Advances in the Study of Ion Transfer at Liquid Membranes with Two Polarized Interfaces by Square Wave Voltammetry

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Abstract
A general analytical expression has been deduced for the \( I/E \) response of the square wave voltammetry corresponding to ion transfer processes in systems with two liquid/liquid polarized interfaces. This expression has been evaluated through the experimental study of a series of quaternary ammonium cations and metal chloro complex anions. We have found that systems with two liquid/liquid polarizable interfaces present the striking advantage that the difference between peak potentials of square wave voltammograms of cations and anions with similar standard ion transfer potential is much greater than in systems with a single polarizable one.

Keywords: Ion transfer, Liquid membranes, Square wave voltammetry, Membranes, Voltammetry

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1. Introduction

As is well known, square wave voltammetry (SWV) and cyclic square wave voltammetry (CSWV) are among the best and most effective techniques developed for the quantitative analysis and the characterization of electrochemical systems. Due to the combination of the main features of cyclic voltammetry and differential pulse techniques, SWV is a fast technique with a strong resolving power and high sensitivity and it is one of the most widely employed techniques in voltammetric studies [1 – 3].

In spite of the great importance that voltammetric studies of ion transfer processes at liquid/liquid interfaces have achieved over the last few decades, as a consequence of its analytical and biological applications [4 – 14], SWV has scarcely been used for this kind of systems [2, 15 – 18]. What is more, to our knowledge, up to date SWV has not been applied in the voltammetric study of the ion transfer at systems as interesting as those with two polarizable liquid/liquid interfaces [8, 10, 11, 14, 19 – 21], probably due to a lack of theory.

It has been demonstrated that the potential window in systems with two polarizable liquid/liquid interfaces is about twice as wide as those with one polarizable interface [11]. The approach with two polarizable interfaces allows a more hydrophobic electrolyte to be used in the membrane phase, since no water-soluble salt of any of its ions is necessary. This leads to a widening in the potential window of the working interface. Moreover, as will be shown here, a striking advantage of these systems with two polarizable interfaces is that they can produce a huge separation between the voltammetric peaks corresponding to any cation and anion of similar standard ion transfer potential. This is mainly due to the different coupled processes that take place at the other interface, which have very different standard ion transfer potential values. All the above is very relevant to electroanalysis and ion sensing because it allows increasing the selectivity of voltammetric methods and amperometric ion sensors based on ion transfer at liquid/liquid interfaces.

In previous papers we have deduced explicit, analytical and very easy manageable expressions for the \( I/E \) response and concentration profiles for the ion transfer at systems with two liquid/liquid interfaces which are valid for any multipotential step technique [21], and more recently we have applied them satisfactorily to the study of the ion transfer of several cationic drugs with different pharmacological activities with DPV technique [22].

For these reasons, and in line with our previous papers [21, 22], the aim of this paper is to lay the basis for the application of the SWV to systems with two polarizable liquid/liquid interfaces and to indicate the parallelism between systems with one [23] and two polarizable liquid/liquid interfaces.

In order to verify the validity of the explicit \( I_{SW}/E \) expression we have studied experimentally the transfer of several cations and anions. From the results it has been possible to determine the standard ion transfer potential of a series of quaternary ammonium cations and metal chloro complex anions distributed over a range of potential of 1200 mV. To the best of our knowledge, this is the first time that the standard ion transfer potential of any anionic metal halo complex has been determined.
For comparison purposes, the same ion transfers have been studied using Cyclic Voltammetry (CV), showing that the fitting between experimental and theoretical values is much better with SWV technique, since the possible ohmic drop effects are greatly reduced due to the differential nature of this technique.

Finally, we have found further experimental evidence that the PVC content in the organic phase, even at relatively high values, does not significantly affect the values of the standard ion transfer potential with respect to the solvent (2-nitrophenyl octyl-ether) alone.

