Physical insights of salt transfer through solvent polymeric membranes by means of electrochemical methods

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A combined voltammetric study of the joint transfer of the two constituting ions of a water-soluble salt has been carried out using normal-pulse voltammetry, linear-sweep voltammetry and square-wave voltammetry in a system with two liquid–liquid polarized interfaces. As a result, we have explained the voltammetric features that allow us to distinguish this uptake from that corresponding to two equally charged ions, in spite of the appearance in both situations of two current peaks with the same sign in both square-wave and linear-sweep voltammograms, and we have found that linear-sweep voltammetry and square-wave voltammetry complement each other excellently.

A theoretical comparison with a system of a single polarized interface has also been made, showing that these systems are much less appropriate for characterizing these salt-ion transfers.

1. Introduction

Ion transfer at the Interface between Two Immiscible Electrolyte Solutions (ITIES) is a fascinating physicochemical process that has attracted the attention of researchers from different fields. Innovative studies have emerged in the literature based on this type of process.1–7 Although some amperometric and voltammetric studies on the ion transfer of salt ions have been reported,8,9 to the best of our knowledge, an in-depth electrochemical interpretation of the joint transfer of the two constituting ions of a water-soluble salt has never been tackled. Within these salts, of particular interest are those resulting from the combination of semi-hydrophobic cations and anions, many of which result in ionic liquids.10 Due to the high utility of ionic liquids in various branches of chemistry11–17 and the fact that they can produce environmental contamination due to their solubility in water,18,19 studies of their aqueous solutions are of great interest.

The novelty of this paper lies in the study of the joint transfer of the two constituting ions of water-soluble salts in membrane systems with one and two liquid–liquid polarized interfaces. Both systems consist of an organic membrane that separates two aqueous solutions, but in the former the polarization phenomenon is only effective at one of the two liquid–liquid interfaces (the sample solution–membrane interface, \( w_1/M \)), while in the latter both interfaces are polarizable.24–29 According to scheme 1 where \( B_i^+A_i^- \) represents the supporting electrolyte of the different phases (\( w_1, M \) or \( w_2 \)), and \( R^+Y^- \) is the salt whose ion transfer will be studied.

Although both systems are of interest, systems with two polarized interfaces have been demonstrated to be more useful for this kind of studies since they have proved to possess a series of striking advantages. They provide a potential window that is about twice that corresponding to systems with a single polarized interface;27 They produce a huge separation between voltammetric responses of any cation and anion with similar standard ion-transfer potential values30 and the half-wave membrane potential of these ions is influenced by their concentration.25,29–31 As will be shown, all these features are very interesting when the joint study of the transfer of the ions of a salt is carried out. For this purpose we have used linear-sweep voltammetry (LSV) and square-wave voltammetry (SWV), and as a result we can explain the voltammetric features that allow this ionic transfer to be distinguished from that corresponding to two equal charged ions, even though in both situations two current peaks with the same sign appear in both square-wave and linear-sweep voltammograms. For the physical explanation of this behavior we have resorted to the use of pulse voltammetry (NPV) since it provides responses that are easier to interpret than those corresponding to multipulse or sweep-potential techniques, because in NPV the membrane is cleaned before each applied potential.

\[ \text{Aqueous phase (} w_1 \text{)} \hspace{1cm} \text{Membrane (} M \text{)} \hspace{1cm} \text{Aqueous phase (} w_2 \text{)} \]

\[ B_i^+A_i^- \text{, } R^+Y^- \]

\[ x \rightarrow -\infty \quad x = 0 \quad x = d \quad x \rightarrow \infty \]

Scheme 1 A schematic view of the system with one polarized liquid–liquid interface (a), and with two polarized liquid–liquid interfaces (b).
2. Experimental section

2.1 Apparatus

The design of the voltammetric ion sensor has been described previously. Briefly, a Pt-wire counter electrode was accommodated inside the inner solution compartment of a Fluka ion-selective electrode (ISE) body, allowing the use of a four-electrode potentiostat. A glass ring of 28 mm inner diameter and 30 mm height, a glass plate, vial and punch were purchased from Fluka for the construction of the membranes.

