Effect of age and chemical treatments on characteristic parameters for active and porous sublayers of polymeric composite membranes

J. Benavente * and M.I. Vázquez

Grupo de Caracterización Electrocinética de Membranas e Interfases, Departamento de Física Aplicada I, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain

Received 24 July 2003; accepted 7 November 2003

Abstract

Changes in the transport parameters and the chemical nature of the surface of composite polyamide/polysulfone membranes due to both aging and treatment with chemical products (HCl, H3NO, and NaOH) have been considered. Hydraulic and salt permeability were obtained from water flow and salt diffusion measurements, respectively, and their values seem to indicate a modification in the structural parameters (porosity/thickness) of aging samples, while HCl and HNO3 treatments will act in the opposite way. Chemical modifications in the membrane surfaces were studied by X-ray photoelectron spectroscopy (XPS), which mainly show the effect of H3NO and HCl on the polyamide active layer of the membranes (polyamide oxidation), but no chemical damage for that sublayer. Electrical characterization of both sublayers of the composite membranes were determined from impedance spectroscopy (IS) measurements using equivalent circuits as models, and these results indicate: (i) a strong increase of the membrane electrical resistance as a consequence of aging, mainly that associated with the active sublayer (30 times higher for an old sample than for a fresh one) and treatment with NaOH; (ii) the reduction of this effect when the samples were treated with HCl and HNO3 solutions. Changes in the values of the electrical resistance of the composite membranes are in agreement with those obtained for permeabilities, but the electrical parameter also allows the determination of the contribution of each sublayer.

© 2003 Elsevier Inc. All rights reserved.

Keywords: Composite membranes; Aging; Chemical treatments; Diffusion; Impedance spectroscopy; XPS

1. Introduction

Membrane processes such as reverse osmosis (RO) and nanofiltration (NF) are now commonly used in water desalting and other separation processes [1, 2]. The membranes used in such systems are usually composite membranes, which can be considered as multilayer systems, in which the phases are coupled in series by infinitely thin layers of aqueous solutions in local equilibrium with both adjacent layers [3]. In the simplest case, RO and NF composite membranes are represented by two homogeneous layers from different materials with different structures and transport properties [1], (i) a thin and dense active layer, and (ii) a thick and porous support, although a nonwoven structure is also commonly used for reinforcement reasons; moreover, a transition or intermediate layer could also exist [1, 4]. It is currently assumed that the active layer controls membrane selectivity and fluxes, but the porous support can also slightly affect them [5–7]. For this reason, modifications of the active or the porous sublayers of composite membranes, which can be due to diverse circumstances (particle deposition, aging, cleaning agents, radiation, etc.), can cause important changes in their transport parameters, as has been reported by different authors [8–10]. Particularly, permeability across polymeric membranes decreases with time, but aging and cleaning agents can also affect the electrical properties of their active layers, which might modify membrane performance when transport of electrolyte solutions is considered [11–13].

In this paper, modifications related to the effect of aging and chemical treatments (solutions 1 M of HCl, HNO3, or NaOH) on the transport parameters for a composite polyamide/polysulfone reverse osmosis membrane are studied. This will permit us to know how the membrane will behave under extreme pH conditions. Chemical variations of the polyamide active layer due to the chemicals products are also considered. Differences in the hydrodynamic and salt permeabilities for the different studied samples

---

* Corresponding author.
E-mail address: j_benavente@uma.es (J. Benavente).
indicate structural changes in the composite membrane, while X-ray photoelectron spectroscopy (XPS) analysis, which was used to determine possible chemical modifications in the polyamide active layer, does not show significant changes to assume polyamide degradation. Moreover, in order to correlate changes in the whole membrane with those corresponding to each sublayer (dense and porous layers), impedance spectroscopy measurements using NaCl solutions at different concentrations were also carried out. Impedance spectroscopy (IS) is an a.c. technique for electrical characterization of material and interfaces based on electrical impedance measurements carried out for a wide range of frequency ($10^{-6}$–$10^9$ Hz). It is a successful tool to determine the electrical properties of heterogeneous systems formed by a series array of layers with different electrical (and even structural) characteristics such as membrane/electrolyte or composite membrane systems, since it allows a separate evaluation of the electrical contribution of each sublayer [14–16]. IS measurements enable us to obtain information about the different sublayers of these heterogeneous systems by using the impedance plots and the equivalent circuits as models, where the different circuit elements are related to the structural/transport properties of the systems [17,18].