2. Experimental

2.1. Apparatus

The design of the voltammetric ion sensor has been described previously [24]. Briefly, a Pt-wire counter electrode was accommodated inside the inner solution compartment of a Fluka ion-selective electrode (ISE) body, which permits the use of a four-electrode potentiostat. A glass ring of 28 mm inner diameter and 30 mm height, glass plate, vial and punch were purchased from Fluka for the construction of the membranes.

2.2. Reagents and Solutions

Poly(vinyl chloride) high molecular mass, 2-nitrophenyl octyl ether (NPOE) and tetrahydrofuran (THF) were Selectrophore products from Fluka. Tetrabasic ammonium tetrakis-(4-chlorophenyl) borate (TDDA-TClPB), tetraphenyl-ammonium chloride (TPACl) and tetrabutyl-ammonium chloride (TBACl), tetraethyl-ammonium tetrakis-(4-chlorophenyl) borate (TDDA-TClPB), tetraethyl-ammonium chloride (TEACl), were purchased from Sigma. Antimony(V) chloride and picric acid were purchased from Merck, and sodium tetrachloroaurate(III) dihydrate was purchased from Semp.

2.2. Reagents and Solutions

A 5 × 10⁻⁴ M tetrachloroaurate(III) solution was prepared by dissolving sodium tetrachloroaurate(III) dihydrate in 5 × 10⁻² M hydrochloric acid solution.

A 5 × 10⁻² M hexachloroantimonite(V) stock solution was prepared by dissolving antimony(V) chloride in concentrated hydrochloric acid solution. Working 5 × 10⁻⁴ M solution was freshly prepared by diluting with 5 × 10⁻² M hydrochloric acid solution.

A 1 × 10⁻² M sodium picrate solution was prepared by dissolving picric acid in water and adding sodium hydroxide solution until a pH 7 was reached. A 5 × 10⁻⁴ M solution was prepared by diluting with 5 × 10⁻² M lithium chloride.

All the other reagents used were of analytical reagent grade. Nanopure water (18-MΩ) prepared with a Milli-Q (Millipore) system was used throughout.

2.3. Membrane Preparation

The membranes were 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

\[ \text{Ag} | \text{AgCl} | 5 \times 10^{-2} \text{M LiCl} | 5 \times 10^{-2} \text{M TDDA-TClPB} | 5 \times 10^{-2} \text{M LiCl}, x \text{ M X}^z | \text{Ag} \]

with \( x = \text{TMA}^+, \text{TEA}^+, \text{TPA}^+, \text{TBA}^+, \text{AuCl}_4^-, \text{SbCl}_4^- \) and \( \text{Pic}^- \). The applied potential, \( E \), is maintained at the preset value by the four-electrode potentiostat that 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 ion \( X^z \) to the organic phase. All computer programs were written in our laboratory.

3. Theory

The potential waveform applied in Square Wave Voltammetry (SWV) technique can be described as a sequence of square wave pulses superimposed on a staircase potential, in agreement with the scheme given in [1]. The net current is the difference between that corresponding to a pulse of odd index (forward, \( I_j \)) and that of the following pulse of even index (reverse, \( I_i \)),

\[ I_{sw} = I_i - I_j \] (1)

This net current \( I_{sw} \) is plotted versus the index potential, defined as an intermediate potential value between each pair of consecutive potential pulses,

\[ E_p^{\text{index}} = E_p + (-1)^p E_{sw} \] (2)

with \( E_p \) being the potential applied during pulse \( p \) (see equation 3 in [18]), and \( E_{sw} \) is the square wave amplitude.

We will apply the SWV technique to the study of the ion transfer through a liquid membrane, which can be described as an organic phase (the membrane, \( M \), that separates two aqueous solutions, \( w_i \) and \( w_o \), with the former containing the ion \( X^z \) (with \( z \) equal to +1 or -1) whose transfer across the interface \( w_i/M \) is going to be analyzed. The cell can be schematically represented as follows:

\[ \text{BA} (w_o) | \text{RY}(M) | \text{BA}, X^z (w_i) \] (1)
where BA is the supporting electrolyte for the aqueous phases w₁ and w₂, and RY are the supporting electrolytes for the organic phase, M. Hereafter, we will call the working interface, w₁/M, “outer” and the w₂/M interface “inner”.

