Transport of NaNO₃ solutions across an activated composite membrane: electrochemical and chemical surface characterizations

J. Benavente*, A. Cañas

Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain

Received 25 February 1998; received in revised form 17 July 1998; accepted 3 November 1998

Abstract

Electrochemical characterization of two different samples of an activated membrane, which consists of a polymeric support containing different amounts of Di-(2-ethylhexyl) phosphoric acid as a carrier, was made by measuring the electrical resistance, salt diffusion and membrane potential for the activated membranes and the polymeric support in contact with NaNO₃ solutions. Transport parameters such as the ion transport numbers and concentration of fixed charge in the membrane, salt and ionic permeabilities at different NaNO₃ concentrations were obtained. A comparison of the different electrochemical parameters obtained with both activated membranes and the polymeric support shows how the carrier affects the transport of NaNO₃ solutions across the activated membranes. On the other hand, chemical composition of the membrane surfaces as a function of the amount of carrier was determined by X-ray photoelectron spectroscopy technique, which also allows an envisagement of the chemical bonding between the carrier and the membrane top layer (polyamide). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquid supported or activated membranes; Impedance spectroscopy; Membrane potential; XPS characterization

1. Introduction

A first attempt to develop high selective membranes was to use liquids as membrane materials and to incorporate in the liquids different carriers, which facilitate the transport of one specific component across the membranes [1–5]. However, one of the most serious obstacles to the application of liquid membranes to industrial separation, even when they were supported in a porous structure (supported liquid membranes or SLMs) was their instability and lifetime [6–8]. SLMs basically consist of an organic solvent immobilized in the pores of a hydrophobic microfiltration membrane, the organic solvent usually contains a carrier which binds selectively to one of the components in the feed solution. SLMs are being developed and studied for the separation and concentration of toxics and/or valuable solutes [9]. Different approaches to stabilize SLMs have been suggested, such as gel formation in the pores of the support [10,11], but also by the application of a thin polymeric top layer, which should avoid the loss of the carrier [12,13]. In a recent paper, Kemperman et al. [14] have described how to obtain this new type of liquid
membrane using long chain quaternary ammonium salts as carriers, and the membrane stability was studied by means of long term permeability experiments with NaNO₃ and NaCl solutions. We will call this new type of supported liquid membranes as activated composite membranes or ACMs.

Not only stability, but other problems arise when dealing with ACMs such as the determination of carrier concentration and its distribution in the membrane, or possible changes in the carrier due to its link to the polymer support. Taking into account that the main advantage of SLMs, their high selectivity in a process when a proper selective complexing agent is chosen as the carrier, is clearly dependent on the carrier properties, the nature of interactions between carriers and the polymeric top layers of activated membranes must be known, since this is a point directly related to their selectivity. On the other hand, different destructive and non-destructive techniques can be used to correlate the concentration of the carrier in the membrane and in the casting solution as was reported in the literature [15], and it was obtained that the electrical resistance of the membrane matrix increases when the concentration of the carrier in the membrane increases [13,15], which permits the use of an electrical parameter determined in situ conditions (in contact with saline solutions) to estimate the degree of activation of these membranes.

In this paper, different characteristic electrochemical parameters for two activated membrane samples obtained by incorporation of different amounts of a carrier (Di-(2-ethylhexyl) phosphoric acid or DEHPA) and the polymeric (polyamide/polysulfone) support were determined. The election of DEHPA as the carrier is related to further possible applications of these activated membranes due to its high rate in the transport of rare earth metals [16]. The electrochemical characterization, carried out with NaNO₃ solutions at different concentrations, permits us to obtain a basic knowledge of the transport parameters of a support electrolyte (NaNO₃) across the activated membranes. Salt diffusion, membrane potential and electrical resistance were measured, and from these experimental results, different transport parameters such as salt and ionic permeabilities, ion transport numbers and fixed charge concentration in the membrane were obtained. Since the membrane surface chemistry can influence its separation properties to a large extent, chemical surface characterization of both activated membranes and the polymeric support was made by means of X-ray photoelectron spectroscopy (XPS). XPS spectra have permitted the assignation of the binding energies of the different elements present in the activated membranes, which gives information about possible interactions between the carrier and the membrane top layer (polyamide). Both types of results, electrochemical and chemical surface characterizations, determined for both activated membranes and the polymeric support show how the presence of the carrier affects, in a more or less extent, the transport of NaNO₃ across the activated membranes as well as the type of chemical bonding between the carrier and the polyamide top layer. This study gives the necessary background prior to attempting the application of these types of activated membranes in the selective transport of valuable metals.

