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Effect of acid/basic solutions contact on ion transport numbers and conductivity for an anion-exchange membrane

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ABSTRACT

Electrical parameters for a commercial positively charged membrane and after submerged for 1 month in 0.1 M acidic solution (HCl) or 0.1 M basic solution (NaOH) were determined by measuring membrane potential and electrical resistance using NaCl solutions. Changes in the values of the cation transport number in the membranes and in the conductivity as a result of chemical treatments were determined, while membrane surface modification was obtained from contact angle measurements. Moreover, the effect of pilot plant wastewaters on both membrane transport number and conductivity have also been determined and compared with those obtained for the model solutions. According to these results, membrane immersion in the HCl solution hardly affects to transport parameters and membrane surface, while the NaOH treatment significantly modified all the studied parameters and its effect is even more important than that caused by plant wastewaters.

Keywords: Charged membranes; HCl/NaOH treatment; Membrane potential; Conductivity; Contact angle

1. Introduction

Electrodialysis is a well established membrane separation process, able to separate positive from negative ions and from neutral solutes, which uses electrical potential difference as driving force [1]. Charged membranes with high concentration of fixed charges and, consequently with high conductivity, are used to control the transport of ions with low ohmic lost. Negatively charged (cation-exchange) membranes allow the passage of positively charged species, excluding practically the transport of anions (negatively charged species, in general), while positively charged (anion-exchange) membranes allow the passage of negatively charged species and they exclude or significantly reduce the transport of positively charged species; moreover, neutral solutes are not affected by membrane charge and they can be separated from charged species or ions by using one of the corresponding kind of membrane [2,3]. In order to make the membranes selective for one kind of ion or charged particles, typical ion-exchange membranes consist of a crosslinked polymer with negatively/

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positively charged groups fixed to the polymeric network which may significantly affect the transport of electrolyte solutions depending on both fixed charge value and membrane structure [4].

Ion-exchange membranes are used in many separation processes being electrodialysis the most important, although the use of cation exchanger membranes for fuel cell application is significantly increasing in the last decade [5,6]. Some traditional electrodialysis applications are separation of amino acids, production of chlorine and caustic soda via the "chlor-alkali" process or even the production of sulfuric acid and caustic soda using bi-polar membranes [1], that is, the union of a cation-exchange membrane and an anion-exchange membrane with an intermediate layer. Other applications of ion-exchange membranes under development is the electrodialytic decontamination of soils polluted by heavy metals [7,8]. In all these applications, membranes are in contact with acid/basic solutions for a certain period of time, which might cause chemical and structural changes which could affect the membrane performance.

The aim of this paper is the estimation of transport and structural modifications in working conditions for a commercial positively charged membrane as a result of its contact with an acidic/basic solution. Pieces of the membrane were immersed in 0.1 M HCl or 0.1 M NaOH solutions for a period of time of 1 month (chemical treatment) and membrane potential and electrical resistance were measured using NaCl solutions at different concentrations. From these results, ion transport numbers and membrane conductivity were determined and the comparison among original and treated membranes gives information on the effect of solution treatment (pH) on characteristic electrochemical parameters. Changes in membrane surface due to acidic/basis solutions contact were also determined from contact angle measurements. Moreover, a comparison of the different parameters obtained for these samples treated with model HCl and NaOH solutions and those determined with a membrane after immersion in wastewater from a laboratory scale electrodialysis pilot plant is also presented and analyzed.

2. Experimental

2.1. Membranes

A positively charged commercial membrane (AR204-SZRA-412 by Ionics, USA) was selected for characterization (sample Ionics(+)), which is a composite membrane prepared from vinyl monomer and acrylic fiber with $–N^+(CH_3)$ radicals to provide it an electropositive character. Pieces of this membrane were maintained one month in 0.1 M solution of HCl or NaOH and the chemically treated membranes will be hereafter named as: Ionics(+)/HCl and Ionics (+)/NaOH, respectively. For comparison, results obtained with a sample of the Ionics(+) membrane after contact with wastewater from a laboratory scale pilot plant for Zn electrodeposition (basically, a H_2SO_4 aqueous solution with Zn^{+2} ions and pH around 1.3) are also analyzed (sample Ionics(+)/PP). Membrane thickness was (590 ± 10) μm.