When an external polarization is applied to this type of membrane system in which there is no common ion among the liquid membrane and aqueous phases, the potential drop across the two interfaces cannot be controlled individually, but the electrochemical processes occurring in both interfaces are coupled by virtue of the same intensity of electrical current (i.e.: \( I(\text{outer interface}) = I(\text{inner interface}) = I \)). If we assume that all phases contain sufficient concentrations of electrolytes such that the different ohmic drops can be neglected, the two interfacial potential differences are related with the potential differences in the outer and inner aqueous solutions. Moreover, for the deduction of Equation 5 it is assumed that the target ion X does not reach the inner interface [21].

We can, therefore, define three index potentials for the SWV response of this system, the membrane index potential, \( E_{p}^{\text{index}} \), given by Equation 2, and also the outer index potential, \( E_{p}^{\text{out index}} \), and the inner index potential, \( E_{p}^{\text{in index}} \), which can be defined as (see [25]):

\[
E_{p}^{\text{out index}} = \left( E_{p}^{\text{out}} - E_{p}^{2p} \right)/2
\]

(3)

\[
E_{p}^{\text{in index}} = \left( E_{p}^{\text{in}} + E_{p}^{2p} \right)/2
\]

(4)

with \( E_{p}^{\text{out}} \) and \( E_{p}^{\text{in}} \) (\( j = 2p - 1 \) or \( j = 2p \)) being the potential differences at the outer and inner interfaces during the \( p \)-th pulse. Note that we have considered that all the index potentials are defined at the midpoint of each square wave cycle [18].

Taking into account that the transfer of the target ion, \( X' \), through the outer interface and the coupled transfer of the ion \( R' \) through the inner one behave in a nernstian way, the expression of the current, \( I \), corresponding to the \( p \)-th potential, \( E_{p} \), can be written in terms of the surfaces concentrations, which are time independent [26],

\[
I_{p} = zFE_{p} \sqrt{D_{X}^{w}/\pi \tau} \sum_{j=1}^{p} \frac{1}{\sqrt{p-j+1}} \left( c_{X}^{w,j-1}(0) - c_{X}^{w,j}(0) \right)
\]

(5)

\[
= zFE_{p} \sqrt{D_{X}^{w}/\pi \tau} \sum_{j=1}^{p} \frac{1}{\sqrt{p-j+1}} \left( c_{R}^{w,j}(d) - c_{R}^{w,j-1}(d) \right)
\]

where \( c_{X}^{w,j}(0) \) and \( c_{R}^{w,j}(d) \) are respectively the surface concentrations of the ion \( X' \) at the outer interface (w₁/M) and of the ion \( R' \) at the inner one (M/w₂), corresponding to \( E_{p} \), \( D_{X}^{w} \), and \( D_{R}^{w} \) are the diffusion coefficients of \( X' \) and \( R' \) in the outer and inner aqueous solutions. Moreover, for the deduction of Equation 5 it is assumed that the target ion \( X' \) does not reach the inner interface [21].

The surface concentrations, \( c_{X}^{w,j}(0) \) and \( c_{R}^{w,j}(d) \), are related with the potential differences in the outer and inner interfaces respectively by:

\[
c_{X}^{w,j}(0) = \frac{c_{X}}{1 + \sqrt{D_{X}^{w}/D_{X}^{o}e^{\eta_{p}}}}
\]

\[
c_{R}^{w,j}(d) = \frac{c_{R}}{e^{\eta_{p}}}
\]

(6)

By combining Equations 6 – 8, it is possible to obtain explicit relationships between the surface concentrations \( c_{X}^{w,j}(0) \) and \( c_{R}^{w,j}(d) \), and the applied potential \( E_{p} \), through the \( g(\eta_{p}) \) function,

\[
c_{X}^{w,j}(0) = c_{X}(1 - g(\eta_{p})); \quad c_{R}^{w,j}(d) = c_{R} \sqrt{D_{R}^{w}/D_{R}^{p}g(\eta_{p})}
\]

