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Electrical Properties of Modified Aromatic Polyamide Membranes

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ABSTRACT

The effects of chemical structure on the values of different electrical parameters measured with novel aromatic polyamide (aramid) membranes were studied. Poly(isophthalamides) containing pendant groups were considered since they can be transformed into dense membranes, suitable for the determination of characteristic transport parameters such as ion transport numbers, electrical resistances and capacitances. Measurements were carried out with the membranes in contact with different NaCl and $MgCl_2$ solutions. Results show that resistance values are strongly dependent on concentration, but membrane capacitance is almost constant for the whole range of concentrations studied ($10^{-3} < C(N) < 5 \times 10^2$). The ionic permeabilities in the membrane were determined from membrane potential and resistance results. The presence of polar side substituents causes lower resistivity in modified polyamides compared with the unsubstituted parent, and the higher the polarity of the substitutent, the lower the resistivity. This trend is valid for both NaCl and $MgCl_2$ solutions.

Key Words. Aromatic polyamides; Dense membranes; Impedance spectroscopy; Membrane potential; Ionic permeabilities

INTRODUCTION

Fully aromatic polyamide membranes have gained great technical importance as barrier materials in ultrafiltration (UF) and reverse osmosis (RO) operations (1, 2). In fact, much effort has been made to develop new polymers that can provide optimal polarity conditions to work as efficient barrier materials for UF and RO (1). The presence of polar groups has been identified as playing a positive role in improving the performance of aromatic polyamide membranes, particularly the flux of water.

Conventional polyamide composite membranes used in technical operations are based on meta-substituted and para-substituted fully-aromatic monomers which react in situ to form an ultrathin active polyamide layer. Theoretically, the chemical structure of these polyamides does not contain polar groups other than amide and some residual free carboxyl groups (3). Therefore, modified aromatic polyamides containing additional polar groups or even ionic groups have been proposed to enhance the polarity and, consequently, the hydrophilicity and water flux (4, 5). Thus, it is interesting to study the effect of chemical modifications on the electrical properties of these materials which must work as specific separation media in aqueous solutions.

In a previous paper the influence of chemical structure on the electrical properties of modified aliphatic-aromatic polyamide membranes was reported (6). It was shown that the presence of polar groups greatly influences the electrical behavior of polyamide membranes. The pyridyl group is strongly polar, and aromatic polyamides containing pyridyl pendant groups have been recently reported as highly hydrophilic materials (7). In this study, poly(isophthalamides) with pyridyl pendant groups were used since they can be processed from solution and be transformed into dense membranes suitable for the determination of characteristic transport parameters. Impedance spectroscopy (IS) was used to determine membrane resistance (or conductivity) and capacitance, but concentration potentials were also measured with different NaCl and $MgCl_2$ solutions. From these results, other characteristic coefficients such as the ionic permeabilities in the membranes, P_i, can be obtained, which provide information about the behavior of these membranes as barriers for the transport of ions. The concentration dependence of these parameters was also studied. The different electrochemical behavior shown by each membrane sample is related to the chemical structure of the individual polymers.

EXPERIMENTAL

Materials

Polymer DDE-I was synthesized from 4,4′-diaminodiphenylether (DDE) and isophthaloyl chloride (IPC) by the conventional low-temperature solution method (8) with essentially quantitative yield.

Polymers DDE-BzI and DDE-PyrI were prepared by polycondensation of DDE with 5-benzoylamino isophthalic acid and 5-(isonicotinoylamino) isophthalic acid, respectively, by the *phosphorylation* method (9), using *N*-methylpyrrolidone (NMP) + LiCl (5%) as the solvent and pyridine/triphenylphosphite as the catalyst system. The yields were over 95%.

Polymer DDE-QPyrI was prepared by treating a solution of polymer DDE-PyrI in NMP with dimethylsulfate (20% molar excess) at 60°C for 8 hours. A polymer concentration lower than 5% (w/v) was used to prevent crosslinking. The modified polymer was isolated by pouring the final solution into methanol and filtering off the yellowish precipitate that formed. It was washed and dried in the usual way. The yield was quantitative. Repeat units for the different polymers are shown in Table 1.

