Surface chemical and electrokinetic characterizations of membranes containing different carriers by x-ray photoelectron spectroscopy and streaming potential measurements: study of the effect of pH

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Received 16 July 2001; Revised 26 November 2001; Accepted 28 December 2001

Two activated membranes containing 200 mM of di-(2-ethylhexyl) phosphoric acid (DEHPA-2) and di-(2-ethylhexyl)dithiophosphoric acid (DTPA-2) as carriers have been studied. The electrokinetic characterization of the membrane/solution interface was carried out by means of tangential streaming potential measurements, with the membranes in contact with an NaCl solution (5 × 10^{-4} M) at different pH (3.5 ≤ pH ≤ 8.5). These measurements allow the determination of the zeta potential, the electrokinetic surface charge density and the isoelectric point of the membranes. Other membrane characteristic parameters such as the acidic dissociation constant or the number of acidic sites per membrane area (density of acidic sites) can be determined if a site dissociation model is used. On the other hand, chemical changes in the membrane surfaces due to contact with solutions at different pH were determined by comparing XPS spectra of the used samples with the original ones. In order to see the influence of each type of carrier on electrokinetic parameters, a comparison with the polymeric base membrane (B0) has also been made. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: activated membranes; stability; XPS characterization; tangential streaming potential; zeta potential; pH modification

INTRODUCTION

Activated carrier membranes (ACMs) are being developed to increase the stability of supported liquid membranes (SLMs), which usually consist of an organic solvent immobilized in the pores of a hydrophobic support that contains a carrier able to link selectively to one of the components of an adjacent mixture. In order to minimize the loss of the carrier reagent during transport across SLMs, Kemperman et al. have optimized the application of a thin polyamide layer covering the impregnated support. Based on this method, different ACMs have been developed by incorporation of different concentrations of two carriers: di-(2-ethylhexyl)phosphoric acid (DEHPA) and di-(2-ethylhexyl)dithiophosphoric acid (DTPA). Electrical, chemical surface and transport characterizations of these membranes were carried out by impedance spectroscopy, x-ray photoelectron spectroscopy (XPS) and the transport of ions across the membranes, which has permitted us to establish a correlation between membrane electrical resistance and the concentration of carrier, to have information about the chemical interactions between the carriers and the polymeric top layer and to determine different characteristic transport parameters for the membranes.

In this work, electrokinetic characterization of the surface of two membranes, one activated with DEHPA and the other with DTPA, was carried out by measuring the streaming potential along the membrane surface or the tangential streaming potential (TSP) at different pH. From these results, the zeta potential and the isoelectric point were determined. Assuming a local dissociation model, the pK_a and the density of acidic sites on the membrane surface N_a were also determined. The study by XPS of the membrane samples before and after electrokinetic measurements allows the possible chemical changes in the surface of the membranes to be investigated owing to their use with aqueous solutions, which could be related to the stability of the two kinds of ACM.

EXPERIMENTAL

Materials

The different studied membranes, two activated and their polymeric support, were prepared in the Analytical
Chemistry Department, Universidad Autonoma de Barcelona (Spain) as described elsewhere. A composite polyamide/polysulphone membrane, the tin polyamide top layer of which was obtained by interfacial polymerization, was used as the support and called B0. The two activated membranes were prepared from solutions containing 200 mls di-(2-ethylhexyl)phosphoric acid and di-(2-ethylhexyl)diithiophosphoric acid, and they will be called hereafter DEHPA-2 and DTPA-2, respectively. The distribution of the carriers across the membranes was determined by x-ray microanalysis and the results indicate that the carrier is mainly concentrated in the polyamide top layer (∼1 µm thickness) and in the upper part of the polysulphone support.

Measurements were carried out at a given NaCl concentration (C = 5 × 10^{-4} M) and pH 3.5–8.5, at 25.0 ± 0.3 °C. The electrolytes used (NaCl, NaOH and HCl) were p.a. grade (Merck). All solutions were prepared with deionized water of conductivity <1.5 µS cm^{-1} and pH 5.6–6.0. The pH of the NaCl solution was changing by adding NaOH and HCl, and measurements were carried out from the higher to the lower pH. Before measuring, the membranes were washed in the cell with distilled water to clean the surfaces.

