Facilitated ion transfer of protonated primary organic amines studied by square wave voltammetry and chronoamperometry

E. Torralba a, J.A. Ortúno b, A. Molina a,*, C. Serna a, F. Karimian c

Departamento de Química Física, Facultad de Química, Universidad de Murcia, Murcia 30100, Spain
b Departamento de Química Analítica, Facultad de Química, Universidad de Murcia, Murcia 30100, Spain
* Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

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Abstract
The transfer of the protonated forms of heptylamine, octylamine, decylamine, procaine and procainamide facilitated by dibenzo-18-crown-6 from water to a solvent polymeric membrane has been investigated by using cyclic square wave voltammetry. The experimental voltammograms obtained are in good agreement with theoretical predictions. The values of the standard ion transfer potential, complexation constant and diffusion coefficient in water have been obtained from these experiments, and have been used to draw some conclusions about the lipophilicity of these species and the relative stability of the organic ammonium complexes with dibenzo-18-crown-6. The results have been compared with those provided by linear sweep voltammetry. Calibration graphs were obtained with both techniques. An interesting chronoamperometric method for the determination of the diffusion coefficient of the target ion in the membrane has been developed and applied to all these protonated amines.

1. Introduction
Organic ammonium ions are important in chemistry and biochemistry [1]. This group of ions includes the protonated forms of some primary amines like aminoacids [2], catecholamines such as the neurotransmitters dopamine [3–5] and serotonin [6], and important biogenic amines, such as histamine [7] and tyramine [8]. Under physiological conditions the corresponding amino group is usually protonated as an ammonium ion [1]. Different classes of organic receptors for organic ammonium ions have been synthesized including crown ethers and calixarenes. The different types of interactions between these receptors and organic ammonium ions have been discussed [1,9,10].

The ion transfer at the liquid–liquid interface is an important phenomenon in systems with two immiscible liquids [11–14], such as those used in liquid–liquid extraction, separations by liquid
membranes, liquid–liquid electrochemistry and ion sensors development, which also serves as a simple model for ion transport across biological membranes. The application of different electrochemical techniques to the study of ion transfer, either simple or facilitated, at the interface between two immiscible electrolyte solutions (ITIES) provides a convenient way to obtain the values of the thermodynamic and kinetic parameters of the different processes involved [12,14,15]. Different strategies developed to overcome the limitations of the traditional experimental studies with ITIES and to broaden its scope of applications were discussed in [16], with special attention to the studies of ion transfer processes through liquid membranes which contain two ITIES, one or both of which can be polarized.

Electrochemical studies reported for the transfer of protonated amines from water to organic solvents have been done mainly for dopamine [3–21], and also for aminoacids [2]. They have made use of voltammetric techniques, mainly cyclic voltammetry (CV) and differential pulse voltammetry (DPV), to determine complexation constants. However, ion transfer studies for homologues of series of protonated primary amines are necessary to elucidate the influence of the organic ammonium chain on the thermodynamic and kinetic parameters associated to the transfer. Exceptions aside [22], little attention has been paid to the diffusional transport of this kind of ions in polymer inclusion membranes (PIM), such as solvent polymeric membranes.

Analytical solutions for the facilitated ion transfer at the interface between two immiscible electrolyte solutions via successive complexation reactions in any voltammetric technique were reported in a previous paper [23]. Based on these studies, simple methods for the quantitative determination of the equilibrium constants and the diffusion coefficients were proposed. The equations deduced have been applied in the present paper to the study of five protonated amines, three long chain alkylamines and, procaine and procainamide by using cyclic square wave voltammetry (CSWV). Due to the improvement of the faradaic-to-background ratio associated to the discrete and differential character of its waveform, this technique provides easier parameterization of the diffusion coefficient of the target ion. Furthermore, a chronoamperometric method for the determination of the diffusion coefficient of the target ion in the membrane is developed and applied to all these protonated amines.