Polymer characterization was carried out using conventional spectroscopic and calorimetric methods; in particular, ^{1}H NMR was used for the determination of chemical structures and differential scanning calorimetry (DSC) was used for the determination of glass transition temperatures. Inherent viscosities (η_{inh}) were measured in NMP for 0.5% polymer solutions at 25 ± 0.1°C.

Dense membranes were prepared by casting polymer solutions (7–10% w/v) in NMP or mixtures of *N,N*-dimethylacetamide (DMA)/NMP. Solvent was evaporated in an air-convection oven at 110°C for 6 hours. Then the films were rinsed in methanol for 24 hours and dried in a vacuum oven at 100°C for 24 hours.

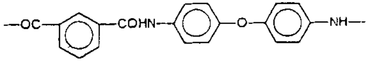
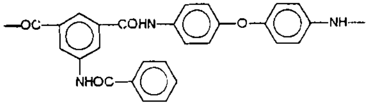
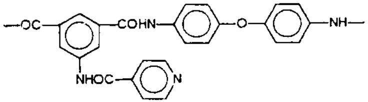
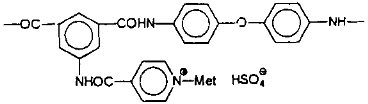
Experimental Setup

Impedance and Concentration Potential Measurements

The experimental device used to measure both impedance spectroscopy and concentration potential is similar to that described in Ref. 10. It basically consists of two half-cells separated by the membrane, which had a free area of 0.7 cm^2.

For IS measurements a frequency response analyzer (FRA, Solartron 1255), controlled by a computer and connected with the solutions in each half-cell via platinum electrodes, was used. The experimental data were

TABLE I
Properties of Modified Polyisophthalamides

Polymer	Repeat unit	η_{inh} (dL/g)	T_g (°C)	$C_{avg}(F) \times 10^{10}$	ϵ
DDE-I		1.36	267	15.2 ± 0.4	21 ± 3
DDE-BzI		0.85	291	3.2 ± 0.2	24 ± 3
DDE-PyrI		0.99	305	6.5 ± 0.2	26 ± 3
DDE-QPyrI		0.89	—[a]	6.8 ± 0.2	40 ± 5

[a] Not observable by DSC.

corrected by software for the influence of connecting cables and other parasite capacitances as indicated in Ref. 11. The measurements were carried out using 100 different frequencies, which ranged between 10^2 and 10^7 Hz, with six different NaCl and $MgCl_2$ solutions (10^{-3} M $\leq C \leq 5 \times 10^{-2}$ M). The solutions on both sides of the membranes had the same concentration.

Concentration potentials were measured with two reversible Ag/AgCl electrodes connected to a digital voltmeter (Yokogawa 7552, 1 GΩ input resistance). The experiments were performed by keeping the concentration ratio of the solutions on both sides of the membrane constant, $c_1/c_2 = \gamma = 2$, for the interval of concentrations $10^{-3} < c(\mathrm{M}) < 10^{-1}$. In all cases the electrode in contact with the low concentration solution (c_2) was grounded; this means $\Delta\phi = \phi(c_1) - \phi(c_2)$.

All measurements were carried out with NaCl and $MgCl_2$ aqueous solutions at a constant temperature of 25.0 ± 0.3°C.

RESULTS AND DISCUSSION

Some physical properties of the aromatic polyamides studied in this paper are listed in Table 1. They were prepared in high yield and high molecular weight (high inherent viscosity), and dense membranes with good mechanical properties could be fabricated by controlled solvent evaporation of cast polymer solutions. Glass transition temperatures in the 275–300°C range are consistent with the fully aromatic chemical structure of these polyamides.

Polymer DDE-QPyrI was prepared by quaternization of the pyridine part of polymer DDE-PyrI with dimethyl sulfate in a solution of NMP. A conversion of approximately 15% after 8 hours of treatment was found by ^{1}H-NMR measurements.