In order to see possible chemical changes in the surface of membranes as a result of their contact with aqueous salt solutions at different pH, membrane samples used in streaming potential measurements or maintained in contact for 10 days with basic (pH 8.3), neutral (pH 5.8) and acid (pH 3.5) 10^{-3} M NaCl solutions were also analysed by XPS. Before XPS analysis, samples were washed many times with distilled water and dried for 24 h at 60 °C; they will be named hereafter by adding a letter after the membrane code: (u) for used membranes, (b) for basic, (n) for neutral and (a) for acid-washed membranes.

**Surface streaming potential measurements**

Measurements of tangential streaming potential (TSP) or streaming potential along the membrane surface were carried out with a system that consists, basically, of a rectangular PMMA cell (15.2 cm² section) with a channel of well-defined dimensions created by the use of a PTFE spacer (thickness 300 ± 10 µm) between two membrane samples. A pump impeller drives the electrolyte solution from a reservoir into the measuring cell, pressure difference (∆P) was measured by a pressure sensor and it varies between 80 and 200 mbar. Characteristic hydrodynamic parameters such as the Reynold number and the hydrodynamic height of the channel are: R = 390 ± 60 and h₀ = 238 ± 17 µm. A high impedance voltmeter (Yokogawa 7552, 1 GΩ input impedance) was used to measure the induced streaming potential (∆V). The TSP measurements for the B0 sample were carried out with Ag/AgCl electrodes; however, damage in the Ag/AgCl electrodes was observed when they were used with DEHPA-2 and DTPA-2 membranes, which was attributed to precipitation of organic silver phosphate in the electrode, so black platinum electrodes were used for measurements with both activated membranes.

**X-ray photoelectron spectroscopy measurements**

Surface chemical characterization was carried out by XPS using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg Kα radiation (300 W, 15 kV, 1253.6 eV) as the excitation source. High-resolution spectra were recorded at 45° take-off-angle by a concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV, using a 720 µm diameter analysis area. Under these conditions the Au 4f/2 line was recorded with 1.16 eV full width at half-maximum (FWHM) at a binding energy (BE) of 84.0 eV. Charge referencing was done against aliphatic/aromatic carbon (C ls-285.0 eV). Survey spectra in the range 0–1200 eV were also recorded at 187.85 eV pass energy. Membranes were irradiated for a maximum time of 20 min to minimize x-ray-induced sample damage. The PHI Access ESCA-V6.0 F software package was used for acquisition and data analysis following the procedure described in detail elsewhere. Atomic concentration percentages of the characteristic membrane elements were determined after subtraction of a Shirley-type background, taking into account the corresponding area sensitivity factor for the different measured spectral regions. The atomic concentration results presented in the next section correspond to the average of three measurements, giving the standard deviation as the error.

**RESULTS AND DISCUSSION**

Tangential streaming potential as a function of applied pressure for the different samples at two given pH values (5.6 and 3.8) is shown in Fig. 1. As can be seen, linear voltage–pressure relationships were obtained for the different membrane samples and electrodes. From the slope of these straight lines, the streaming potential coefficient, ζ = (∆V/∆P), was determined. Zeta potential (ζ) was obtained from the streaming potential coefficient by using the Helmholtz–Smoluchowski expression

\[
\zeta = (\eta/\varepsilon_0 \varepsilon_r) (\Delta V/\Delta P) = (\eta/\varepsilon_0 \varepsilon_r) \phi
\]

where η and λ are the solution viscosity and conductivity, respectively, and ε₀ and ε_r are the vacuum permittivity and

![Figure 1](image-url)
the solution dielectric constant. Once the zeta potential is determined, the electrokinetic surface charge density \( \sigma_e \) can be obtained by

\[
\sigma_e = (2\varepsilon_o \varepsilon_r k T / z e) \sin h (z e \zeta / 2 k T)
\]

where \( \varepsilon \) is the thickness of the electrical double layer, \( z \) is the valency of the ion, \( e \) is the elementary charge, \( k \) is the Boltzmann constant and \( T \) is the temperature of the system.