2. Experimental

2.1. Materials

Activated and inactivated (polymeric support) membranes were prepared in the Analytical Chemistry Department, Universidad Autonoma de Barcelona (Spain), and kindly submitted by Dr. M. Valiente and Dr. M. Muñoz. The procedure followed to obtain the different membranes is indicated in [15]: the polysulfone membrane (PS), maintained on an un-woven support, was obtained by phase inversion technique, while a thin top layer of polyamide containing different concentrations of the carrier was obtained by interfacial polymerization [14,17], and it was dried in an oven at 60°C for 10 min. Di-(2-ethylhexyl) phosphoric acid (DEHPA) was used as a carrier, and the two different activated membranes were obtained using different amounts of DEHPA in the casting solution (400 and 700 mM of DEHPA). These membrane samples were thereafter named ACM-4 and ACM-7, respectively; while the untreated membrane (the polyamide/polysulfone support) will be called PPS.

Aqueous NaNO₃ solutions at different concentrations were used. The reagent was of analytical grade from Merck (Darmstadt, Germany) and the water was obtained with a Milli-Q system (Millipore, Bedford,
MA). Measurements were carried out at a constant temperature (25.0±0.3°C) and pH (6.7±0.3).

2.2. Surface characterization

The surface chemical composition of ACM-4, ACM-7 and PPS membranes was determined by X-ray photoelectron spectroscopy (XPS) using a PHI 5700 Multi-Technique System. High resolution scan of C1s, O1s, N1s, P2s and S2p lines was performed at 45° take-off angle, with a 720 μm spot and working in the pass energy constant mode at 29.350 and 0.125 eV per step. As an energetic source of photoionization, Mg Kα X-rays (15 kV, 300 W) were used for residual pressure ranging between 5.0×10⁻⁷ and 3.0×10⁻⁷ Pa. The 29.350 eV passing energy was setup to take high resolution spectra. The line Au4f7/2 recorded with the conditions selected had a full width at half-maximum (FWHM) of 1.16 eV. The work function of the spectrometer was determined with the Au4f7/2 peak at a binding energy of 84.00 eV. Intensity ratios were converted into atomic concentration ratios by using Physical Electronic (PC-ACCESS Multitechnique V6.0F) software. Binding energies of the analyzed peaks were determined by setting the C1s component due to aliphatic carbon at a value of 284.8 eV and fitting the spectra with different chemical state bands using Gaussian–Lorentzian peak shape.

2.3. Electrochemical characterization

The experimental device used for the different electrochemical measurements is similar to that indicated elsewhere [18], and it basically consists of two half-cells separated by the membrane with a free area of 0.64 cm², which was supported by rubber rings. To minimize the concentration–polarization at the membrane/solution interfaces, a magnetic stirrer was placed at the bottom of each half-cell, which had a stirrer rate of 500 rpm.