(14)
Introducing Equations 14 into Equation 5 when a system with two polarizable liquid/liquid interfaces is considered [21], or from Equations 6–11 of [23] for a system with a single polarizable interface, we obtain the following elegant expression for the current corresponding to the \( p \)-th potential, \( E_p \):

\[
I_p = zFA \sqrt{\frac{D_{w,r}^0}{\pi \epsilon_r}} \sum_{j=1}^{p-1} \left( \frac{1}{\sqrt{p-j+1}} (F(\eta_{j-1}) - F(\eta_j)) \right)
\]

(15)

with \( F(\eta) = -g(\eta) \) and \( F(\eta_0) = 0 \) for the liquid membrane system discussed in this paper and,

\[
F(\eta) = \begin{cases} 
\frac{1}{1+e^\theta} & j \geq 1 \\
1 & j < 1
\end{cases}
\]

(16)

if a system with a single polarizable interface is considered [23].

As can be seen from Equations 9, 15 and 16, the expression for the current-potential response to the application of any multipotential step sequence to the system with two polarizable liquid/liquid interfaces is formally identical to that obtained for the system with a single polarizable interface [23], since the method followed for its deduction is based on the same premises.

Note that, in agreement with Equation 10 of [23] and Equation 10 of this paper, \( \eta \) presents an analogous form for systems with one or two polarizable interfaces, but the half-wave potential expression is different, it is given by Equation 11 in the latter case and by

\[
E^{1/2} = \frac{\Delta^{w,0}_{M,X}}{\varepsilon_X} + \frac{RT}{zF} \ln \sqrt{\frac{D_{w,F}^0}{D_{w,F}^1}}
\]

(17)

in the former [24].

Now we are able to write the expression for the SWV response for both types of systems by combining Equations 1 and 15

\[
I_{sw} = I_{p-1} - I_p = I_d(t) \left[ \sum_{j=1}^{p-1} (F(\eta_j) - F(\eta_{j-1})) \left( \frac{1}{\sqrt{2p-j+1}} \right) - 1 \right] + \frac{1}{\sqrt{2p-j}} + F(\eta_{2p}) - F(\eta_{2p-1})
\]

(18)

where \( r \) is the duration of each potential pulse and \( I_d(t) \) is given by

\[
I_d(t) = zFAc_X \sqrt{\frac{D_{w,F}^0}{\pi \epsilon}}
\]

(19)

4. Results and Discussion

Scheme 1 shows the potential-time waveform used in SWV calculated from Equation 1 of [18]. In this figure we have plotted the applied potential, \( E \), (red line) and its distribution between the outer interface, \( E^{out} \), (blue line) and the inner interface \( E^{in} \), (green line) calculated from Equation 8. As can be observed in the central part of the cyclic sweep, the outer potential, \( E^{out} \), follows the same trend as the applied potential, \( E \), in such a way that, in this zone, the outer interface presents a behavior similar to that of a system with single polarizable interface (see below). Concerning the inner interface, \( E^{in} \) is quite sensitive to the external polarization at both extremes of the cyclic sweep, becoming independent of the potential in the central zone of the same.

In this figure, we have also observed that, in line with previous calculations at both extremes of the cyclic sweep, becoming independent of the potential in the central zone of the same.

In Inset of Scheme 1 we can see how the potential pulses are distributed unequally between both outer and inner interfaces.

In Figure 1 it has been plotted the \( I/E \) curves corresponding to the direct and to the reverse scans (solid line and empty circles, respectively) by taking as abscissa three different potentials: the applied potential, \( E \) (Figure 1a), the outer potential, \( E^{out} \) (Figure 1b) and the inner potential, \( E^{in} \) (Figure 1c). These figures include the net current calculated from Equation 18, and also the forward, \( I_f \), and reverse, \( I_r \), currents calculated from Equation 15.