Figures 2 and 3 show the dependence of zeta potential and electrokinetic surface charge density with pH for the different membranes (represented by two separated figures because different kinds of electrodes were used). Less negative zeta potential values were obtained for the DEHPA-2 membrane than for the DTPA-2 membrane but no difference in their isoelectric point was found, as can be seen in Table 1, where the values for the three membrane samples are indicated; the acidic character of polyamide membranes has also been reported by other authors.\(^{17,18}\)

Assuming a local dissociation model,\(^{9}\) the surface charge density due to the dissociation of acidic groups \( \sigma_{s,a} \) can be expressed as a function of the density of dissociated groups \( N_a \) by

\[
\sigma_{s,a} = -[e N_a / (1 + 10^{pK_a - pHs})]
\]

where \( pH_s \) corresponds to the pH at the membrane surface.\(^{9}\) If there is no other charge on the membrane wall, then

**Figure 2.** (a) Zeta potential and (b) electrokinetic surface charge density as a function of pH for the B0 membrane. Line corresponds to fitting data curve using a local dissociation model.

**Figure 3.** (a) Zeta potential and (b) electrokinetic surface charge density as a function of pH for DEHPA-2 (open circles) and DTPA-2 (open triangles) membranes. Dashed and dotted lines correspond to fitting data curves using a local dissociation model for DEHPA-2 and DTPA-2, respectively.

**Table 1.** Electrokinetic and membrane characteristic parameters: isoelectric point (i.p.), acidity constant \( pK_a \) and density of acidic sites \( N_a \) for the different membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>i.p.</th>
<th>( pK_a )</th>
<th>( N_a ) (m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>3.8</td>
<td>5.0 ± 0.1</td>
<td>( 4.5 ± 0.1 ) \times 10(^{15})</td>
</tr>
<tr>
<td>DEHPA-2</td>
<td>3.7</td>
<td>4.5 ± 0.2</td>
<td>( 3.6 ± 0.3 ) \times 10(^{15})</td>
</tr>
<tr>
<td>DTPA-2</td>
<td>3.6</td>
<td>4.5 ± 0.1</td>
<td>( 4.6 ± 0.2 ) \times 10(^{15})</td>
</tr>
</tbody>
</table>

\( \sigma_{s,a} = \sigma_e \) and \( N_a \) and \( pK_a \) (parameters characteristic of the membrane surface) can be calculated from the electrokinetic surface charge density \( \sigma_e \). In Figs 2(b) and 3(b) the dotted lines represent the fitting of the experimental data for activated and B0 support membranes according to this model. Values for \( pK_a \) and \( N_a \) for the three studied membranes are also shown in Table 1. These results are coincident with the previous graphical observations: DTPA-2 acid properties are more similar to non-activated membrane than DEHPA-2, although these results indicate that, in general, the carrier hardly affects the membrane/solution interface electrical properties.