Membrane resistance values were determined by impedance spectroscopy (IS) technique. Impedance measurements were obtained by means of an impedance analyzer (Solartron 1260) controlled by a computer and connected with the solutions in each half-cell via platinum electrodes. The experimental data were corrected by the software for the influence of connecting cables and other parasitic capacitances. The measurements were carried out with 0.01 V as maximum voltage and using 100 different frequencies, which ranged between 60 Hz and 1 MHz, for six different NaNO₃ solutions (10⁻³ M ≤ C ≤ 5×10⁻² M). The solutions on both sides of the membranes had the same concentration. To ensure that no concentration gradient exists in the membranes, they were immersed for at least 18 h in a solution of a given NaNO₃ concentration, and they were maintained during 3 h under alternating current at a frequency of 1 kHz.

In diffusion measurements the membranes were initially separating a concentrated solution (C₁=0.01 M) and distilled water (C₂=0). Changes in the solution on side 2 were recorded vs. time by means of a conductivity cell connected to a digital conductivity meter (Radiometer CDM 83).

Membrane potential, Δφ, or electrical potential difference between both sides of the membranes caused by a concentration gradient was measured by two reversible Ag/AgCl electrodes connected to a digital voltmeter (Yokogawa 7552, 1 GΩ input resistance). The electrodes were in contact with the electrolyte solutions via saline bridges. Δφ values were measured by keeping the concentration ratio of the solutions at both sides of the membrane constant, γ=C₂/C₁=2, for C₁ ranging between 10⁻³ and 5×10⁻² M. In these measurements the electrode placed into the diluted solution was grounded, this means Δφ=φ₂−φ₁.

For diffusion and membrane potential measurements three series of measurements were carried out with each membrane and the results presented in this paper correspond to their average values. In order to see if the working conditions produce appreciable changes in the activated membranes due to a loss of the carrier, impedance measurements with the ACM-4 membrane for the whole range of concentrations were repeated after each experimental determination of the other electrochemical parameters (diffusion and membrane potential).

3. Results and discussion

Some characteristic geometrical parameters of the membrane themselves (without considering the un-
woven support) such as dry and wet membrane thickness ($\delta^{\text{dry}}$ and $\delta^{\text{wet}}$, respectively) and water content, $W$ (grams of water/gram of wet membrane), were determined and their values are shown in Table 1. The slight increase in the water content presented by both activated membranes is attributed to the hydration of the carrier DEHPA [19].

Chemical composition of the different elements present in the surface of the membranes was determined by X-ray photoelectron spectroscopy (XPS), and their percentages are indicated in Table 2. These results show that the increase of the carrier in the casting solution used to obtain the activated membranes hardly affects the chemical composition of the membrane surface; in fact, a comparison of the O/C and O/P ratios for both ACMs samples shows that their surfaces are almost completely covered by DEHPA, since these ratios are very close to DEHPA stoichiometric ratios, which is also confirmed by the drastic decrease in the N$_{1s}$ concentration in both activated membranes. The carrier surplus must be mainly distributed into the polymeric support, as was reported elsewhere [15]; in any case, the small differences found in the N$_{1s}$ and P$_{2p}$ atomic concentrations ($c$(N$_{1s}$)$_{\text{ACM-4}}$<c(N$_{1s}$)$_{\text{ACM-7}}$ and $c$(P$_{2p}$)$_{\text{ACM-4}}$<c(P$_{2p}$)$_{\text{ACM-7}}$) agrees with a higher amount of DEHPA in the surface of the ACM-7 membrane.

Membrane electrical parameters were obtained from impedance (a.c.) measurements. Analysis of a.c. data is often carried out by a complex plane method, which involves plotting the impedance imaginary part vs. the real part ($\tilde{Z}_{\text{img}}$ vs. $\tilde{Z}_{\text{real}}$). When plotted on a linear scale, the equation for a parallel resistance–capacitor ($RC$) circuit gives rise to a semi-circle in the $\tilde{Z}$ plane. The semi-circle has intercepts on the axis $\tilde{Z}_{\text{real}}$ at $R_{\infty}$ ($\omega \to \infty$) and $R_0$ ($\omega \to 0$), where ($R_{\infty}$−$R_0$) is the resistance of the system [21]. The maximum of the semi-circle equals 0.5 ($R_{\infty}$−$R_0$) and occurs at frequency $\omega=\omega C=1$, where $RC$ is the relaxation time. However, complex systems may present different relaxation times, and in these cases, the impedance plot is a depressed semi-circle and a non-ideal capacitor, which is called a constant phase element (CPE), is considered; the CPE admittance is expressed by [21]

$$Q(\omega) = Y_0(j\omega)^n,$$

(1)