In order to show the suitability of CSWV and LSV as analytical tools for determining the ion concentration of long chain protonated alkylamines in solution, calibration plots were obtained with both techniques.

2. Experimental

2.1. Apparatus

The design of the voltammetric ion sensor has been described previously [16]. Briefly, a Pt wire counter electrode was accommodated inside the inner solution compartment of a Fuka ion-selective electrode (ISE) body. A glass ring of 28 mm inner diameter and 30 mm height, and a glass plate were purchased from Fuka for the construction of the membranes.

2.2. Reagents and solutions

Poly (vinyl chloride) high molecular weight, 2-nitrophenyl octyl ether (NPOE) and tetrahydrofuran (THF) were Selectophore products from Fluka. Tetraethylammonium chloride (TEACI), sodium tetrathylphlhorbore (NaTPB), heptylamine (HA), octylamine (OA), decylamine (DA), p-aminobenzoic acid diethyl diethylaminoethyl ester (procaine, PN), 4-amino-N-(2-(diethy lamino) ethyl) benzamide (procainamide, PD) and dibenzo-18-crown-6 (DB18C6) were purchased from Sigma. Magnesium sulfate (MgSO4) was purchased from Merck. Crystal violet was purchased from Riedel-de Haen in the form of chloride (CVCI). All the other reagents used were of analytical reagent grade. Nanopure water (18 MΩ) prepared with a Milli-Q (Millipore) system was used throughout. Crystal violet tetrathorpborbore (CV-TPB) was obtained as a precipitate by mixing an aqueous solution of crystal violet with an aqueous solution of sodium tetrathylphlorbore in equimolar amounts. 10−4 M solutions of the ammonium salts of the different species assayed were prepared by solving the corresponding amine in MgSO4 5 × 10−3 M and adding hydrochloric solution to adjust the pH of about 6 to convert the amine to its protonated form. Tetraphorphborbore salts of each protonated amine (HA–TPB, OA–TPB, DA–TPB, PN–TPB and PD–TPB) were precipitated by mixing an aqueous solution of the corresponding protonated amine with an aqueous solution of NaTPB in equimolar amounts.

2.3. Membranes preparation

Three different kinds of membranes were prepared. For the simple ion transfer measurements the membranes were prepared by dissolving 200 mg NPOE, 100 mg PVC and 10.4 mg CV-TPB in 3 ml of tetrahydrofuran. For the facilitated ion transfer measurements 5.4 mg of DB18C6 were also added to the solution. For the determination the diffusion coefficients in the membrane of the different amines by chronoamperometry, the membranes were prepared by adding the necessary amount of the tetrathylphlorbore...
salt of each protonated amine to the first solution mentioned to get a concentration of $5 \times 10^{-3}$ M (see the cell schemes given below).

The corresponding solutions were poured into two glass rings resting on a glass plate and were left overnight to allow the solvent THF to evaporate slowly. A 6-mm diameter piece of each membrane was cut out with the punch and incorporated into a modified ISE body as described above.

2.4. Electrochemical measurements

The electrochemical cells used can be expressed as Ag/AgCl | $5 \times 10^{-2}$ M CVCl | $5 \times 10^{-2}$ M CV-TPB (Membrane) | $5 \times 10^{-2}$ M MgSO$_4$, $10^{-4}$ M X$^-$ | $3$ M KCl/AgCl/Ag for the simple ion transfer LSV and SWV measurements, with $X^{-} = HA^-$, OA$^-$, DA$^-$, PN$^-$ and PD$^-$. Ag/AgCl | $5 \times 10^{-2}$ M CVCl, $5 \times 10^{-2}$ M CV-TPB, $5 \times 10^{-4}$ M DB18C6 (Membrane) | $5 \times 10^{-2}$ M MgSO$_4$, $10^{-4}$ M X$^-$ | $3$ M KCl/AgCl/Ag for the facilitated ion transfer LSV and SWV measurements.