2.2 Reagents and solutions

High-molecular-mass poly(vinyl chloride) PVC, 2-nitrophenyl octyl ether (NPOE) and tetrahydrofuran (THF) were Selectophore products from Fluka. Tetradodecylammonium tetrakis-(4-chlorophenyl) borate (TDDA-TClPB) and tetraethylammonium chloride (TEA Cl) were purchased from Sigma. Other parameters are given in the notation. The half-wave potentials, \( E_{1/2} \), are taken from ref. 29 and are given in the notation. The half-wave potentials, \( E_{1/2} \), are taken from ref. 29 and are given in the notation.

2.3 Membrane preparation

The membrane was prepared by dissolving 200 mg NPOE, 100 mg PVC and 17.2 mg TDDA-TClPB in 3 ml of tetrahydrofuran. This solution was poured into the glass ring resting on the glass plate and was left overnight to allow the solvent to evaporate slowly. A 6 mm diameter piece was cut out with the punch and incorporated into the modified ISE body described above.

2.4 Electrochemical measurements

The electrochemical cell used can be expressed as

\[
Ag|AgCl|5 \times 10^{-3} M \text{ LiCl} | 4 \times 10^{-3} M \text{ TDDA-TClPB} \quad 5 \times 10^{-5} M \text{ LiCl} \quad x \text{ M} \begin{array}{c} \text{ R}^+ \text{ Y}^- \text{ ISE} \quad \text{ Y}^+ \text{ R}^- \text{ AgCl} | Ag \end{array}
\]

with \( R^+ Y^- = \text{EMIm}^+ \text{Otf}^-, \text{BMPyr}^+ \text{TFSI}^-, \text{BMIm}^+ \text{PF}_6^-, \text{THTDP}^+ \text{Cl}^-, \text{TEA}^+ \text{Cl}^- \), and \( \text{Na}^+ \text{Pic}^- \). The applied potential, \( E \), is maintained at the preset value by the four-electrode potentiostat, which applies the necessary potential between the right and left counter electrodes and allows automatic compensation of the Ohmic potential drop. A positive current corresponds to the transfer of positive charge from the aqueous phase which contains the target salt \( R^+ Y^- \) to the organic phase, or of negative charge in the opposite direction. All computer programs were written in our laboratory.

3. Results and discussion

Fig. 1 shows the theoretical normal-pulse voltammograms (Fig. 1a), together with the experimental (dotted lines) and theoretical (solid lines) linear-sweep voltammograms obtained for a sweep rate of 5 mV s\(^{-1}\) (Fig. 1b), and the experimental (circles) and theoretical (lines) square-wave voltammograms obtained for a square-wave amplitude of 50 mV (Fig. 1c), corresponding to the transfer of the salt BMPyrTFSI from water to the solvent polymeric membrane. LSV and square-wave voltammograms were obtained by making two different and independent potential sweeps in opposite directions, from negative to positive potential and vice versa. Dash and solid arrows show the direction of each scan.

Theoretical curves from Fig. 1a were obtained using

\[
I = zF \sqrt{D_{X^+}^w} \pi r c_{X^+} \sqrt{\frac{e^2 + 8e^2 - e^4}{4}}
\]

with

\[
\eta = \frac{zF}{RT} (E - E_{M,X^+}^{1/2})
\]

where \( X^+ \) can be either of the two ions of the salt, i.e. \( X^+ = R^+ \) or \( Y^- \). Other parameters are given in the notation. The half-wave membrane potential in the systems with two polarized interfaces, \( E_{M,X^+}^{1/2} \), takes the following form

\[
E_{M,X^+}^{1/2} = E_M^{0V} - RT \ln \lambda
\]

\[
E_M^{0V} = \Delta_M \phi_{X^+}^{0V} - \Delta_M \phi_{Y^-}^{0V}
\]

\[
\lambda = \sqrt{\frac{D_{X^+}^w D_{Y^-}^w \pi r c_{X^+} c_{Y^-}^{0V}}{D_{X^+}^{0V} D_{Y^-}^{0V}}}
\]

It is important to highlight that, the form of eqn (5) depends on the ion that is transferred across the inner interface, \( B^+ \), coupled to the transfer of the target ion across the outer one. In our case \( B^+ = \text{Cl}^- \) for \( X^+ = R^+ \), and \( B^+ = \text{Li}^+ \).
for $X^z = Y^-$, i.e. the ions transferred at both interfaces have contrary signs ($z = -z'$).