2. Material and methods

2.1. Material

A commercial composite polyamide/polysulfone membrane for reverse osmosis kindly submitted by PRIDESA (Barcelona, Spain) was studied. In order to see the effect of aging and chemical treatments on the membrane, new samples taken from a packet which had already been opened for two years, were used (membrane PAC-O); some of these samples were chemically treated by maintaining each one for 24 h in one of the solutions 1 M HCl, 1 M HNO$_3$, and 1 M NaOH, and they will hereafter be named as PAC-A, PAC-B, and PAC-C, respectively. For comparison, some results previously obtained with a fresh sample from the same packet (membrane PAC-F) are also presented [19].

Electrochemical measurements were carried out in aqueous NaCl solution at different concentrations ($10^{-3}$ M < c < $5 \times 10^{-2}$ M), at room temperature $t = (25.0 \pm 0.3)$ °C and standard pH (6.0 ± 0.2). Before use, the membranes were immersed for at least 12 h in a solution of appropriate concentration.

2.2. Transport and electrical measurements

Hydraulic permeability was determined from water flux measurements, which were carried out in a tangential test cell (Minitan S, Millipore). The cell has recirculation of both the feed and the permeate solutions, and two screen separators of polypropylene were placed above and below the membrane, which has an area of 59 cm$^2$ [20]. The initial volume in feed and permeate reservoirs was 500 cm$^3$, while the applied pressure ranged between 150 and 500 KPa.

Salt diffusion and impedance spectroscopy measurements were carried out in a dead-end test cell similar to that described elsewhere [21]. The membrane was tightly clamped between two glass half-cells using silicone rubber rings. In order to minimize concentration–polarization at the membrane surfaces, a magnetic stirrer was placed at the bottom of each half-cell and its speed rate was externally controlled; measurements were carried out at a stirring rate of 525 rpm.

In salt diffusion measurements the membrane was initially separating a concentrated solution ($c_1$) from a diluted one (initially distilled water, $c_2 = 0$). Changes in the solution on side 2 were recorded versus time by means of a conductivity cell connected to a digital conductivity meter (Radiometer CDM 83). In order to see the effect of concentration gradients on salt permeability, two concentrated solutions ($c_1 = 10^{-2}$ and $5 \times 10^{-2}$ M) were used. A conductivity cell was also placed in reservoir 1 to control the constancy of concentration $c_1$.

Impedance spectroscopy (IS) measurements were carried out using an impedance analyzer (Solartron 1260) controlled by a computer. The experimental data were corrected by software as well as the influence of connecting cables and other parasite capacitances. The measurements were carried out using 100 different frequencies in the range 10–$10^7$ Hz at a maximum voltage of 0.01 V, the solutions at both sides of the membrane having the same concentration.

2.3. X-ray photoelectron spectroscopy measurements

Surface chemical characterization of the different membrane samples was carried out by X-ray photoelectron spectroscopy (XPS) spectra, which were obtained using a Physical Electronics PHI 5700 spectrometer with nonmonochromatic Mg K$_\alpha$ radiation as excitation source (300 W, 15 kV, 1253.6 eV). High-resolution spectra were recorded at a given takeoff angle $\alpha = 45^\circ$ by a concentric hemispherical analyzer operating in the constant pass energy mode at 29.35 eV, using a 720-µm-diameter analysis area. Under these conditions the Au4f$_{5/2}$ line was recorded with 1.16 eV fullwidth at half maximum (FWHM) at a binding energy of 84.0 eV [22]; charge referencing was done by setting the C–C peak at 284.6 eV. Survey spectra in the range 0–1200 eV were recorded at 187.85 eV of pass energy. Membranes were irradiated for a maximum time of 15–20 min to minimize X-ray induced sample damage [23]; the pressure in the analysis chamber was maintained lower than $5 \times 10^{-6}$ Pa. A PHI Access ESCA-V6.0 F software package was used for acquisition and data analysis [24].

Taking into account the material used and the XPS experimental conditions, the depth studied is around 6–7 nm [25,26]. Since the thickness of the polyamide active layer is between 0.1 and 1 µm [1], only the polyamide top layer will be considered in this study. Atomic concentration percentages of the polyamide characteristic elements (C, O,
and N) were determined from the different measured spectral regions by taking into account the corresponding area sensitivity factor [27].