The following cell was used for the chronoamperometric determinations Ag/AgCl | $5 \times 10^{-2}$ M MgCl$_2$, $5 \times 10^{-2}$ M CV-TPB, $5 \times 10^{-4}$ X-TPB (Membrane) | $5 \times 10^{-2}$ M MgSO$_4$, $10^{-4}$ M X$^-$ | $3$ M KCl/AgCl/Ag with X$^-$ = HA$^-$, OA$^-$, DA$^-$, PN$^-$ and PD$^-$. The applied potential, $E$, is maintained at the pre-set 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 ion X$^-$ to the organic phase. All computer programs were written in our laboratory. Each experiment was measured by triplicate.

2.5. Chemical structures

![Chemical structures](image)

2.5.1. Interaction between DB18C6 and alkyl-ammonium cations

![Interaction diagram](image)

where solid arrows indicate a facilitated ion transfer process in which the complexation takes place at the bulk of the organic phase; and dashed arrows indicate the situation in with the complexation takes place at the interface.

3. Results and discussions

3.1. Square wave and linear sweep voltammograms

The potential–time waveforms used in LSV and in CSWV, and the general procedure to obtain the theoretical LSV and CSWV I/E responses for the non-kinetically controlled facilitated ion transfer of an ion liable to several equilibrium complexation reactions in both the aqueous and the organic phases were described in reference [23]. From the general equations deduced in this reference, the theoretical expressions corresponding to the particular situation in which the ion transfer is followed by a unique complexation reaction in the organic phase can be easily deduced.

Fig. 1 shows the experimental background-corrected LSV and CSWV voltammograms (left and right panels, respectively), for the simple and the facilitated ion transfer (grey and black circles) of the ammonium forms of the different analytes assayed.

Solid lines indicate the theoretical LSV and CSWV curves, which were obtained by using

$$I_{LSV} = \frac{\eta_{LP}}{V} \left( \frac{2\eta_{LP}}{RT} \right)^p \sum_{j=1}^n \frac{1}{\pi^2} \left( F_{1j} (\eta_{j-1}) - F_{1j} (\eta_j) \right)$$

for the LSV recordings, and

$$I_{CSWV} = \eta_{LP} \left( 1 + \sum_{j=1}^{2p-1} F_{1j} (\eta_{j-1}) - F_{1j} (\eta_{j-1}) \right) \left( \frac{1}{\sqrt{2p-j+1}} - \frac{1}{\sqrt{2p-j}} \right)$$

for the CSWV ones (see reference [23] for the technique waveform and notation for the symbol definitions) $F_{1j}(\eta_j)$ in Eqs. (1) and (2) and is the function that contains the dependence with the applied potential

$$F_{1j}(\eta_j) = \frac{1}{1 + \Omega e^{\eta_j p}}$$

with

$$\eta_j = \frac{F_{1j} (E_p - \Delta \phi_M \phi_{N_M}^{0})}{RT} + \frac{D_{M}^{\Delta \phi}}{\Omega} \left( \frac{D_{M}^{\Delta \phi}}{\Omega} \right)^{1/2}$$