In Fig. 1b and c, theoretical curves were obtained by taking $E_{M,X^z}^{1/2}$ and $A \sqrt{D_C^{X^z}}$ as adjustable parameters, and experimental data was fitted to the theoretical equations for reversible ion transfer using

$$I_p = zFA \sqrt{\frac{D_C^{X^z}}{\Delta E \pi C_{X^z}}} \sum_{j=1}^{p} \left( \frac{1}{\sqrt{p-j+1}} (g(\eta_j) - g(\eta_{j-1})) \right)$$

(6)

for the linear-sweep voltammograms (by introducing the condition $\Delta E \leq 0.01 \text{ mV}^{29,33}$); and

$$I_{sw} = I_{2p-1} - I_{2p} = zFA \sqrt{\frac{D_C^{X^z}}{\pi \Delta E}} \left[ \sum_{j=1}^{2p-1} (g(\eta_{j+1}) - g(\eta_j)) \frac{1}{\sqrt{2p-j+1}} - \frac{1}{\sqrt{2p-j}} \right] + g(\eta_{2p-1}) - g(\eta_{2p})$$

(7)

for the square-wave voltammograms. For eqn (6) and (7), $g(\eta_p)$ is the function that contains the dependence on the applied potential, $E_p$, as follows,

$$g(\eta_p) = \frac{\sqrt{2e\eta_p + 8e\eta_p - e^{\eta_p}}}{4}$$

(8)

$$\eta_p = \frac{zF}{RT}(E_p - E_{M,X^z}^{1/2})$$

(9)

with $g(\eta_0) = 0$, and other parameters defined in the notation.

As can be seen from both figures, a good agreement between theoretical and experimental data was obtained for both LSV and SWV techniques. From Fig. 1a it can be seen that when the successive transfer of two ions of opposite charge takes place (i.e. the ions that constitute any $R^+ Y^- \text{ salt}$), two well-separated waves appear which correspond to the anion transfer (negative current) and to the cation transfer (positive current), respectively. This behavior can be easily explained since for potential values that fulfill $E < E_{M,Y^z}^{1/2}$, the limit current for the anion transfer, is reached (i.e. $c_{Y^z}^{c,-}(0) = 0$, while the surface concentration for the cation is $c_{Y^z}^{c,+}(0) = c_{salt}^{c,+}$). The interfacial concentration of the anion reaches its initial value, $c_{Y^z}^{c,-}(0) = c_{Y^z}^{c,-}(0) = c_{salt}^{c,+}$, for applied potential values between the half-wave membrane potentials of the two salt-ions, $E_{M,X^z}^{1/2} < E < E_{M,R^+}^{1/2}$. In these conditions the current becomes nil since the interfacial concentrations of the two ions are the same ($c_{Y^z}^{c,-}(0) = c_{Y^z}^{c,+}(0) = c_{salt}^{c,+}$), i.e. the initial conditions are re-established. For applied potentials that fulfill $E \gg E_{M,R^+}^{1/2}$, the limit current for the cation transfer is reached.

**Fig. 1** Theoretical normal-pulse voltammograms (Fig. 1a), experimental (dotted lines) and theoretical (solid lines) linear-sweep voltammograms (Fig. 1b), and experimental (circles) and theoretical (lines) square-wave voltammograms (Fig. 1c), obtained for a $2.5 \times 10^{-3} \text{ M}$ solution of BMPyrTFSI by carrying out two different and independent sweeps in opposite directions: from negative to positive potentials (indicated by dash arrows, $E_{fin} = -0.7 \text{ V}$, $E_{fin} = 0.5 \text{ V}$) and vice versa (indicated by solid arrows, $E_{fin} = 0.5 \text{ V}$, $E_{fin} = -0.7 \text{ V}$). Theoretical curves in Fig. 1a were calculated from eqn (1) by using the optimal $E_{M,X^z}^{1/2}$ and $A \sqrt{D_C^{X^z}}$ obtained from the fitting of Fig. 1c: $E_{M,BMPyr^+}^{1/2} = 311 \text{ mV}$, $E_{M,TFSI^-}^{1/2} = -494 \text{ mV}$, $A \sqrt{D_C^{BMPyr^+}} = 5.9 \times 10^{-4} \text{ cm}^3 \text{ s}^{-1/2}$, $A \sqrt{D_C^{TFSI^-}} = 6.24 \times 10^{-4} \text{ cm}^3 \text{ s}^{-1/2}$ and $\tau = 1 \text{ s}$. Theoretical curves in Fig. 1b and c were calculated from eqn (6) and (7) by taking $E_{M,X^z}^{1/2}$ and $A \sqrt{D_C^{X^z}}$ as adjustable parameters. Fig. 1b: $\Delta E = 0.01 \text{ mV}$, $v = 5 \text{ mV s}^{-1}$. Fig. 1c: $E_{fin} = 50 \text{ mV}$, $E = 10 \text{ mV}$, $\tau = 0.3 \text{ s}$, $T = 298.15 \text{ K}$.  

