ V}$ in Fig. 3a and -0.0225 V in Fig. 3b); but the peak currents of reaction 4 are much lower ($\Phi_p = 0.067$ in Fig. 3a and 0.010 in Fig. 3b) than the peak currents of reaction 3 ($\Phi_p = 0.191$ in Fig. 3a and 0.175 in
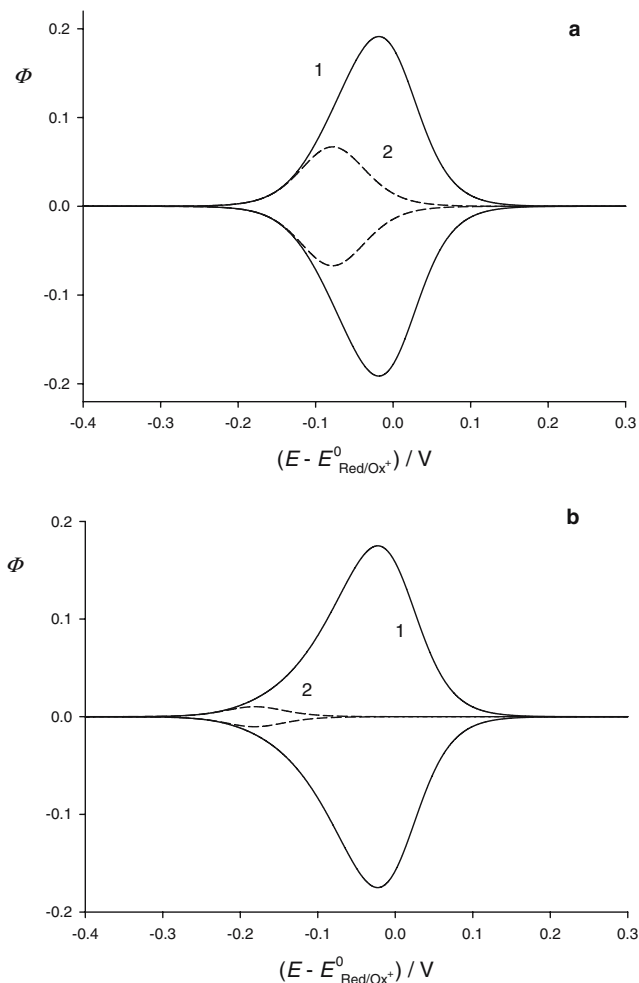
Fig. 3b). Obviously, the transfer of M^+ from RTIL into water is thermodynamically favored, but this ion can carry only a small current because its initial concentration in RTIL is very low. Therefore, under these conditions, it is more probable that the oxidation of the compound Red in the film is coupled to the transfer of anion X^- from water into RTIL according to reaction 3.

Figure 4 shows the dependence of CV peak potentials of reaction 3 on the logarithm of ratio of bulk concentration of electrolyte MX in water and the initial concentration of compound Red in the film of RTIL. If the partition coefficient $K_{tr,MX}^{w \to RTIL}$ is smaller than 10^{-3}, the peak potential is a linear function of $\log[MX_{(w)}]^*$, with the slope -59 mV (see curve 3). At higher values of the partition coefficient, the relationship between E_P and $\log[MX_{(w)}]^*$ is a curve with the slope that decreases as $\log[MX_{(w)}]^*$ increases. Finally, if $K_{tr,MX}^{w \to RTIL} > 1$, the peak potential is independent of $[MX_{(w)}]^*$ and defined by Eq. 23. Therefore, if E_P depends on the concentration of electrolyte in water, the electrode reaction 3 is more probable than the electrode reaction 4; but if E_P does not depend on $[MX_{(w)}]^*$, then both reactions are equally probable.

The relationships shown in Fig. 4 must be taken in consideration if the solubility of a certain ion in RTIL is estimated on the basis of the results of electrochemical measurements.

Conclusions

For a RTIL-confined redox reaction coupled to a charge compensating ion transfer across the RTIL/aqueous elec-

Fig. 3 Dimensionless cyclic voltammograms of (1) the electrode reaction 3 and (2) the electrode reaction 4. $\Delta_w^{RTIL}\phi_{M^+}^\theta = -0.2$ V (a) and -0.3 V (b); $\Delta_w^{RTIL}\phi_{X^-}^\theta = 0.1$ V, $[MX_{(w)}]^*/[Red]^* = 100$
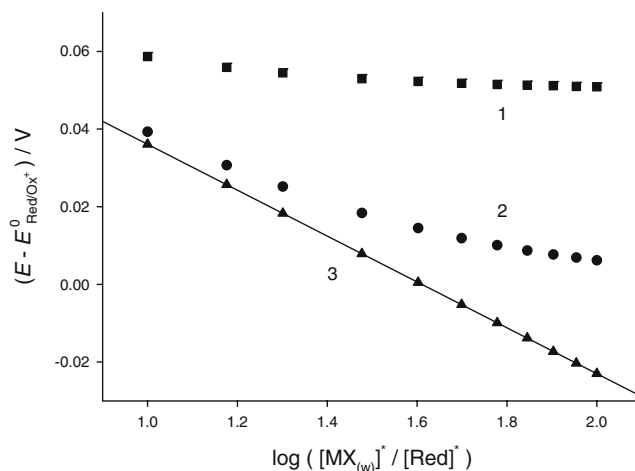

Fig. 4 Cyclic voltammetry of the electrode reaction 3. The relationship between peak potentials and the logarithm of the ratio of bulk concentration of the electrolyte MX in water and the initial concentration of compound Red in RTIL. $\Delta_w^{RTIL}\phi_{X^-}^\theta = 0.1$ V; $\Delta_w^{RTIL}\phi_{M^+}^\theta = 0$ V (1), -0.1 V (2) and -0.4 V (3); $K_{tr,MX}^{w \to RTIL} = 0.143$ (1), 2.04×10^{-2} (2), and 5.92×10^{-5} (3)

trolyte interface, the dependence of the formal potential on the electrolyte concentration may give valuable hints on the direction of ion transfer. This, however, is only possible if the transfer of the ions constituting the RTIL from there to the aqueous phase is excluded. Preliminary experiments with a RTIL of extremely low solubility in water, i.e., a very hydrophobic RTIL, have shown that even in such case the transfer of one of the RTIL ions to water may occur provided that very hydrophilic ions are present in the aqueous phase (Quentel et al., manuscript in preparation). We are also aware that the partition of a salt as described by Eq. 1 is not the only possibility to get ions from the aqueous phase into the RTIL: It is possible that an ion exchange is operative, i.e., that the anions of the RTIL leave the RTIL phase and anions of the aqueous electrolyte enter the RTIL. The same may occur with the cations. For a safe interpretation of voltammetric data, e.g., the dependence of formal potentials on ion concentrations, it is absolutely necessary to study the partition of ions in independent experiments, e.g., by ion chromatographic measurements.

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