Other symbols are given in the nomenclature. By making $K = 0$ in Eqs. (5) and (6), Eqs. (1) and (2) and become those corresponding to the simple ion transfer [23]. It can be noted that a relatively good agreement between theoretical and experimental data was obtained in all cases. Thus, for example, for the case of OA$^-$ (Fig. 1c and d), the correlation coefficients resulting from the adjustment between experimental and theoretical data were 0.982 and 0.942 for the positive SWV peaks corresponding to the simple and facilitated ion transfer, respectively, and 0.873 and 0.949 for the LSV voltammograms.
Fig. 1. Experimental (circles) and theoretical (lines) LSV and CSW voltammograms (left and right panels, respectively) for the simple (grey circles) and the facilitated (black circles) ion transfer of the ammonium forms of the different analytes assayed. Theoretical curves were obtained from Eqs. (1) and (2) and for LSV and CSWV, respectively. LSV parameters: $v = 5 \text{ mV s}^{-1}$ and $\Delta E = 0.01 \text{ mV}$. CSWV parameters: $E_{SW} = 50 \text{ mV}$, $E_S = 10 \text{ mV}$, $t = 0.5$. Optimum $E_{1/2}$ values (in mV) for the simple and the facilitated ion transfers, respectively: (a) (HA$^+$, LSV): 357.4 $\pm$ 2.7 and 157.7 $\pm$ 0.7; (b) (HA$^+$, CSWV): 344.0 $\pm$ 1.1 and 173.0 $\pm$ 0.1; (c) (OA$^+$, LSV): 322.7 $\pm$ 1.2 and 130.7 $\pm$ 1.2; (d) (OA$^+$, CSWV): 315.7 $\pm$ 0.6 and 134.7 $\pm$ 4.0; (e) (DA$^+$, LSV): 259.7 $\pm$ 4.0 and 107.7 $\pm$ 6.6; (f) (DA$^+$, CSWV): 262.3 $\pm$ 1.2 and 108.3 $\pm$ 4.1; (g) (PN$^+$, LSV): 323.0 $\pm$ 1.0 and 304.0 $\pm$ 0.1; (h) (PN$^+$, CSWV): 323.6 $\pm$ 0.9 and 298.0 $\pm$ 0.1; (i) (PD$^+$, LSV): 342.7 $\pm$ 1.5 and 345.0 $\pm$ 2.3; (j) (PD$^+$, CSWV): 341.0 $\pm$ 1.0 and 326.3 $\pm$ 1.5. Optimum $D_{X+}$ values (in $\text{cm}^2 \text{s}^{-1}$) are gathered in Table 3.
Theoretical expressions of the CSWV and LSV peak coordinates of the non-kinetically controlled facilitated ion transfer process.

<table>
<thead>
<tr>
<th>CSWV</th>
<th>LSV</th>
</tr>
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<tbody>
<tr>
<td>$E_{peak,CSWV}^{\text{CSWV}} = E_{peak,LSV}^{\text{CSWV}} = E^{1/2}$ (T1.1)</td>
<td>$E_{peak,LSV} = E^{1/2} + 1.095RT$ (T1.2)</td>
</tr>
<tr>
<td>$E_{peak,CSWV}^{\text{CSWV}} = E_{peak,LSV}^{\text{CSWV}} = E^{1/2}$ (T1.3)</td>
<td></td>
</tr>
<tr>
<td>$E_{peak,CSWV}^{\text{CSWV}} =</td>
<td>\text{peak current}</td>
</tr>
</tbody>
</table>

Table 1

<table>
<thead>
<tr>
<th>$X^+$</th>
<th>$\Delta W_{\text{CSWV}}^{\text{CSWV}}$</th>
<th>$\Delta W_{\text{CSWV}}^{\text{LSV}}$</th>
<th>CSWV</th>
<th>LSV</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA$^+$</td>
<td>57.03 ± 0.1</td>
<td>69.2 ± 0.1</td>
<td>69.2 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>OA$^+$</td>
<td>28.7 ± 0.6</td>
<td>34.4 ± 1.2</td>
<td>34.4 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>DA$^+$</td>
<td>24.7 ± 1.2</td>
<td>28.6 ± 4.1</td>
<td>28.6 ± 4.1</td>
<td></td>
</tr>
<tr>
<td>PN$^+$</td>
<td>36.7 ± 0.9</td>
<td>34.8 ± 1.1</td>
<td>34.8 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>PD$^+$</td>
<td>54.0 ± 1.0</td>
<td>54.4 ± 1.6</td>
<td>54.4 ± 1.6</td>
<td></td>
</tr>
</tbody>
</table>

The data in Table 1 is drawn from a study involving the CSWV and LSV techniques, which were used to determine the potential and diffusion coefficients of the facilitated ion transfer of the various ions. The data was obtained through experiments involving the transfer of ions from one phase to another, and the results were used to calculate the theoretical expressions for the CSWV and LSV peak coordinates. The calculations were based on the experimental data and the theoretical expressions described in the literature. The results are presented in Table 1, which provides a summary of the calculated values for each ion studied.