3. Results and discussion

3.1. Hydrodynamic and salt permeabilities

The hydraulic permeability, \( L_p \), is one of the parameters most commonly used for membrane characterization, and it establishes the relationship between the pressure difference applied to the membrane and the volume of solution flowing through it: \( J_v = L_p \Delta P \). Fig. 1 shows the water flow versus applied pressure for the different membrane samples, while \( L_p \) values obtained from the slopes of these straight lines are indicated in Table 1. Results show a decrease in the permeability of the aging sample with respect to the new one, but it can also be observed that chemical treatments affect this parameter in two opposite ways: increasing \( L_p \) value when HCl and NaNO\(_3\) solutions were used, and decreasing \( L_p \) value in the case of NaOH.

Salt permeability through a membrane can be determined from salt diffusion measurements. According to Fick’s first law, the salt flux through a membrane (for a quasi-steady state) can be written as

\[
J_s = P_s (c_1 - c_2),
\]

where \( J_s \) is the diffusive salt flux, \( P_s \) is the salt permeability in the membrane, and \( c_1 \) and \( c_2 \) are the external concentrations. On the other hand, the molar salt flux through the membrane at any time instance is given by

\[
J_s = (1/S_m)(dn/dt) = (V_0/S_m)(dc_2/dt),
\]

where \( V_0 \) is the volume of the solution at the side of concentration \( c_2 \) and \( S_m \) represents the membrane area. From Eqs. (1) and (2) the following expression is obtained (assuming \( c_1 \) is constant),

\[
(d\sigma/dc) = (S/V_0)(d\sigma/dc_e)P_s \Delta c,
\]

where \( (d\sigma/dc)_e \) is an electrolyte characteristic parameter (for a given temperature). Variation in the conductivity of the solution \( c_2 \) as a function of time for aging and chemically treated samples at the same concentration gradient (\( \Delta c = 0.05\) M) is shown in Fig. 2a, while a comparison of diffusion measurements for fresh and aging membranes at different concentration gradients can be seen in Fig. 2b. According to Eq. (3), salt permeability through the different samples can be determined from the slopes of the straight lines shown in Fig. 2, and their values are also indicated in Table 1. These results show a decrease in the value of salt permeability in all the membrane samples when the concentration increases, but also significant differences among the different samples. Aging membrane presents a salt permeability much lower than fresh membrane, while permeability values for HCl- and HNO\(_3\)-treated samples are appreciably higher than that for the PAC-O.

Results from both hydrodynamic permeability and salt diffusion measurements indicate a modification of the membrane structure (morphology) as a result of aging. Taking into account the results indicated in Table 1, the following sequence of values for hydraulic and salt resistances (\( R_H = 1/L_p \) and \( R_S = 1/P_s \)) for the different samples was obtained:

\[
R_H(\text{PAC-C}) > R_H(\text{PAC-O}) > R_H(\text{PAC-B})
\]
\[
> R_H(\text{PAC-A}) > R_H(\text{PAC-F}),
\]
\[
R_S(\text{PAC-C}) > R_S(\text{PAC-O}) > R_S(\text{PAC-B})
\]
\[
> R_S(\text{PAC-A}) > R_S(\text{PAC-F}).
\]

As can be observed, similar tendencies were obtained for both parameters. Since both resistances are inversely re-

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( L_p ) (m(^3)/s/Pa)</th>
<th>( \Delta c = 0.01) M</th>
<th>( \Delta c = 0.05) M</th>
<th>( (R_p/R_T) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC-F(^a)</td>
<td>( 10 \times 10^{-12} )</td>
<td>( (41 \pm 3) \times 10^{-9} )</td>
<td>( (30 \pm 5) \times 10^{-9} )</td>
<td>( (0.86 \pm 0.01) )</td>
</tr>
<tr>
<td>PAC-O</td>
<td>( (4.5 \pm 0.2) \times 10^{-12} )</td>
<td>( (14 \pm 1) \times 10^{-9} )</td>
<td>( (7.7 \pm 0.6) \times 10^{-9} )</td>
<td>( (0.30 \pm 0.06) )</td>
</tr>
<tr>
<td>PAC-A</td>
<td>( (6.0 \pm 0.3) \times 10^{-12} )</td>
<td>( (28 \pm 2) \times 10^{-9} )</td>
<td>( (19.6 \pm 0.9) \times 10^{-9} )</td>
<td>( (0.70 \pm 0.08) )</td>
</tr>
<tr>
<td>PAC-B</td>
<td>( (5.1 \pm 0.2) \times 10^{-12} )</td>
<td>( (24 \pm 3) \times 10^{-9} )</td>
<td>( (13.8 \pm 0.8) \times 10^{-9} )</td>
<td>( (0.83 \pm 0.09) )</td>
</tr>
<tr>
<td>PAC-C</td>
<td>( (2.5 \pm 0.2) \times 10^{-12} )</td>
<td>( (13 \pm 1) \times 10^{-9} )</td>
<td>( (6.1 \pm 0.5) \times 10^{-9} )</td>
<td>( (0.74 \pm 0.06) )</td>
</tr>
</tbody>
</table>