Figure 1 (a and b) shows the impedance plots ($-Z_{\mathrm{img}}$ vs Z_{real}) obtained by impedance spectroscopy measurements for the DDE-I and DDE-QPyrI membranes, respectively, at a given concentration ($C = 0.005$ N) with NaCl and $MgCl_2$ solutions. Similar curves were obtained with the other membranes and concentrations studied. Two dielectric relaxations were obtained for the entire range of frequencies; they correspond to the contributions of both the membrane ($10^2 \leq f(\mathrm{Hz}) \leq 10^5$) and electrolyte solution ($10^5 \leq f(\mathrm{Hz}) \leq 10^7$).

Analysis of ac data was carried out by a complex plane method (12) which involves plotting the impedance imaginary part against the real part (Z_{img}) versus the real part (Z_{real}). When plotted on a linear scale, the equation for a parallel resistance-capacitor (RC) circuit gives rise to a semicircle in the Z^* plane (similar to each of those shown in Fig. 1). The

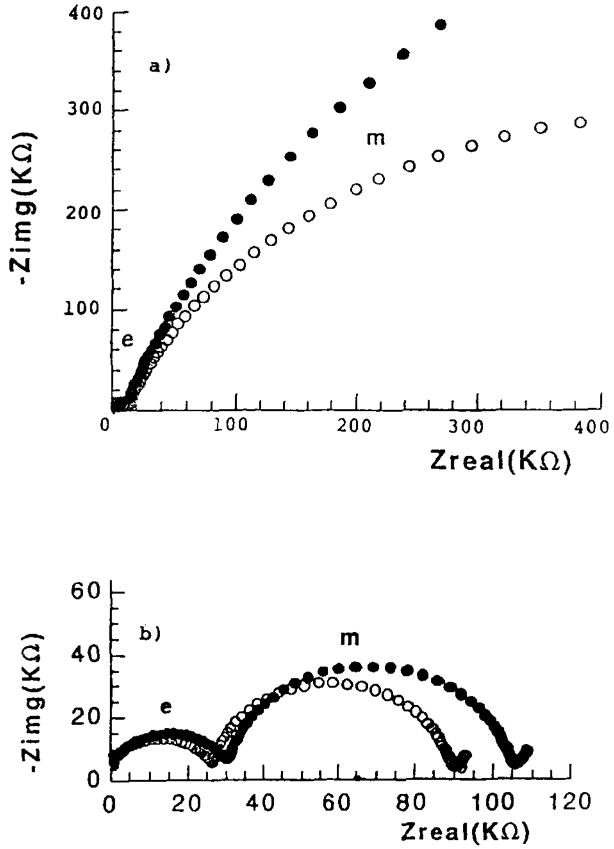


FIG. 1 Impedance plots (Z_{real} vs $-Z_{img}$) at a given concentration $C = 0.005$ M: (○) NaCl, (●) $MgCl_2$. (a) DDE-QPyrI membrane. (b) DDE-I membrane.

semicircle has intercepts on the Z_{real} axis at $R_\infty(\omega \rightarrow \infty)$ and $R_0(\omega \rightarrow 0)$, where $(R_\infty - R_0)$ is the resistance of the system and ω is the angular frequency. The maximum of the semicircle equals $0.5(R_\infty - R_0)$ and occurs at a frequency ω such that $\omega RC = 1$, where RC is the relaxation time.

In all cases the experimental impedance values were fitted to a circuit which consists of a series association of two RC elements: one of them corresponds to the membrane (R_mC_m), and the other to the electrolyte solution (R_eC_e). Only the membrane contribution will be considered in the following discussion. Analysis of the impedance curves by means of a nonlinear program (13) permits us to determine both the resistance and capacitance values of each membrane sample for the different concentrations and electrolytes studied. Quite good agreement between experimental and calculated values was obtained in all cases (error intervals lower than 5%).

Concentration dependence on both membrane resistance and capacitance values was considered. For comparison, in order to avoid the effect of the different membrane thicknesses in these results, the specific resistance $R^* = R_m/d_m$ is shown in Fig. 2 as a function of the salt concentration.