3.2. Determination of standard ion transfer potentials and diffusion coefficients

The standard ion transfer potential of each ion $X^+$ was calculated with both LSV and CSWV techniques from the difference between the experimentally obtained half-wave potential of this ion $E_{1/2}$ and that of the reference ion TEA$^+$, according to the procedure described in [16]. The value of $\Delta W_{\text{TEA}}^{\text{CSWV}}$ was 21 mV obtained from [28] who also used a 2:1 (m:m) NPOE PVC membrane was used.

Table 2 gathers the $\Delta W_{\text{CSWV}}^{\text{CSWV}}$ values obtained from the different ions assayed. From our knowledge, $\Delta W_{\text{CSWV}}^{\text{CSWV}}$ for the protonated form of the aliphatic amines HA, OA and DA have not been reported to date with exception of DA that was reported in [23].

Several conclusions can be drawn from this table. As can be seen, the standard ion transfer potential values obtained with CSWV and LSV are quite similar; therefore, CSWV and LSV are adequate for the determination of this parameter. Moreover, $\Delta W_{\text{CSWV}}^{\text{CSWV}}$ obtained for PN$^+$ and PD$^+$ with both techniques matches very well with the values previously reported [29], which is indicative of the goodness of the determination procedure. By comparing the $\Delta W_{\text{CSWV}}^{\text{CSWV}}$ values obtained for the homologues HA$^+$, OA$^+$ and DA$^+$ we can see that when the alkyl chain length increases in an $\text{CH}_3 - \text{CH}_2$ — unit (from OA to DA) a shift of nearly 53 and 63 mV is observed in the $\Delta W_{\text{CSWV}}^{\text{CSWV}}$ values obtained with CSWV and LSV, respectively. Furthermore, an increase of just one $\text{CH}_2$ — unit (from HA to OA) give rise to a displacement of approximately 28 mV for CSWV and 34 mV for LSV; which is almost coincident with 53/2 and to 63/2. Thus, a clear pattern can be established for the influence of the alkyl chain length in the standard ion transfer potential, and consequently in the lipophilicity of this species.

In all the cases studied, the CSWV technique allowed for a more accurate quantification of the peak heights than LSV because of the improvement of the faradaic-to-background current ratio that CSWV provides, and so, CSWV was selected as preferential technique for the determination of the different diffusion coefficients in water, $D_{\text{W}}$, by fitting the experimental data to the theoretical equations. The effective area ($A_{\text{eff}}$) of the two kinds of membranes was calculated from the fitting of the experimental TEA recordings, by taking $D_{\text{W}}$ for TEA as (9.3 ± 0.7) × 10$^{-6}$ cm$^2$s$^{-1}$ [30]. Thus, we obtained $A_{\text{eff}}$ = 0.209 ± 0.007 cm$^2$ for the simple ion transfer membranes and $A_{\text{eff}}$ = 0.151 ± 0.004 cm$^2$ for the facilitated ones. This difference can be mainly attributable to the different bulge of the membranes once mounted in the electrode body.