\(^a\) \( L_p \) value submitted by the manufacturer.
lating to membrane porosity and directly to membrane thickness, these results could be due to a reduction in the pore size/increase of pore length. On the other hand, HCl and HNO$_3$ treatments seem to act to open the membrane structure, while as a result of treatment with NaOH the membrane presents a tighter structure, according to the decrease in both $L_p$ and $P_s$ values obtained for the PAC-C sample.

On the other hand, transport of solute and solute through membranes can be described in a phenomenological way [3]. In the phenomenological treatment, only “thermodynamic forces” and their resulting fluxes are considered and the membrane is treated as a black box. A parameter to characterize the selectivity of a membrane is the retention coefficient, $S = 1 - (c_f/c_p)$, where $c_f$ and $c_p$ are the feed and permeate concentrations, respectively. The retention can be related to the solvent flux, $J_v$, the solute permeability, $P_s$, and the rejection coefficient, $\sigma$, by the expression [1]

$$S = \left[\sigma(1 - \exp Pe)\right]/\left(1 - \sigma\exp Pe\right),$$

with $Pe$ being the Péclet number, $Pe = -J_v(1 - \sigma)/P_s$. A comparison between experimental and calculated retention values for membrane PAC-O is shown in Fig. 3. Rather good agreement was obtained, which can be taken as proof of the reliability of $P_s$ results obtained from diffusion experiments.

### 3.2. XPS study

Chemical characterization of the membrane surfaces was carried out by XPS. Relative atomic concentrations (a.c.%) of the elements present in the surface of the different membrane samples (polyamide active layer) were determined by XPS analysis and the percentages obtained are indicated in Table 2. Small concentrations (less than 0.5%) of noncharacteristic polyamide elements (sulfur, chlorine, etc.) were also found. Similar figures for noncharacteristic membrane material elements (even higher) have been reported in the literature [26,28]; they are usually considered as impurities and they are attributed to environmental contamination or residual products from membrane manufacturing. In this case, due to the fact that sulfur is a characteristic element of the polysulfone support layer, its value is also indicated in Table 2, since the increase in the atomic concentration of sulfur would indicate the damage of the polyamide active layer for chemically treated samples. As can be observed in Table 2, a practically constant value for the sulfur a.c.% in the different samples was obtained, which indicates that it can be

### Table 2

<table>
<thead>
<tr>
<th>Membrane</th>
<th>(Cl$_x$) (%)</th>
<th>(O$_x$) (%)</th>
<th>(N$_x$) (%)</th>
<th>(S$_x$) (%)</th>
<th>O/C</th>
<th>N/C</th>
<th>N/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC-F</td>
<td>75.0±0.3</td>
<td>13.7±0.3</td>
<td>11.0±0.2</td>
<td>0.30±0.01</td>
<td>0.183</td>
<td>0.147</td>
<td>0.803</td>
</tr>
<tr>
<td>PAC-O</td>
<td>76.0±0.6</td>
<td>12.6±0.4</td>
<td>11.2±0.6</td>
<td>0.20±0.02</td>
<td>0.166</td>
<td>0.147</td>
<td>0.889</td>
</tr>
<tr>
<td>PAC-A</td>
<td>71.1±0.9</td>
<td>18.9±0.4</td>
<td>9.6±0.5</td>
<td>0.40±0.08</td>
<td>0.266</td>
<td>0.135</td>
<td>0.508</td>
</tr>
<tr>
<td>PAC-B</td>
<td>68.5±0.3</td>
<td>21.5±0.2</td>
<td>9.7±0.4</td>
<td>0.30±0.04</td>
<td>0.314</td>
<td>0.142</td>
<td>0.451</td>
</tr>
<tr>
<td>PAC-C</td>
<td>70.9±0.4</td>
<td>18.2±0.2</td>
<td>10.6±0.1</td>
<td>0.30±0.02</td>
<td>0.257</td>
<td>0.150</td>
<td>0.582</td>
</tr>
</tbody>
</table>