As can be observed, the \( I_{sw}/E \) curves corresponding to the direct scan and to the absolute value of the reverse scan are perfectly superimposable, which implies that the \( I_{sw}/E \) curves corresponding to the direct and inverse scans are symmetrical with respect to the potential axis. This is due to the reversible behavior of the ion transfers which take place in both interfaces of the liquid-liquid membrane. For these reasons SWV technique is an excellent tool for analyzing the reversibility of charge transfer processes [27]. It can be also observed from the same figure that the square wave signal obtained in Figure 1b is formally similar to that obtained when only one interface is considered, whereas that obtained in Figure 1c presents a sharp fall at negative potentials. This different behavior is due to the unequal distribution of the applied potential between the outer and inner interfaces, indicated by Scheme 1.

Figure 2 shows the \( |I_{sw}|/E \) curves corresponding to the direct and to the reverse scans of the square wave (solid line and empty circles, respectively) for a system with only one

and with two polarizable interfaces, calculated for a square wave pulse amplitude of 50 mV by using Equation 18.

As can be seen, in the two cases considered, i.e. a single or two liquid-liquid polarizable interfaces, the \( |I_{sw}|/E \) curves corresponding to the direct and reverse scans are superimposable, since all the ion transfer processes considered are reversible, as has been discussed previously. It can be also observed in this figure that, in line with previous
considerations [21, 22], the curves corresponding to the system with two liquid-liquid polarizable interfaces are lower and wider than those corresponding to the system with a single polarizable interface. Moreover, the peaks (of the direct and reverse scans) obtained when two polarizable interfaces are considered are shifted 8 mV with respect to those obtained for the system with a single polarizable one, i.e. the half wave potential for the system with two polarizable interfaces can be easily determined from the peak potential by means of

$$E_{\text{peak}}(\text{mV}) \approx E_M^{1/2} \pm 8$$  \hspace{1cm} (20)$$

for $E_m = 50$ mV (with the upper sign for cations and the lower one for anions), whereas when only one interface is considered, $E_{\text{peak}} = E_M^{1/2}$ regardless of the square wave potential (see Eq. 17).

The influence of the ionic concentration on the SWV response was studied using different concentrations of TPA$^+$. The experimental voltammograms obtained are shown in Figure 3. As can be seen, the increase of the concentration of the target ion has a double effect: an increase of the peak current and a shift of the peak potential toward more positive values through an increase of $E_M^{1/2}$ (see Equations 11 – 13), thus behaving in a similar way to that previously observed using DPV technique [22].

The plot of peak current vs. TPA$^+$ concentration is shown in the insert figure. A linear relationship was obtained within the concentration range studied with a regression coefficient of 0.999. These results show that SWV technique is also a good analytical tool for the determination of ion concentration in systems with two liquid-liquid polarizable interfaces.

Figure 4 shows the experimental (black points) and theoretical (solid grey line) SWV and CV voltammograms (Figures 4a and 4b, respectively), corresponding to the transfer of several ions from the water to a solvent polymeric membrane. We have studied four quaternary ammonium cations, two metal chloro complex anions and the picrate anion, and their transfer potentials are distributed into a range of potential over 1200 mV.

In both figures the theoretical curves were obtained by using $E_M^{1/2}$ and $A \sqrt{D_M}$ as adjustable parameters. Experimental data were fitted to the theoretical equations for a reversible ion transfer process using Equation 18 for square wave voltammetry and Equation 15 for cyclic voltammetry (by making $|\Delta E| = 0.01$ mV, as discussed in previous papers [21]). As can be seen, the fitting of the experimental values to the theoretical equations is much better in SWV than in CV.

To obtain these theoretical data, we have taken into account that, under the experimental conditions used, the ion which is transferred across the inner interface is that of the support electrolyte of the inner aqueous phase (BA, see Scheme 1). Hence, the flux of the target ion, $X^z$, and the coupled flux of the ion $B^z$ (with $z' = -z$) are opposite, and Equations 8b, 12 and 13 take the following form:

$$E_{\text{in}} = \frac{E_{\text{fin}}}{450 \text{ mV}}$$
$$D_{E_s} = 10 \text{ mV}$$
$$E_{\text{sw}} = 50 \text{ mV}$$
$$t = 1 \text{ s}$$
$$A = 0.081$$
$$\Delta_0^+ \phi_X^y = -50 \text{ mV}$$
$$\Delta_0^+ \phi_R^y = -150 \text{ mV}$$
$$c_{R}^+ = 50 \text{ mM}$$
$$D_X^+ = D_R^+ = 10^{-5} \text{ cm}^2 \text{s}^{-1}$$
$$D_X^R = 10^{-5} \text{ cm}^2 \text{s}^{-1}$$