Given the independence of the CSWV and LSV peaks with the diffusion coefficient in the membrane as is clearly seen in Eqs. (T1.4) and (T1.5), chronoanopemetry under limiting current conditions for the egress of each ion from the membrane was chosen as the technique for the determination of $D_{\text{W}}$. Membranes containing X-TBP were prepared for each protonated amine assayed. In this case, the inner solution contained MgCl$_2$ to avoid cation exchange in the inner interface, thus involving a two polarized interfaces cell configuration [31], [32] (see Sections 2.3 and 2.4 in Section 2). To our knowledge this kind of experimental setup for the determination of organic diffusion coefficients in solvent polymeric membranes has not been previously reported. Due to the importance of diffusion coefficients of ionophores and ionophore–ion complexes in plasticized polymeric membranes for some performance characteristics of ionophore-based ion-selective electrodes and bulk optodes, several methods have been developed for their determination [33]. These include optical [34,35], electrochemical [33,36] and radiochemical methods [37].
Fig. 2 depicts the experimental background-corrected chronoamperograms obtained with the different X–TPB membranes built. Solid lines indicate the theoretical curves, obtained by using the Cottrell expression

\[ I(t) = F A c \sqrt{D_M X / \pi t} \tag{7} \]

As can be seen, a good agreement between theoretical and experimental data is obtained in all cases. The \( D_W X \) and \( D_M X \) values obtained by fitting the experimental recordings to the theoretical equations for CSWV (Eq. (2)) and for chronoamperometry (Eq. (7)) are gathered in Table 3.

As far as we know, there are no precedent studies on the diffusion coefficients of HA and DA, so the values stated in the present work must be considered as they are. Winkelmann et al. determined photometrically \( D_W X \) for OA as \( 3.7( \pm 1.1) \times 10^{-5} \text{cm}^2 \text{s}^{-1} \) [38] which matches totally with the value obtained here \( (3.5 \times 10^{-5}) \). On the other hand, Samec et al. determined \( D_W X \) for the procaine by cyclic voltammetric experiments as \( (6 - 7) \times 10^{-6} \text{cm}^2 \text{s}^{-1} \) [39], which is also close with the \( 9 \times 10^{-6} \) value obtained here.

### 3.3. Complexation equilibrium constants

The values for the equilibrium complexation constant with the crown ether DB18C6 for the different ammonium cations studied...
were obtained by
\[
K = \frac{D_{X^+}^M}{D_{X^+}^M} e^{\left(FRT\right)\Delta E^{1/2} - 1}
\] (8)
which was derived from Eq. (T1.3) of this paper. \(\Delta E^{1/2}\) in this equation represents the difference between the half-wave potentials of the simple and the facilitated ion transfer process for a given ion, which is given by
\[
\Delta E^{1/2} = E_{\text{simple}}^{1/2} - E_{\text{facilitated}}^{1/2} = \frac{RT}{F} \ln \left( \frac{D_{X^+}^M}{D_{X^+}^M} \left(1 + K\right) \right)
\] (9)

For our determinations we assumed \(D_{X^+}^M \approx D_{X^+}^M\).

Table 4 shows the \(K\) values obtained by substituting the experimental \(\Delta E^{1/2}\) values obtained from the CSWV and LSV recordings for the different protonated amines assayed.

The results provided for the two techniques coincide quite well, so CSWV and LSV techniques can be used to obtain the \(K\) values. Moreover, \(K\) for the aliphatic amines HA, OA and DA is much higher than for the aromatic PD and PN, which might be attributable to lower steric hindrances for the formation of the HA–DB18C6, OA–DB18C6 and DA–DB18C6 complexes. A small decrease in the complexation constant values with 18-crown-6 was reported for

### Table 3

<table>
<thead>
<tr>
<th>(X^+)</th>
<th>(\left[ D_{X^+}^M \pm \sigma \right] \cdot 10^3)</th>
<th>(\left[ D_{X^+}^M \pm \sigma \right] \cdot 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA+</td>
<td>4.2 ± 0.1</td>
<td>2.0 ± 0.8</td>
</tr>
<tr>
<td>OA+</td>
<td>3.5 ± 0.1</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>DA+</td>
<td>1.0 ± 0.1</td>
<td>3.6 ± 0.4</td>
</tr>
<tr>
<td>PN+</td>
<td>0.9 ± 0.1</td>
<td>1.2 ± 0.4</td>
</tr>
<tr>
<td>PD+</td>
<td>1.2 ± 0.1</td>
<td>1.7 ± 0.5</td>
</tr>
</tbody>
</table>

Table 4

Complexation constant values obtained with CSWV and LSV.