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(i.e., $c_{y_0}^c(0) = 0$, while the surface concentration for the anion fulfills $c_{y_0}^a(0) = c_{y_0}^a = c_{salt}^a$).

From the above interpretation it is clear that with NPV it is easy to distinguish if two successive ion transfers correspond to ions of opposite sign as occur with the anion and the cation in the case of a salt, giving rise to two waves of different sign (as occurs in Fig. 1a), or ions of the same sign which could be present in the sample, which gives two waves of the same sign (as shown in Fig. 2a).

In Fig. 1b and c, the successive transfer of two opposite charged salt ions is also considered as in Fig. 1a, but using other electrochemical techniques that are more powerful and more easily applicable than the NPV technique. We have used LSV (Fig. 1b) and SWV (Fig. 1c). It is clear that the two peaks which appear in each scan of both figures correspond to the transfer of the anion and the cation. However, as these two peaks do not have different current signs it is difficult to determine if they correspond to ions with the same charge or with opposite charge. This distinction is simple when using LSV (Fig. 1b) since, as can be observed, in the case of opposite charged ions a greater fall in current is always observed at the beginning of the experiment, which corresponds to the transfer of the anion into the membrane if the potential is scanned from negative to positive values or to the transfer of the cation into the membrane if the potential is scanned in the opposite way. This current fall is followed by a current peak of opposite sign due to the back transfer of the ion already extracted from the membrane into the aqueous phase. This behavior is not observed in the case of NPV since, as a single-pulse technique, the initial equilibrium conditions are re-established after each applied potential, and therefore the current associated with back-ion transfers is not possible since the membrane is clear of salt-ions and the sign of the current indicates the charge of the ion uptake. With regard to the second peak of the LSV scan, it always corresponds to the transfer of the other ion of the salt from the aqueous phase into the membrane.

From Fig. 1b, it also can be seen that in the case of the transfer of the ions of a salt, the LSV current tends to zero between both ion-transfer processes (for $E_{M,Y} < E < E_{M,R}^{cw}$, i.e. the initial equilibrium is re-established as in the case of NPV (see Fig. 1a). However, when the transfer of two equal-sign ions is considered, for example, two cations as presented in Fig. 2b, the LSV scan from negative to positive potentials presents zero initial current, and the current between both ion-transfer processes is always different from zero, since it tends to the limit current value of the first ion transfer, as shown in Fig. 2b.

Fig. 1a (NPV) and 1b (LSV) are key to the physical explanation of the square-wave voltammograms given in Fig. 1c since, due to the subtractive character of the SWV technique ($I_{sw} = I_{2p-1} - I_{2p}$), the morphology of its signal makes it difficult to know if the two successive ion transfers observed in Fig. 1c correspond to ions with equal or opposite charge.
voltagograms corresponding to the successive transfer of two oppositely charged ions \((R^+ Y^-)\) from water to the solvent polymeric membrane against a system with only one polarized interface. With the aim of comparing the results obtained with both types of systems we have chosen \(\Delta M^* \phi_{0}^R = \Delta M^* \phi_{0}^{\text{BMPyr}^+}\) and \(\Delta M^* \phi_{0}^Y = \Delta M^* \phi_{0}^{\text{TFSI}^-}\) (see Table 1). These theoretical curves were also obtained from eqn (1), (6) and (7), taking into account that, for these systems the \(g(\eta_p)\) function needs to be changed for \(-1/(1 + J_p)\), being