$T = 298.15$ K
In order to obtain the values of the ion transfer potential of the ions under study, we have chosen two reference ions, TEA$^+$ for the analyzed cations and Pic$^-$ for the anions analyzed. The standard ion transfer potential of each ion $X^\pm$ was calculated from the difference between the half-wave potentials obtained (by using Eq. 20) from the peak potentials of the SWV voltammogram of this ion and of the corresponding reference, TEA$^+$ or Pic$^-$. Thus, by applying Equations 20, 11, 22 and 23, with the same square wave amplitude ($E_{sw} = 50$ mV) and concentrations for both ions, and taking into account the relation between formal and standard ion transfer potentials, the following expressions are obtained:

$$E_{M,X}^{1/2} - E_{M,TEA}^{1/2} = \Delta_{M,X}^{\phi^0} - \Delta_{M,TEA}^{\phi^0} + \frac{RT}{F} \ln \left( \frac{D_{TEA}^{M}}{D_{X}^{M}} \frac{c_{TEA}^{X}}{c_{X}^{TEA}} \right) \quad (24)$$

when the target ion is a cation, and

$$E_{M,X}^{1/2} - E_{M,Pic}^{1/2} = \Delta_{M,X}^{\phi^0} - \Delta_{M,Pic}^{\phi^0} - \frac{RT}{F} \ln \left( \frac{D_{TEA}^{M}}{D_{Pic}^{M}} \frac{c_{TEA}^{Pic}}{c_{Pic}^{TEA}} \right) \quad (25)$$

when the target ion is an anion. $\gamma_j^i$ and $D_j^i$ are the activity and the diffusion coefficient of ion $j$ in phase $i$, respectively. These differences are independent of the ion transfer at the inner interface. It is important to highlight that under the experimental conditions used, the two last terms of the right hand side in the above equations are practically zero. So, in order to determine $\Delta_M^{\phi^0}$, we have used $\Delta_M^{\phi^0}_{TEA} = 21$ mV, which was obtained from [26], where a 2/1 (m/m)
NPOE/PVC membrane was used, and for $\Delta_{\text{m}}^* \phi_{\text{NPOE}}^{0} = -17 \text{ mV}$, which was obtained from [9], where a 4/1 (m/m) NPOE/PVC membrane was used.

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

When we compare the values of the standard ion transfer potentials obtained in this work with those previously reported for membranes with different ratios PVC/NPOE [9, 29, 30], no significant differences are observed. This extends the observation that the presence of PVC in the membrane composition does not alter the standard ion transfer potential values with respect to the plasticizer NPOE alone to higher PVC contents [9, 22].

It can be also seen from Table 1 that the difference between the standard ion transfer potentials of TMA$^+$ and...
Ion Transfer at Liquid Membranes

Fig. 4. Experimental SWV (a) and CV (b) voltammograms obtained for $5 \times 10^{-4}$ M solutions of several ions (shown on the curves). Solid lines correspond to the theoretical curves calculated from Equation 18 for SWV and from Equation 15 for CV. (a) $E_0 = 50$ mV, $E_i = 10$ mV, $\tau = 0.5$ s and the following values of $A_D/E_C$: TMA$, 5 \times 10^{-4}$; TMA$, 4.9 \times 10^{-4}$; TPA$, 4.5 \times 10^{-4}$; TPA$, 3.8 \times 10^{-4}$; SbCl$_6^-$, $3.3 \times 10^{-4}$; AuCl$_6^-$, $4.9 \times 10^{-4}$; Pic$, 3.7 \times 10^{-4}$. $T = 298.15$ K. (b) $\Delta E = 0.01$ mV, $v = 5$ mV/s and the following values of $A_D/E_C$: TMA$, 4.2 \times 10^{-4}$; TMA$, 4.1 \times 10^{-4}$; TPA$, 4.0 \times 10^{-4}$; TPA$, 3.8 \times 10^{-4}$; SbCl$_6^-$, $3 \times 10^{-4}$; AuCl$_6^-$, $3.8 \times 10^{-4}$; Pic$, 3.8 \times 10^{-4}$. $T = 298.15$ K.