<table>
<thead>
<tr>
<th>(X^+)</th>
<th>([\log(K) \pm \sigma])</th>
<th>([\log(K) \pm \sigma])</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSWV</td>
<td>LSV</td>
<td>CSWV</td>
</tr>
<tr>
<td>HA+</td>
<td>2.89 ± 0.01</td>
<td>3.37 ± 0.01</td>
</tr>
<tr>
<td>OA+</td>
<td>3.07 ± 0.07</td>
<td>3.26 ± 0.03</td>
</tr>
<tr>
<td>DA+</td>
<td>2.59 ± 0.07</td>
<td>2.68 ± 0.11</td>
</tr>
<tr>
<td>PN+</td>
<td>0.24 ± 0.02</td>
<td>0.32 ± 0.04</td>
</tr>
<tr>
<td>PD+</td>
<td>−0.11 ± 0.07</td>
<td>−0.04 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Experimental SWV voltammograms obtained for solutions of \(X^+\) of different concentrations (shown, in mM, on the figures). \(\Delta E_{r} = 10\) mV, \(E_{swv} = 50\) mV, \(r = 0.5\) s. (b) Plot of the peak current vs. concentration.
the smallest homologues ammonium, methyl-ammonium and ethyl-ammonium, which reduced for longer alkyl chains (butyl-ammonium) [40]. In line with these reported results, no significant difference between the $K$ values for the long chain alkylamines studied here has been observed.

3.4. Calibration plots

In order to demonstrate the suitability of SWV and LSV techniques as analytical tools for the determination of the protonated alkylamines, Figs. 3 and 4 depict the influence of the concentration of OA$^+$ in the experimental SWV and LSV voltammograms corresponding to its facilitated ion transfer by DB18C6.

As can be seen, the peak current in both SWV and LSV techniques increases linearly with the concentration of alkylamine, in agreement with what is predicted by Eqs. (T1.4) and (T1.5). With respect to the peak position, it remains constant for the SWV voltammograms in the whole range of concentrations assayed as predicted, but a shift to positive potentials is observed in the LSV peaks as the concentration is increased.

The plot of peak current vs concentration are shown in each case below the main figure, together with the regression plot and the corresponding regression coefficient, which was near 0.99 for both techniques (see figures). The detection limit values calculated as the alkylamine concentration corresponding to three times the standard deviation of the blank were $3 \times 10^{-2}$ and $2 \times 10^{-6}$ M for LSV and SWV, respectively. The results show that both SWV and LSV could be used to determine the concentration of this kind of organic ammonium ions.

4. Conclusions

The facilitated ion transfer of the protonated forms of three long chain alkylamines, and procaine and procainamide by DB18C6 have been studied by means of cyclic square wave voltammetry.

The standard ion transfer potentials, complexation constant values and diffusion coefficients for the ions assayed have been obtained from the fitting of the experimental values to the theoretical equations proposed in a previous paper. The suitability of the determination procedures have been tested by comparing the results obtained with the previous reported values if available, and also by comparing the CSWV results with those provided by LSV.

Some interesting conclusions have been drawn from these experiments in relation with the lipophilicity of the alkylamines and with the stability of the alkylamine and aryline complexes; as for example that an increase of a $-\text{CH}_2-$ unit in the alkyl chain of the alkylamine produces a decrease of the standard ion transfer potential of approximately 30 mV, or that the alkylamine complexes with DB18C6 are notably more stable than the aryline ones.

A chronoamperometric method for the determination of the diffusion coefficients of the target ion in the membrane has been developed and applied to all these protonated amines.
The goodness of CSVV and LSV as analytical tools for determining the ion concentration in unknown solutions of long chain alkylamines is studied.

Acknowledgements

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