### Table 1

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$W$ (%)</th>
<th>$\delta^{\text{dry}}$ (µm)</th>
<th>$\delta^{\text{wet}}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSP</td>
<td>47.7±0.4</td>
<td>66.4±1.1</td>
<td>75.2±1.2</td>
</tr>
<tr>
<td>ACM-4</td>
<td>51.2±0.6</td>
<td>64.3±2.3</td>
<td>73.2±2.1</td>
</tr>
<tr>
<td>ACM-7</td>
<td>55.6±0.8</td>
<td>74.1±2.2</td>
<td>83.0±1.2</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Element</th>
<th>SSP</th>
<th>ACM-4</th>
<th>ACM-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic concentration (%)</td>
<td>Atomic concentration (%)</td>
<td>Atomic concentration (%)</td>
<td></td>
</tr>
<tr>
<td>C$_{1s}$</td>
<td>80.06</td>
<td>75.78</td>
<td>75.74</td>
</tr>
<tr>
<td>O$_{1s}$</td>
<td>9.49</td>
<td>18.53</td>
<td>18.50</td>
</tr>
<tr>
<td>N$_{1s}$</td>
<td>9.58</td>
<td>1.09</td>
<td>0.96</td>
</tr>
<tr>
<td>P$_{2s}$</td>
<td>0.49</td>
<td>4.37</td>
<td>4.62</td>
</tr>
<tr>
<td>S$_{2s}$</td>
<td>0.38</td>
<td>0.22</td>
<td>0.17</td>
</tr>
</tbody>
</table>
where \(Y_0(\Omega s^{-n})\) and \(n\) are two empirical parameters \((0 \leq n \leq 1)\). In these cases an equivalent capacitance, \(C^{eq}\), can be determined by the following relationship [22]:

\[
C^{eq} = \frac{(R_0 Y_0)^{1/n}}{R_0}.
\]

(2)

Fig. 2(a) and (b) shows the impedance plots \((-Z_{img} vs. Z_{real}\)) obtained by impedance spectroscopy measurements for the three membranes. Similar curves were found with the different concentrations studied. Two dielectric relaxations were obtained for the whole range of frequencies, this means
two different semicircles, which correspond to the contribution of both membrane \( (60 \leq f \text{ (Hz)} \leq 6 \times 10^4) \) and electrolyte solution \( (6 \times 10^4 \leq f \text{ (Hz)} \leq 10^6) \). The experimental values were fitted to a circuit formed by a series association of two sub-circuits:

1. the electrolyte part, which is represented by a resistance, \( R_e \), in parallel with a capacitor, \( C_e \), and it is written as: \( (R_eC_e) \);
2. the membrane itself, which consists of a parallel association of a resistance, \( R_m \), and a non-ideal capacitor, \( Q_m \), and it is written as \( (R_mQ_m) \).

Fig. 2. Impedance plots: (a) membrane SSP; (b) membrane ACM-4 (×) and ACM-7 (○).
Fig. 3. Concentration dependence for the membrane electrical resistance: (○) PPS, (△) ACM-4 and (□) ACM-7.

Only the membrane contribution will be considered in the following discussion. Analysis of the impedance curves by means of a non-linear program [23] permits us to determine the resistance of each membrane sample, and relative errors lower than 10% were obtained in all cases.