\[
J_p = e^{\eta_p} \frac{p \geq 1}{p = 0}
\]

with \(\eta_p\) given by eqn (2) from ref. 30. The half-wave potential for the system with a single polarizable interface is \(3^2\)

\[
E^{1/2} = \Delta M^* \phi_{X^2}^p + \frac{RT}{2F} \ln \sqrt{\frac{D_{X^0}^{p}}{D_{X^2}^{p}}}
\]

As in Fig. 1b and c, in Fig. 3b and c two independent potential sweeps have been theoretically studied, from negative to positive values (dashed line) and vice versa (solid line).

Comparing Fig. 3 with Fig. 1, it can be observed that for any of the three electrochemical techniques used, the responses corresponding to the transfer of the ions of a salt are much less separate when a membrane system of a single polarizable interface is used, and can even overlap (the current does not fall to zero between them). For example, the separation between the voltammetric signals corresponding to the salt ions that are presented in Fig. 3a–c is approximately 190 mV, in contrast with the nearly 820 mV that is observed in the system with two polarizable interfaces (see Fig. 1a–c and also Table 1), i.e. the voltammetric signals of the salt ions are separated approximately four-times more in this system. This constitutes a huge advantage when ions with opposite charge are studied, as shown in Fig. 4.

Fig. 4 shows the experimental and theoretical square-wave voltamograms obtained using a square-wave amplitude of 50 mV corresponding to the transfer from water to the solvent polymeric membrane of the cations and the anions of different salts, together with those of TEA\(^+\) and Pic\(^-\) as reference ions. Experimental data were fitted to theoretical equations for the reversible ion-transfer process (eqn (7)) using \(E^{1/2}_{M,X^2}\) and

\[
\begin{align*}
\text{Fig. 3} & \quad \text{Theoretical normal-pulse voltammograms obtained from eqn (1) (Fig. 3a), and theoretical LSV (Fig. 3b) and SWV (Fig. 3c) voltammograms obtained from eqn (6) and (7), respectively, for the successive transfer of two ions with opposite charge \((R^+ Y^-)\) in a system with only one polarized interface by making the same two different and independent sweeps as in Fig. 1: from negative to positive potentials (dash line, \(E_{\text{in}} = -0.7 \text{ V}, \ E_{\text{in}} = 0.5 \text{ V}\) and vice versa (solid line, \(E_{\text{in}} = 0.5 \text{ V}, \ E_{\text{in}} = -0.7 \text{ V}\). Dash and solid arrows show the direction of the sweep in each case.} \\
\end{align*}
\]

\[
\begin{align*}
c_{\text{H}_2} & = 2.5 \times 10^{-4} \text{ M}, \\
\Delta \phi_{0}^R & = 24 \text{ mV}, \ \Delta \phi_{0}^Y & = 9 \text{ mV}. \ 
\text{Fig. 3a: } A \sqrt{D_{R^2}^{p}} = 5.9 \times 10^{-4} \text{ cm}^2 \text{s}^{-1/2}, A \sqrt{D_{Y^2}^{p}} = 6.24 \times 10^{-4} \text{ cm}^2 \text{s}^{-1/2}, \tau = 1 \text{ s}. \ 
\text{Fig. 3b: } A \sqrt{D_{R^2}^{p}} = 7.8 \times 10^{-4} \text{ cm}^2 \text{s}^{-1/2}, A \sqrt{D_{Y^2}^{p}} = 6.6 \times 10^{-4} \text{ cm}^2 \text{s}^{-1/2}, \Delta \phi_{\text{H}_2} = 0.01 \text{ mV}, \ v = 5 \text{ mV} \text{s}^{-1}. \ 
\text{Fig. 3c: } A \sqrt{D_{R^2}^{p}} = 5.9 \times 10^{-4} \text{ cm}^2 \text{s}^{-1/2}, A \sqrt{D_{Y^2}^{p}} = 6.24 \times 10^{-4} \text{ cm}^2 \text{s}^{-1/2}; \ E_{\text{sw}} = 50 \text{ mV}, \ E_{\text{in}} = 10 \text{ mV}, \tau = 0.3 \text{ s}. \ T = 298.15 \text{ K}. 
\end{align*}
\]
Table 1 Standard ion-transfer potentials and peak-to-peak separation values obtained from SWV