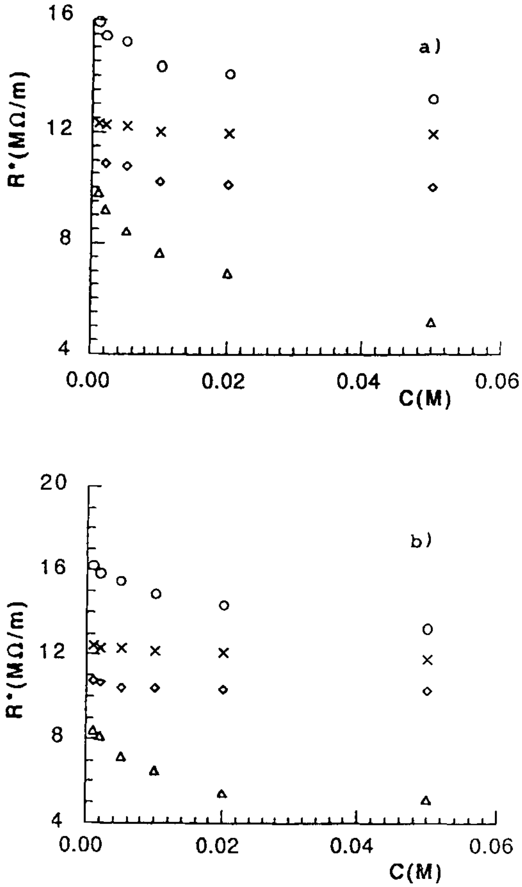


FIG. 2 Specific membrane resistance, $R^* = R_m/\delta$, versus external salt concentration. (○) DDE-I, (×) DDE-Bz, (◇) DDE-PyrI, (△) DDE-QPyrI. (a) NaCl solutions. (b) $MgCl_2$ solutions.

From this, a decrease of R^* values when the concentration increases can be observed; the lowest one corresponds to the DDE-I membrane (around 17%). However, for the more polar DDE-QPyrI membrane a decrease around 45% with both electrolytes was obtained; this can be attributed to the absorption of electrolyte into the membrane matrix (14). The results also show that the membrane resistance values are strongly dependent on the chemical nature of the membrane. They clearly decrease when the polymer chains contain more polar or ionic groups.

However, membrane capacitances are almost independent of both concentration and electrolyte, and their average values, C_{avg}, are shown in Table 1. From C_{avg}, assuming the membranes behave as plate plane capacitors, the polymer dielectric constants were determined (for a hydrated state), and their values are also indicated in Table 1. These results agree with the polar nature of the aromatic polyamide membranes.

Concentration potential values as a function of the salt concentration, $1/c_1$, are shown in Fig. 3 for two membrane samples (DDE-I and DDE-QPyrI) with both electrolytes. Differences due to both the chemical nature of the membrane and the electrolyte can be seen in the experimental points shown in this figure. Almost linear relationships between $\Delta\phi$ and $1/c_1$ were obtained in most cases except for the DDE-QPyrI membrane (with $MgCl_2$

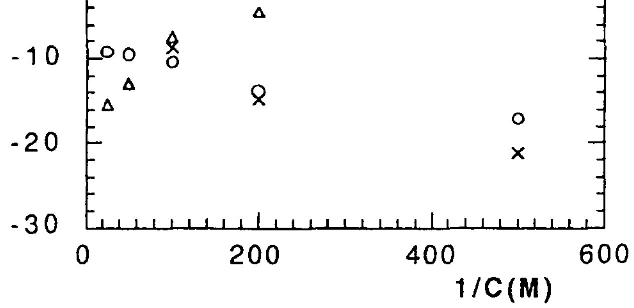


FIG. 3 Concentration potential, $\Delta\phi$, versus external salt concentration $1/c_1$, for two membrane samples. NaCl solutions: (○) DDE-I, (△) DDE-QPyrI. $MgCl_2$ solutions: (◇) DDE-I, (×) DDE-QPyrI.

solutions mainly). This could be due to a Donnan potential contribution in the membrane potential values at the lowest concentrations ($c_1 < 5 \times 10^{-3}$ M).