Dependence of $R_m$ values with NaNO$_3$ concentration is shown in Fig. 3. The decrease of membrane resistance when the concentration increases is attributed to the electrolyte invasion into the membrane structure. In order to determine the resistance of the membrane matrix (without any electrolyte contribution) $R_m$ values were fitted to the following expression:

$$R_m(C) = R_0 - aC^b,$$

where $R_0$ represents the matrix resistance (at $C=0$), while $a$ and $b$ are two empirical parameters. Calculated $R_0$, $a$ and $b$ values for each membrane are given in Table 3 (the correlation coefficients were higher than 0.95); an increase of the matrix resistance as a result of the increase of concentration of carrier in the casting solution was found as was also reported in the literature [13,15]; this increase is attributed to a higher compaction of the carrier filling the pores of the polymeric support and as a result of this, the membranes present a more compact structure. This fact allows the use of a physical parameter, the membrane resistance, as a tool to estimate the content of carrier in activated membranes from in situ measurements. The different values determined for the ACM-4 by the fitting of the resistance values obtained after measurements of salt diffusion and membrane potential ($R_0^{I}$ and $R_0^{II}$, respectively) are also indicated in Table 3. Results show a slight decrease of membrane matrix resistance as a consequence of its functioning, which must be due to a small loss (or higher hydration) of the carrier.

Concentration dependence of equivalent capacitance is not as strong as electrical resistance and the following average values were obtained:

PPS: \( \langle C^{eq} \rangle = (1.17 \pm 0.15) \times 10^{-10} \text{ F} \),

ACM-4: \( \langle C^{eq} \rangle = (0.7 \pm 0.3) \times 10^{-10} \text{ F} \),

ACM-7: \( \langle C^{eq} \rangle = (6.8 \pm 1.3) \times 10^{-10} \text{ F} \).

These results show a higher dispersion in the values determined with both activated membranes in comparison with the polymeric support, which could also be due to the hydration or solution uptake by the carrier.

Variation of concentration ($C_2$) vs. time in diffusion experiments for both activated membranes, ACM-4 and ACM-7, and the polymeric PPS one are shown in Fig. 4 ($\Delta C = C_1 - C_2 = 0.01 \text{ M NaNO}_3$). According the Fick’s first law, the salt flux through a membrane, $J_s$ (for a quasi-steady state) can be written as

$$J_s = P_s(C_1 - C_2),$$

where $P_s$ is the salt permeability in the membrane. On the other hand, the molar salt flux through the membrane at any time is given by

$$J_s = \left( \frac{1}{S} \right) \frac{dn}{dt} = \left( \frac{V_0}{S} \right) \left( \frac{dC_2}{dt} \right),$$

where $V_0$ is the volume of the solution at the side of concentration $C_2$, and $S$ is the membrane area.

From Eqs. (4) and (5) the following expression is obtained:

$$\frac{dC_2(t)}{dt} = \left( \frac{S}{V_0} \right) P_s(C_1 - C_2).$$

Table 3

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$R_0^I$ ($\Omega \text{ m}^2$)</th>
<th>$a$ (Ω mol$^{-1}$)</th>
<th>$b$</th>
<th>$R_0^{II}$ ($\Omega \text{ m}^2$)</th>
<th>$R_0^{III}$ ($\Omega \text{ m}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSP</td>
<td>44.5</td>
<td>0.72×10$^6$</td>
<td>0.0034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACM-4</td>
<td>85.6</td>
<td>1.34×10$^6$</td>
<td>0.0011</td>
<td>72.3</td>
<td>64.6</td>
</tr>
<tr>
<td>ACM-7</td>
<td>146.7</td>
<td>2.22×10$^6$</td>
<td>0.0009</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
By means of Eq. (6), from the slopes of the straight lines indicated in Fig. 4, the values of the salt permeability in each membrane sample were obtained. \( P_s \) values are given in Table 4. These results indicate that the presence of the carrier DEHPA does not clearly affect the permeability of NaNO\(_3\) across the membranes.