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Delta \phi_{\text{PTEA}}^{m}/\text{mV}$</th>
<th>$\Delta \phi_{\text{P}}^{m}/\text{mV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF$_6^-$</td>
<td>-68 ± 2</td>
<td>862</td>
</tr>
<tr>
<td>BMIm$^+$</td>
<td>-12 ± 1</td>
<td></td>
</tr>
<tr>
<td>TFSI$^-$</td>
<td>9 ± 1</td>
<td>821</td>
</tr>
<tr>
<td>BMPyr$^+$</td>
<td>24 ± 1</td>
<td></td>
</tr>
<tr>
<td>Otf$^-$</td>
<td>-204 ± 2</td>
<td>1004</td>
</tr>
<tr>
<td>EMIm$^+$</td>
<td>-6 ± 2</td>
<td></td>
</tr>
<tr>
<td>THTDP$^+$</td>
<td>-399 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

$A\sqrt{D_C}$, as adjustable parameters. As can be seen, a very good fit was obtained in all cases.

The standard ion-transfer potential of each ion $X^*$, was calculated from the difference between the half-wave membrane potentials obtained from SWV curves of that ion and of the corresponding reference (TEA$^+$ for cations and Pic$^-$ for anions) using the same square-wave amplitude and concentration for both ions. Thus, by applying eqn (3)-(5) and taking in the relation between formal and standard potential, the following equation is obtained when the target ion is a cation, $R^+$, and

$$E_{M,Y^-}^{1/2} - E_{M,Pic}^{1/2} = \Delta \phi_{\text{PTEA}}^M - \Delta \phi_{\text{PTEA}}^{0} + \frac{RT}{F} \ln \left( \frac{D_{\text{MTEA}}^{0}}{D_{\text{MTEA}}^{+}} \right)$$

$$+ \frac{RT}{F} \ln \left( \frac{D_{\text{MTEA}}^{0}}{D_{\text{MTEA}}^{+}} \right)^{1/2}$$

(12)

when the target ion is an anion, $Y^-$. Under the experimental conditions used, the last two terms of the right hand side in eqn (12) and (13) are practically zero, such that, in order to determine $\Delta \phi_{\text{PTEA}}^{0}$ and $\Delta \phi_{\text{PTEA}}^{0}$ we have used $\Delta \phi_{\text{PTEA}}^{0} = 21 \text{ mV}$ and $\Delta \phi_{\text{PTEA}}^{0} = -17 \text{ mV}$, the former obtained from ref. 34 where a 2:1 (m/m) NPOE–PVC membrane was used, and the latter obtained from ref. 26 where a 4:1 (m/m) NPOE–PVC membrane was used.

The average values obtained for the standard ion-transfer potentials of the different salt-ions by using SWV are shown in the first column of Table 1.

As can be seen in Fig. 4 and also in the second column of Table 1, the peak separation between the voltammetric responses of the salt-ions, $\Delta \phi_{\text{P}}$, becomes higher as the lipophilicity of these ions decreases. This behavior can be easily explained by the following equation

$$\Delta \phi_{\text{P}} \simeq 16 + \Delta \phi_{\text{F}}^{0} + \Delta \phi_{\text{Y}}^{0} - \Delta \phi_{\text{Y}}^{0} + \Delta \phi_{\text{Y}}^{0}$$

$$- \Delta \phi_{\text{F}}^{0} - \frac{RT}{F} \ln \left( \frac{\prod D_{i}^{0}}{D_{i}^{+}} \frac{c_{\text{Cl}}^{0}}{c_{\text{Cl}}^{+}} \right)$$

(14)

which has been obtained using eqn (3)-(5) from the present paper and eqn (20) from ref. 30, and taking into account that in our membrane system $\text{Cl}^-$ is transferred at the inner interface when the target ion is a cation, $R^+$, and $\text{Li}^+$ is transferred when the target ion is an anion, $Y^-$. As can be seen from this equation, for a fixed electrolyte in the inner aqueous solution the peak-to-peak separation depends on the difference between the standard ion-transfer potentials of the coupled ions, which increases as the lipophilicity of these ions decreases, on the diffusion coefficients of the same and on the initial concentration of the salt assayed, $c_{\text{Cl}}^{0}$. This last dependence is of particular interest, since it allows the peak positions of the salt-ions to be tuned slightly in order to discriminate between their signals and those corresponding to possible interfering ions.