However, the surface chemical composition of the activated membranes is very different from the non-activated membrane, as can be observed by XPS. Table 2 shows atomic
Table 2. Relative atomic concentration and some interesting ratios between them for fresh and TSP used membranes (u)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>%C</th>
<th>%O</th>
<th>%N</th>
<th>%P</th>
<th>%S</th>
<th>N/O</th>
<th>N/P</th>
<th>P/O</th>
<th>P/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>77.6±0.8</td>
<td>9.8±0.4</td>
<td>12.6±0.4</td>
<td>—</td>
<td>—</td>
<td>1.29</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B0(u)</td>
<td>71±1</td>
<td>18.9±0.9</td>
<td>10.0±0.5</td>
<td>—</td>
<td>—</td>
<td>0.529</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DEHPA-2</td>
<td>77.5±0.1</td>
<td>14.8±0.3</td>
<td>4.2±0.4</td>
<td>3.4±0.1</td>
<td>—</td>
<td>0.284</td>
<td>1.24</td>
<td>0.230</td>
<td>—</td>
</tr>
<tr>
<td>DEHPA-2(u)</td>
<td>69.4±0.5</td>
<td>20.9±0.3</td>
<td>9.2±0.2</td>
<td>0.5±0.1</td>
<td>—</td>
<td>0.440</td>
<td>18.4</td>
<td>0.024</td>
<td>—</td>
</tr>
<tr>
<td>DTPA-2</td>
<td>78±1</td>
<td>12.8±0.9</td>
<td>3.3±0.1</td>
<td>2.1±0.1</td>
<td>4.0±0.1</td>
<td>0.258</td>
<td>1.57</td>
<td>0.164</td>
<td>0.525</td>
</tr>
<tr>
<td>DTPA-2(u)</td>
<td>72.7±0.2</td>
<td>17.2±0.8</td>
<td>3.2±0.2</td>
<td>2.4±0.3</td>
<td>4.4±0.5</td>
<td>0.186</td>
<td>1.33</td>
<td>0.140</td>
<td>0.545</td>
</tr>
</tbody>
</table>

Figure 4. Comparison of the shape of C 1s, O 1s, N 1s and P 2p spectra for DEHPA-2 (open circles), DEHPA-2(u) (solid circles), DTPA-2 (open triangles) and DTPA-2(u) (solid triangles) samples. (a) Comparison of S 2p spectra for DTPA-2 (open triangles) and DTPA-2(u) (solid triangles) samples. (b) Comparison of C 1s spectra for B0 (cross), B0(u) (asterisk) and DEHPA-2(u) (solid circles) samples.

concentrations for the fresh and used samples; only chemical elements in the polyamide matrix (carbon, oxygen and nitrogen) and in the carrier (carbon, oxygen and phosphorus, and also sulphur in DTPA-activated samples) appear in concentrations higher than 0.5%. The N/O ratio for B0 is higher than the polyamide theoretical values, which indicates the presence of nitrogen-containing impurities that were removed during the electrokinetic measurements, as well as phosphorus and sulphur (<0.5% in B0 sample) impurities. The increase of oxygen found for the B0(u) sample can be due to hydration of the polyamide membrane.

In the activated membranes, phosphorus, sulphur (only for DTPA sample) and oxygen are the characteristic elements of the carriers, whereas nitrogen is only characteristic of the polyamide. Then, the decrease of phosphorus and the increase of nitrogen content in the used sample with respect to fresh DEHPA-2 activated membrane indicate a decrease of the carrier amount on the membrane surface. However, this effect is not observed in DTPA-2-activated membrane, where the contact of the membrane with aqueous solutions at different pH only produces an increase of oxygen and a decrease of the carbon concentration.

Figure 4 shows C 1s, O 1s, N 1s and P 2p spectra for DEHPA-2 and DEHPA-2(u) and DTPA-2 and DTPA-2(u) samples, where broadening of the C 1s signal mainly towards high binding energy (BE) (relative increase of oxygen-containing carbon compounds) and an increase of the oxygen band at ~533.0 eV can be observed for both used samples. These features also happen for the non-activated membrane [see Fig. 4(b)] and could be related to membrane hydration. The maximum of the N 1s signal shifts slightly to higher BE in both used activated membranes, and the same happens for the P 2p signal in the DTPA-2(u) sample, whereas in DEHPA-2 samples the bad quality of the P 2p spectra for the used samples (owing to the low phosphorus content) does not allow this observation; both effects could be due also to water molecule interaction, although non-significant changes in the shape of these two spectra as a result of the use of the membranes are observed. The removal of the carrier on the surface of the DEHPA-activated membrane is also observed in the shape of the XPS signal by the higher broadening of the O 1s spectra for the DEHPA-2(u) sample, the spectrum being very similar to that of B0(u) [see Fig. 3(b)]. On the other hand, a comparison of the shape of the S 2p
spectra for DTPA-2 and DTPA-2(u) samples [Fig. 4(a)] shows a higher amount of $S^{VI}$ atoms at ~168.5 eV in the fresh sample than in the used sample, probably sulphur atoms in a high oxidative environment; these results seem to indicate that although the DTPA carrier is not removed from the surface of this membrane, the aqueous solutions could change its chemical state. The removal of DEHPA carrier during the measurement process can justify the lower density of acidic chemical state. The removal of DEHPA carrier during the use of the DEHPA-2-activated samples [Fig. 4(a)] shows that the carrier remains on the surface, although its selective properties could be altered because changes in its chemical state also exist. These changes are mainly due to the membrane washing process, independently of the acid or basic character of the solutions.