From concentration potential and conductance values ($\lambda = 1/R_m$), the ionic permeabilities through the membranes, P_i, can be determined by the following expressions (15, 16):

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

$$P_+ + P_- = \lambda RT/F^2S(z_i^2c_i) \qquad (2)$$

where P_+ and P_- are the cation and anion permeabilities, respectively, S is the membrane area, z_i is the valency of each ion, R and F are the gas and Faraday constants, respectively, T is the temperature of the system, and γ is the concentration ratio ($\gamma = c_1/c_2 = 2$). Conductance values at the average concentration, $\langle c\rangle = [c_1 + c_2]/2$, were obtained by extrapolation of the results indicated in Fig. 2.

Variation of the ionic permeabilities with concentration is shown in Fig. 4 for two membrane samples with both electrolytes. In all cases a decrease of P_+ and P_- values was obtained when the concentration was increased. This is more evident at low concentrations ($1.5 \times 10^{-3} \leq c$(M) $\leq 7.5 \times$

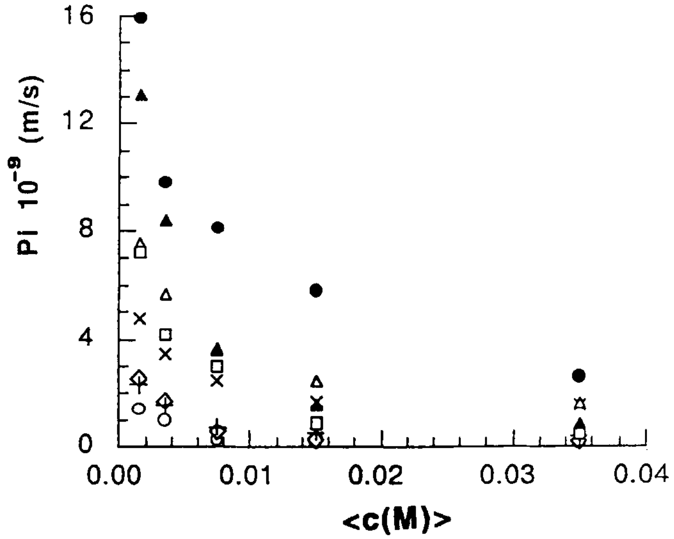


FIG. 4 Ionic permeabilities, P_i, versus average concentration $\langle c(M)\rangle$. NaCl solutions, DDE-PyrI: P_+: (○) and P_-: (◇); DDE-QPyrI: P_+: (×) and P_-: (△). $MgCl_2$ solutions, DDE-BzI: P_+: (+) and P_-: (▲); DDE-PyrI; P_+: (□) and P_-: (●).

10^{-3}), but at high concentrations ($7.5 \times 10^{-3} \leq c(\mathrm{M}) \leq 3.5 \times 10^{-2}$) an almost constant value for the permeability was obtained, mainly for the anionic permeability. The same kind of concentration dependence was obtained for the other membrane samples. A comparison of the results found with both electrolytes shows that $MgCl_2$ solutions give higher permeability values, which may be due to a more hydrated environment and, for this reason, a decrease of interactions with the membrane matrix. It is worth noting that in all cases the permeabilities obtained for each membrane sample for the cations are higher than those determined for the anion, which agrees with the weak negative character attributed to these polymeric membranes.

With both electrolytes the sequence for the ionic permeabilities is P_i(DDE-I) < P_i(DDE-BzI) < P_i(DDE-PyrI) < P_i(DDE-QPyrI). These results clearly show that an increase of polar groups in the polymers improves the water permeability through a membrane but also increases the transport of ions across the membrane.

In conclusion, we can state that the chemical composition of aromatic polyamides greatly affects their electrical parameters, as shown by transport experiments carried out on aramid membranes with the same backbone and different pendant groups. The most relevant effect was observed for quaternized pyridine pendant groups. These ionic groups bring about a large increase in both conductivity and dielectric constant compared with the unmodified aramide DDE-I, as well as in the permeability of ions through the membrane. These results confirm that for the design of novel polyamide membranes, the electrical properties and the permeabilities of specific ions should be considered, and equilibrium between the transport of water and ions should be obtained.

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