Fig. 2. Conductivity of solution in half-cell 2, $\sigma_2$, versus time. (a) Comparison among different samples ($c_1 = 0.05$ M NaCl): (■) membrane PAC-O, (○) membrane PAC-A, (Δ) membrane PAC-B, (◇) membrane PAC-C, $\Delta c = 0.05$ M. (b) Comparison for two different samples and NaCl concentration gradients: $\Delta c = 0.05$ M, membrane PAC-F (▼) and membrane PAC-O (■); $\Delta c = 0.01$ M, membrane PAC-F (▼) and membrane PAC-O (○).

Fig. 3. Salt retention, $S$, versus volume flux, $J_v$, for PAC-O sample ($c = 0.016$ M NaCl). Points: experimental values; solid line: theoretical values.
considered as an impurity, and only the polyamide active layer is studied.

As can be seen in Table 2, values obtained for PAC-F and PAC-O samples hardly differ from each other, which indicates that structural changes associated to membrane aging cannot be correlated with any chemical modification of the active layer. However, some differences can be observed in the c.a. values for the chemically treated samples, mainly an increase in the concentration of oxygen and a small decrease in the nitrogen concentration. Concentration ratios of these elements are also indicated in Table 2. These results show very good agreement between N/C experimental and theoretical values ([N/C]T = 0.143) for the different samples. In the case of PAC-F and PAC-O membranes the N/O experimental ratio hardly differs from the theoretical one ([N/O]T = 1), but its value clearly decreases when chemically treated samples are considered.

Fig. 4 shows the C1s, O1s, and N1s spectra for the different membrane samples. As can be seen in Fig. 4, there are no significant differences in the shapes of the O1s and N1s spectra, although a broadening and increase in the intensity of the O1s signal for the three treated samples, as well as a loss of symmetry of that treated with HNO3, can clearly be observed. C1s spectra were fitted by considering three different carbon contributions: (i) aliphatic/aromatic (plus adventitious carbon) at 284.7 eV B.E. (carbon CA); (ii) the peak at 286.1 eV B.E. corresponding to –C–O– or –C–N– links (CB); (iii) carbon CC, which presents a peak at 287.9 eV B.E., due to C=N or O=C–N links. Fig. 5 shows experimental and fitted signals as well as those corresponding to carbons CA, CB, and CC for the HCl-treated sample. Table 3 shows the percentages of the total area assigned to the different types of carbon for membrane PAC-O and treated samples. It can be seen how chemical treat-

![Figure 4](image1.png)

**Fig. 4.** XPS spectra for polyamide characteristic elements. Membrane PAC-O (■), PAC-A (○), PAC-B (△) and PAC-C (×).

![Figure 5](image2.png)

**Fig. 5.** Deconvolution of C1s signal for sample PAC-A: carbon CA (---), carbon CB (-----), carbon CC (-----).

**Table 3**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CA (%)</th>
<th>CB (%)</th>
<th>CC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC-O</td>
<td>69.0</td>
<td>22.0</td>
<td>9.0</td>
</tr>
<tr>
<td>PAC-A</td>
<td>61.2</td>
<td>22.7</td>
<td>15.5</td>
</tr>
<tr>
<td>PAC-B</td>
<td>58.6</td>
<td>26.8</td>
<td>14.5</td>
</tr>
<tr>
<td>PAC-C</td>
<td>65.9</td>
<td>19.5</td>
<td>14.7</td>
</tr>
</tbody>
</table>
ments increase the proportion of O=\text{C–N} links as a result of polyamide oxidation, but an increase in C=\text{N} links for \text{HNO}_3-treated membrane was also found. In any case, taking into account XPS results, it can be assumed that the changes obtained in the transport parameters for aging and chemically treated membranes cannot be attributed to chemical degradation of the polyamide active layer, and they must be related to structural (morphological) changes in the sublayers of the composite membrane.