The value of the standard ion-transfer potential for the ionic liquid cation BMIm$^+$ obtained is in acceptable agreement with results we previously reported using a system with a single polarizable interface, thus showing the reliability of the procedure for the determination of standard ion potentials.

In the case of the salt THTDP$^+$ Cl$^-$, consisting of a very hydrophobic cation and a very hydrophilic anion, only the peak corresponding to the cation can be observed, which appeared in the middle of the potential window. The transfer of water-soluble phosphonium salts may be very important...
because they accumulate selectively in cancer cells, which has been exploited for anti-tumor therapies.35

The separation achieved between the potential peaks corresponding to the cation and anion of the different ionic liquid salts assayed can be exploited for the simultaneous determination of the concentration of both ions in real samples.

4. Conclusions

In this paper, we have demonstrated that linear-sweep voltammetry and square-wave voltammetry complement each other effectively to distinguish if two successive ion transfers correspond to ions of opposite sign (i.e., the ions that constitute a \( R^+ Y^- \) salt) or to ions of equal sign, even though two voltammetric peaks of the same sign are observed for both kind of ion transfers in both LSV and SWV techniques. The use of normal-pulse voltammetry helps to interpret the experimentally observed behavior.

The use of the linear-sweep voltammograms permits us to distinguish easily both situations, since in the case of opposite charged ions a large fall in current is observed at the beginning of the experiment and the current tends to zero between both ion-transfer processes; while when the transfer of two equal sign ions is considered, the initial current is null and the current between both ion-transfer processes is always different from zero, since it tends to the limit current value of the first ion transfer.

In contrast, the square-wave voltammograms of both kinds of ion transfers do not present significant differences and, consequently, this technique barely permits us to distinguish if the two successive ion transfers correspond to ions with opposite or equal charge sign. However, SWV provides better defined peaks than LSV, showing better resolution and high sensitivity, and it allows for more accurate quantification.

We have also demonstrated that systems with two liquid–liquid polarized interfaces are more advantageous for the analysis of the transfer of the two ions consisting of a salt than those with a single polarizable one, since the voltammetric signals of the ions have much greater separation in this kind of systems.

5. Notation

\( X^+ \) ion that is transferred at the sample solution–membrane interface (outer interface) or target ion.

\( Y^- \) ion that is transfer at the reference solution–membrane interface (inner interface) coupled to the transfer of the target ion at the outer one.

\( \bar{A} \) area of the outer interface.

\( F \) Faraday constant, 96485.3 C.

\( R \) molar gas constant, 8.31447 J mol\(^{-1}\) K\(^{-1}\).

\( T \) working absolute temperature.

\( D_{i0}^p \) diffusion coefficient of the ion \( i \) in phase \( p \), being \( p = w_1 \) (sample aqueous solution), \( w_2 \) (reference solution) or \( M \) (membrane).

\( c_i^0 \) initial concentration of the ion \( i \).

\( c_i^0(0) \) interfacial concentration of the ion \( i \) in phase \( p \).

\( \gamma_i^0 \) activity of the ion \( i \) in phase \( p \).

\( \Delta_{M}^{w} \phi_i^0 \) standard molar ion-transfer potential of the ion \( i \).

\( \Delta_{M}^{w} \phi_i^0 = \Delta_{M}^{w} \phi_i^0 + \frac{RT}{F} \ln \left( \frac{c_i^0}{c_i^0(0)} \right) \) \\

\( \nu \) sweep rate in LSV.

\( \Delta E \) pulse amplitude in square voltage.

\( E_{sw} \) square wave amplitude in SWV.

\( \tau \) duration of each applied potential.

References


18 L. Zhao, Y. Liao and Z. Zhang, Clean, 2007, 35, 42.