Fig. 5 shows the membrane potential as a function of the salt concentration (\( \Delta \phi \) vs. \( 1/C_2 \)). Straight lines were obtained for the three membranes in the range of concentrations studied. For slightly charged membranes, Aizawa et al. [24] proposed the following relationship between \( \Delta \phi \) and \( 1/C_2 \):

\[
(\Delta \phi = (RT/F)[(1 - 2t_+)(\ln \gamma + 2(\gamma - 1)t_+ t_- X/\gamma C_2)],
\]

where \( X \) is the concentration of fixed charge in the membrane, \( \gamma = C_1/C_2 = 2 \) the ratio between the concentration of both external solutions, \( t_+ \) and \( t_- \) the cation and anion transport numbers, respectively; \( R \) and \( F \) the gas and Faraday constants, and \( T \) is the temperature of the system. Eq. (7) represents a linear relationship between \( \Delta \phi \) and \( 1/C_2 \), and it allows the determination of both the fixed charge and the transport numbers of the ions in the membrane by the fitting of the experimental points. \( X, t_+ \) and \( t_- \) values for the different membrane samples are shown in Table 4. These results show the influence of the carrier in the membrane fixed charge:

- The polyamide/polysulfone membrane presents a weak cationic exchanger character, which is attributed to the adsorption of Cl\(^-\) ions into the matrix structure, as was reported in the literature for commercial membranes made from similar polymers [25–27].
- The activated membranes have a small positive charge, which is due to the mono-sodium salt formed when DEHPA is in contact with NaNO\(_3\).

### Table 4
Salt permeability (\( P_s \)), cation and anion transport numbers (\( t_+ \) and \( t_- \)), concentration of fixed charge (\( X \)), cationic and anionic permeabilities (\( P_+ \) and \( P_- \)) and salt permeability \( P_s^* \) for the different membrane samples

<table>
<thead>
<tr>
<th></th>
<th>PPS</th>
<th>ACM-4</th>
<th>ACM-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_s ) (m/s)</td>
<td>(4.4±0.3)×10(^{-8})</td>
<td>(6.5±0.4)×10(^{-8})</td>
<td>(4.9±0.3)×10(^{-8})</td>
</tr>
<tr>
<td>( t_+ )</td>
<td>(0.547±0.009)</td>
<td>(0.414±0.016)</td>
<td>(0.432±0.018)</td>
</tr>
<tr>
<td>( t_- )</td>
<td>(0.453±0.009)</td>
<td>(0.586±0.017)</td>
<td>(0.578±0.018)</td>
</tr>
<tr>
<td>( X ) (M)</td>
<td>–(3.0±0.7)×10(^{-3})</td>
<td>+(6.3±1.6)×10(^{-3})</td>
<td>+(5.2±0.8)×10(^{-3})</td>
</tr>
<tr>
<td>( P_+ ) (m/s)</td>
<td>(1.28±0.18)×10(^{-8})</td>
<td>(2.9±0.04)×10(^{-8})</td>
<td>(2.41±0.16)×10(^{-8})</td>
</tr>
<tr>
<td>( P_- ) (m/s)</td>
<td>(1.32±0.08)×10(^{-8})</td>
<td>(6.2±0.08)×10(^{-8})</td>
<td>(3.4±0.3)×10(^{-8})</td>
</tr>
<tr>
<td>( P_s^* ) (m/s)</td>
<td>(1.3±0.3)×10(^{-8})</td>
<td>(4.0±0.9)×10(^{-8})</td>
<td>(2.8±0.4)×10(^{-8})</td>
</tr>
</tbody>
</table>
aqueous solutions [19]. It should be pointed out that the fixed charge in both activated membranes is practically independent of the amount of the carrier, as can be observed from the values in Table 4, if the error interval is considered.