3.3. Impedance spectroscopy

In order to correlate the modifications due to the effect of aging and chemical treatments in the whole composite membrane with that corresponding to each sublayer, impedance spectroscopy measurements were carried out. A comparison of the Bode plots obtained with the PAC-F and PAC-O samples (\(-Z_{\text{img}}\) vs \(f\) and \(Z_{\text{real}}\) vs \(f\)) in contact with the same NaCl solution is shown in Figs. 6a and 6b. In this picture different relaxation processes can be observed, which correspond to the dense active layer (a.l.) and the porous sublayer (p.l.) of the composite membrane and the electrolyte solution (e) placed between the membrane and the electrodes. For comparison, impedance values obtained with the electrolyte solution alone, at the same concentration, are also shown in Fig. 6 and, as can be observed, very good concordance between the values assigned to the electrolyte in the heterogeneous system (composite membrane/NaCl solution) and those directly measured was obtained. These diagrams allow the determination of the range of frequencies associated with each relaxation process and for the systems drawn in Fig. 6 are: dense layer, \(10 \leq f\) (Hz) \(\leq 10^4\); porous layer, \(10^4 – 2 \times 10^5\) Hz; and electrolyte, \(10^5 – 10^7\) Hz. In general, the value of the maximum frequency associated with the relaxation process in the active layer decreases when the membrane presents a closer structure.

The analysis of impedance data is usually carried out by the complex plane \(Z^*\) method, which involves plotting the impedance imaginary part (\(-Z_{\text{img}}\)) versus the real part (\(Z_{\text{real}}\)). A single parallel R–C circuit gives rise to a semicircle in the \(Z^*\) plane, such as that shown in Fig. 7 for the electrolyte solution, which has intercepts on the \(Z_{\text{real}}\) axis at \(R_\infty\) (\(\omega \to \infty\)) and \(R_0\) (\(\omega \to 0\)), \((R_0 – R_\infty)\) being the resistance of the system. The maximum of the semicircle equals 0.5(\(R_0 – R_\infty\)) and it occurs at a frequency such that \(\omega RC = 1\), \(RC\) being the relaxation time [29]. However, complex systems usually present a distribution of relaxation times and the resulting plot is a depressed semicircle; in such cases a nonideal capacitor, which is called a constant phase element (CPE), is considered [29]. The impedance for the CPE is expressed by \(Q(\omega) = Y_0(\omega^{\sigma n})\), where the admittance \(Y_0\) (\(\Omega s^{-n}\)) and \(n\) are two empirical parameters (\(0 \leq n \leq 1\)). A particular case is obtained when \(n = 0.5\); then the circuit element corresponds to a “Warburg impedance” (W), which is associated with a diffusion process according to Fick’s first law.

Experimental impedance data (\(-Z_{\text{img}}\) vs \(Z_{\text{real}}\)) obtained with aging and chemically treated samples are shown in Fig. 8 (\(c = 2 \times 10^{-3}\) M \text{NaCl}), where the equivalent circuit associated with each system is also indicated. Similar types of curves were obtained for the other concentrations studied. These diagrams show that (i) HCl treatment clearly reduces the aging effect on the active layer of the PAC-O membrane, while the treatment with \text{HNO}_3 also affects the porous sublayer; (ii) the use of \text{NaOH} solution for chemical treatment increases the electrical resistance of both active and porous sublayers (opposite to that observed with the two other treatments).

The fitting of the impedance experimental points by means of a nonlinear program [30] allows the determination of the different circuit parameters. Dependence of \(R_a\)
and $R_p$ values with salt concentration for PAC-F and PAC-O membranes is shown in Fig. 9a. In all cases, a decrease of the membrane electrical resistance when the salt concentration increases was found, which is attributed to the concentration dependence of the electrolyte filling the membrane matrix [18,31]. As can be observed, for the fresh PAC-F sample the higher contribution to the total membrane electrical resistance corresponds to the thick and porous support, while for aging PAC-O sample the active layer part is much higher. In fact, the following average ratios for the whole interval of concentration were obtained:

\[
\langle \frac{R_{\text{PAC-O}}}{R_{\text{PAC-F}}} \rangle = (6.0 \pm 0.7),
\]

\[
\langle \frac{R_{\text{a-PAC-O}}}{R_{\text{a-PAC-F}}} \rangle = (30 \pm 7),
\]

\[
\langle \frac{R_{\text{p-PAC-O}}}{R_{\text{p-PAC-F}}} \rangle = (2.0 \pm 0.4).
\]

According to these results, aging strongly affects the active layer, although its effect on the porous sublayer is sensitively lower.