The removal of carrier in the DEHPA-2 membrane observed by XPS provokes a decrease in the value of the density of acid sites for this membrane in comparison with the DTPA-2 sample.

Acknowledgements

We thank Professor Valiente’s research group, Departamento de Química Analítica, Universidad Autónoma de Barcelona, España, for preparing the activated membranes, and Junta de Andalucía (Grupo FQM 258) for partial financial support.

REFERENCES


### Table 3. Relative atomic concentration obtained for samples washed with $10^{-3}$ m NaCl solutions at pH 8.3 (b), pH 5.8 (n) and pH 3.5 (a)

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C</th>
<th>%O</th>
<th>%N</th>
<th>%C</th>
<th>%O</th>
<th>%N</th>
<th>%P</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b)</td>
<td>70.0±0.5</td>
<td>20.4±0.5</td>
<td>9.6±0.1</td>
<td>71.3±0.8</td>
<td>19.4±0.7</td>
<td>8.8±0.1</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td>(n)</td>
<td>70.2±0.7</td>
<td>20.6±0.8</td>
<td>9.3±0.1</td>
<td>76.2±0.6</td>
<td>17.1±0.5</td>
<td>6.1±0.1</td>
<td>0.6±0.1</td>
</tr>
<tr>
<td>(a)</td>
<td>71.9±0.4</td>
<td>18.5±0.6</td>
<td>9.6±0.3</td>
<td>72.5±0.2</td>
<td>17.7±0.3</td>
<td>9.0±0.1</td>
<td>0.7±0.1</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Surface electrokinetic characterization of two activated membranes containing di-(2-ethylhexyl)phosphoric acid and di-(2-ethylhexyl)dithiophosphoric acid as carriers and comparison with the base non-activated polyamide membrane have shown that the carrier hardly affect the electrokinetic properties of the membrane/solution interface. The three membranes present a slight acid behaviour in contact with sodium chloride solutions.

X-ray photoelectron spectroscopy has shown that the use of the DEHPA-2-activated membranes with aqueous NaCl solutions at different pH provokes a decrease in the amount of carrier on the membrane surface. For the DTPA-2-activated sample the carrier remains on the surface, although its selective properties could be altered because changes in its chemical state also exist. These changes are mainly due to the membrane washing process, independently of the acid or basic character of the solutions.

In order to determine the influence of the acid or basic medium on the observed chemical changes due to the use of activated membranes in the electrokinetic measurements, samples that have been in contact only with basic, neutral or acid solution were also studied by XPS. Atomic concentrations are reported in Table 3 for the non-activated and the DEHPA-2-activated membrane. For each sample, atomic concentration values at the three studied pHs are very similar, and they are comparable to the corresponding used membranes, which suggest that the basic or acid character of the aqueous solutions is not the main factor for the observed chemical changes. The shape of the different signals for (b), (n) and (a) samples is also very similar to those of the used samples. These results suggest that the influence of washing with water is higher than the influence of diluted aqueous solution pH on the stability of the activated membranes, although it is necessary to point out that XPS is a surface sensitivity technique (maximum depth ~4–9 nm).