From membrane potential and resistance (or conductance $\lambda=1/R$) values, the ionic permeabilities through a membrane, $P_i$, can be determined by the following equations [28]:

$$P_+/P_- = \exp[(F/RT)\Delta\phi] - \gamma(1 - \gamma \exp[(F/RT)\Delta\phi]), \quad (8)$$

$$P_+ + P_- = RT/F^2\Sigma_i(z_i^2C_i), \quad (9)$$

where $P_+$ and $P_-$ are the cation and anion permeabilities, $z_i$ their valencies, and the other parameters have already been indicated. Conductance values at the average concentration of the external solutions used in membrane potential measurements, $C_{avg}$, were obtained by the interpolation of the results presented in Fig. 3. Average values of the ionic permeabilities in the range of concentrations studied, $\langle P_+ \rangle$ and $\langle P_- \rangle$, are also shown in Table 4. A comparison of the ionic permeabilities obtained for the different membranes shows lower values for the PPS than for both activated membranes, but it also shows the lower value of the cationic permeability in ACM-4 and ACM-7 compared with the anionic permeability, which agrees with the positive fixed charge obtained for these membranes from membrane potential results.

Assuming for salt and ionic permeabilities a relationship similar to that obtained for diffusion coefficients (for 1:1 electrolytes, $P_i = P_+P_-/[P_+ - P_-]$), salt permeability at the concentration gradient measured in diffusion experiments ($P^*_s$) was estimated by interpolation of $P_+$ and $P_-$ results. $P^*_s$ values are also shown in Table 4. Quite a good agreement between both $P_i$ and $P^*_s$ values was obtained taking into account the different experimental conditions under which both parameters were determined.

4. Conclusions

Electrochemical and chemical surface characterizations of two different samples of an activated membrane containing different amounts of Di-(2-ethylhexyl) phosphoric acid (DEHPA) as a carrier and the polyamide/polysulfone support were obtained by measuring the membrane impedance, salt diffusion and membrane potential when the membranes were in contact with NaNO$_3$ solutions, and using X-ray photoelectron spectroscopy (XPS) technique, respectively.

- XPS results show that the surface of both activated membranes are completely covered by the carrier, and the increase of carrier in the casting solution, does not correspond to an increase in the surface of the membrane. A comparison of binding energies and peaks associated to characteristic elements for both activated membranes and the polymeric support indicates changes in the chemical state of these elements, which is due to an ionic bonding between the carrier and the membrane top layer (polyamide).

- Electrochemical characterization allows the determination of different transport parameters when the membranes are in contact with NaNO$_3$ solutions: salt and ionic permeabilities, fixed charge concentration, ion transport numbers and membrane conductance. As a consequence of the carrier, a small positive fixed charge for both activated membranes was obtained from membrane potential measurements, which is attributed to the formation of the mono-sodium salt, while the negative charge presented by the polymeric support which is due to the adsorption of Cl$^-$ ions. Impedance spectroscopy measurements permit us to determine separately both membrane and electrolyte electrical resistance; the increase of the membrane electrical resistance when the concentration of carrier in the membrane increases is due to a higher compaction of the carrier filling the pores of the polymeric support. This fact allows the use of this physical parameter to correlate the degree of activation of these membranes (content of carrier) by means of a non-destructive technique and when they are in working conditions (in contact with electrolyte solutions).

Acknowledgements

Thanks are due to Dr. M. Valiente, Dr. M. Muñoz and M. Oleinikova, Analytical Chemistry Department, Universidad Autonoma de Barcelona (Spain) for membrane preparation; Dr. E. Rodríguez-Castellón,
Inorganic Chemistry Department, Universidad de Málaga (Spain) and M.J. Ariza for helping us with the XPS analysis. We also thank Dirección General de Ciencia y Tecnología and Comisión Interministerial de Ciencia y Tecnología (Projects: PB95-0487 and MAT-0970-C03-01, respectively) and Junta de Andalucía for financial support.

References