A more realistic model for composite membranes should consider a transition or intermediate sublayer between the highly porous support (usually, an ultrafiltration membrane) and the dense active layer; if this sublayer is partially included in the two other layers, a simple bilayer model can be used. However, due to the different thicknesses estimated for both sublayer (less than 1 µm in the case of the dense layer and 50–100 µm for the porous one [11]), the inclusion of a part of the transition layer in the active sublayer will greatly

---

**Fig. 8. Nyquist plots for aging and chemically treated membrane samples. $c = 0.002$ M NaCl.**

**Fig. 9. Electrical resistance for composite membrane ($R_T$), active layer ($R_a$), and porous layer ($R_p$) versus NaCl concentration.** (a) membrane PAC-F: $R_T$ (▲), $R_a$ (▲), and $R_p$ (△); membrane PAC-O: $R_T$ (■), $R_a$ (●), and $R_p$ (○); membrane PAC-A: $R_a$ (●) and $R_p$ (○); membrane PAC-B: $R_a$ (▲) and $R_p$ (△); membrane PAC-C: $R_a$ (●) and $R_p$ (○).
increase its thickness and, consequently, its electrical resistance, which is directly dependent on thickness; however, it will cause a reduction in both hydraulic and salt permeabilities. On the other hand, its effect on the thick porous support will be much lower. As can be seen, this assumption is in agreement with the result obtained for the membrane characteristic parameters determined from different kinds of measurements.

The effect of chemical treatments on the electrical resistances of dense and porous layers can be observed in Fig. 9b. It was obtained that HCl and HNO3 treatments reduce the electrical resistance of the aging membrane, mainly that associated with the active layer, which presents practically the same values after both kinds of treatments; oppositely, NaOH treatment increases the electrical resistance of the composite membrane. In fact, the sequence of total electrical resistance values, $R_T$, for the different samples is $R_T(\text{PAC-C}) > R_T(\text{PAC-O}) > R_T(\text{PAC-B}) > R_T(\text{PAC-A}) > R_T(\text{PAC-F})$. This sequence is similar to that previously obtained for hydrodynamic and salt resistance, in agreement with their similar kind of dependence on geometrical parameters. Moreover, IS measurements allow the estimation of the contribution of each sublayer. Average values for the ratio of the porous layer/total membrane electrical resistance, $(R_p/R_T)$, obtained for the studied samples in the whole interval of NaCl concentrations studied are also indicated in Table 1. As can be observed, the electrical resistance of the porous support for chemically treated samples represents $(76 \pm 7)\%$ of the total electrical resistance, which does not differ very much of the value corresponding to the fresh membrane ($(85 \pm 2)\%$), while for the aging sample the higher contribution corresponds to the dense active layer (approximately 70%).

4. Conclusions

We have stated that aging and chemicals (HCl, HNO3, and NaOH solutions) can affect the structure of both sublayers of composite polyamide/polyisulfone membranes, causing variations in the membrane transport parameters. Particularly, modifications in the hydraulic and salt permeabilities through the composite membrane have been obtained.

Chemical characterization of the membrane surfaces has been carried out by X-ray photoelectron spectroscopy analysis. As a result of the chemical treatments slight modifications in the surfaces of the polyamide active layers of the different samples were obtained, which are attributed to polyamide oxidation, but they have not caused degradation of this sublayer. Modification of transport parameters might be related to changes in the membrane structure.

Impedance spectroscopy measurements have permitted us to determine the electrical resistance of both dense and porous sublayers. Results show the strong increase of the membrane electrical resistance, this being more significant for the thin and dense polyamide active sublayer. A three-layer model for the composite membrane (active, transition, and porous sublayers) could explain the membrane structural changes determined from permeability and electrical resistance values by assuming pore reduction in the intermediate layer, which can be considered as an increase in the thickness of the dense sublayer.

Acknowledgments

We thank the Comisión Interministerial de Ciencia y Tecnología (Spain) for financial support (Project MAT2000-1140) and Professor Rodriguez Castellón (Departamento de Química Inorgánica, Universidad de Málaga, Spain) for helping us in XPS analysis.

References