SbCl$_6^-$ is nearly 40 mV, which is in contrast with the approximately 800 mV observed between the peaks corresponding to the square wave voltammograms of these ions in Figure 4a. The huge peak separation achieved is mainly due to the great difference between the formal potentials of the ions that are transferred at the inner interface (Cl$^-$ is transferred coupled to TMA$^+$ transfer, and Li$^+$ is transferred coupled to SbCl$_6^-$ transfer). This provides this system of two polarizable interfaces with a high resolving power for the study of species with opposite charge but with similar standard ion transfer potential, in comparison to the system with a single polarizable one.

The high standard ion transfer potential value found for the hexachloroantimonate(V) anion compared to the values reported for common inorganic anions from water to NPOE [9, 29] explains the high selectivity of a SbCl$_6^-$-selective electrode reported for the determination of antimony(V), based on an anion exchanger dissolved in an NPOE/PVC membrane [31]. Interestingly, the potentiometric selectivity coefficient $K_{\text{SbCl}_6^-/\text{AuCl}_6^-}$, calculated from the corresponding standard ion transfer potentials obtained here (shown in Table 1) by using the expression:

$$\log K_{\text{SbCl}_6^-/\text{AuCl}_6^-} = \frac{E^0_{\text{SbCl}_6^-} - E^0_{\text{AuCl}_6^-}}{0.0592}$$

was $\log K = 2.1$ which matches reasonably well the experimental value ($\log K = 1.8$) reported in the above-mentioned paper, in spite of the ratio of NPOE to PVC in the mentioned electrode being as low as 1/2 (m/m). This encourages the experimental determination of standard ion transfer potentials to plasticized polymeric membranes to predict the selectivity of potentiometric ion selective electrodes.

4. Conclusions

The explicit analytical equation obtained in this paper for the $I/E$ response of the SWV technique in systems with two liquid-liquid polarizable interfaces provides simple criteria to characterize the reversibility of the ion transfer.

The application of SWV allows us to obtain accurate values of the standard ion transfer potential of a series of quaternary ammonium cations and metal chloro complex anions distributed into a wide range of potential (approximately 1200 mV).

A remarkable advantage of the system with two liquid-liquid polarizable interfaces is that it produces a separation between voltammetric peaks corresponding to cations and anions with similar standard ion transfer potential much greater than systems with a single polarizable interface. This can be exploited to increase the selectivity of voltamperometric and amperometric ion sensing.

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Table 1. Comparison between the standard ion transfer potentials obtained in this paper (from Eqs. 20, 11, 22–25) and those previously reported.

<table>
<thead>
<tr>
<th>X$^-$</th>
<th>$\Delta E^0/\phi^0_N$ (mV)</th>
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<tbody>
<tr>
<td></td>
<td>Ratio NPOE/PVC</td>
</tr>
<tr>
<td>-------</td>
<td>----------------</td>
</tr>
<tr>
<td>TMA$^+$</td>
<td>139 ± 1</td>
</tr>
<tr>
<td>TPA$^+$</td>
<td>100 ± 1</td>
</tr>
<tr>
<td>TBA$^+$</td>
<td>221 ± 1</td>
</tr>
<tr>
<td>SbCl$_6^-$</td>
<td>178 ± 2</td>
</tr>
<tr>
<td>AuCl$_6^-$</td>
<td>51 ± 2</td>
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SWV has proven to be a very good technique for the study of the ion transfer at membrane systems, permitting to obtain accurate results in a fast and simple way.

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