2.2. Concentration potential and electrical resistance measurements

Measurements of membrane potential were performed with NaCl solutions in a dead-end test cell similar to that described elsewhere [9], which basically consist of two glass half-cells with the membrane placed between both cells and two magnetic stirrers in the bottom of each cell to minimize concentration-polarization at the membrane surfaces (solutions stirring rate of 540 rpm). Cell potentials (ΔE) were measured with two reversible Ag/AgCl electrodes, one placed in each half-cell, and connected to a digital voltmeter (Yokohama 7552, 1 GΩ input resistance). Measurements were carried out by keeping constant the concentration of the solution at one side of the membrane ($C_f = 0.01$ M) and gradually changing the concentration of the solution at the other side (0.01 M $\leq C_v \leq$ 0.1 M), at room temperature (25 ± 2) °C and standard pH (5.8 ± 0.3) [6].

Electrical resistance of the different membranes was measured with an AC bridge at a frequency of 100 kHz with the samples in wet state, that is, after immersion for 24 h in a 0.01 M NaCl solution. Then, the membranes were taken out and their surfaces dried with paper previously to put in the test-cell, which consists of a Teflon support with two Pt electrodes, and closed with screws [10].

2.3. Contact angle measurements

Changes in the membrane surfaces as a result of chemical treatment were determined from contact angle measurements, which were performed by the sessile drop method using distilled water drops of 5 μL and a Teclis T2010 instrument equipped with a video system. Measurements were carried out on both membrane faces covering 2 × 2 cm area.

3. Results and discussion

Cell potential, ΔE, is the electrical potential difference measured at both sides of a sample separating two solutions of the same electrolyte but different activities (or concentrations in the case of diluted solutions). Membrane potential, $\Delta\Phi_{\mathrm{mbr}}$, values were obtained by subtracting the electrode potential ($\Delta\Phi_{\mathrm{elect}} = (RT/F)\ln\ (C_f/C_v)$), to the measured cell potential values, that is, $\Delta\Phi_{\mathrm{mbr}} = \Delta E - \Delta\Phi_{\mathrm{elect}}$. Fig. 1(a) shows membrane potentials as a function of the logarithm of the concentration ratio of the NaCl solutions at both sides of the membranes, where significant differences depending on the treatment with acidic, basic or wastewater solutions can be observed, but in all cases linear relationships were obtained.

Among the different electrochemical parameters associated to the diffusive transport of ions or charged solutes (ionic mobility, transport number and diffusion coefficient), ion transport number, t_i, which represents the fraction of the total electric current transported by one ion ($t_i = I_i/I_T$) is commonly used [2]. Taking into account t_i definition, $\Sigma_i\ t_i = 1$, in the case of single salts, the following relation between cation and anion transport numbers exists: $t_+ + t_- = 1$. For an ideal cation-exchange membrane, $t_+ = 1$, and the cell potential measured between two solutions of activities a_1 and a_2, at both membrane sides, presents its maximum value [11]:

$$\Delta E_{\max} = -(2RT/F)\ln(a_2/a_1) \approx -(2RT/F)\ln(C_v/C_f) \quad (1)$$

where R and F are the gas and Faraday constants, T is the thermodynamic temperature of the system; as was already indicated concentrations are usually used instead of activities in the case of diluted solutions, where C_f and C_v represent the values of fixed ($C_f = 0.01$ M) and variable solutions, respectively. Cation transport number through a non-ideal membrane for a given pair of solution concentrations can be estimated by [11]: $t_+ = \Delta E/\Delta E_{\max}$, while anion transport number can then be determined by $t_- = 1 - t_+$.

Fig. 1(b) shows the variation of Cl^- transport number with the average concentration of the solutions at both membrane sides ($C_{\mathrm{avg}} = (C_f + C_v)/2$) for the studied membranes, and their average values $\langle t_{Cl^-}\rangle$ are indicated in Table 1, where the error interval corresponds to standard deviation. For comparison, solution anion transport number ($t^o_{Cl^-}$, [12]) is also indicated in Fig. 1 as a dashed-dotted line, and differences between solution ($t^o_{Cl^-}$) and membranes (t_{Cl^-}) transport number values are an indication of the barrier effect of each particular membrane. As can be observed in both Fig. 1(b) and Table 1, different t_- values were obtained depending on the membrane chemical treatment, that is, depending on the solution where the ion-exchange membrane had previously been submerged. Particularly, HCl treatment slightly reduces the value of the anion transport number (around 4%), but its reduction in the case of NaOH treatment is around 20%, even higher than that obtained for the wastewater solution (~11%). These differences seem to indicate changes in the Ionics(+) membrane (bulk phase and/or surface) associated to the chemical treatments. This effect is usually analyzed by determining the ionic permselectivity, $S(i)$,of the membrane [11]:

$$S(i) = (t_i - t_i^o)/(1 - t_i^o) \quad (2)$$

where t_i and t_i^o represent the ion transport number in the membrane and in solution, respectively. Anion

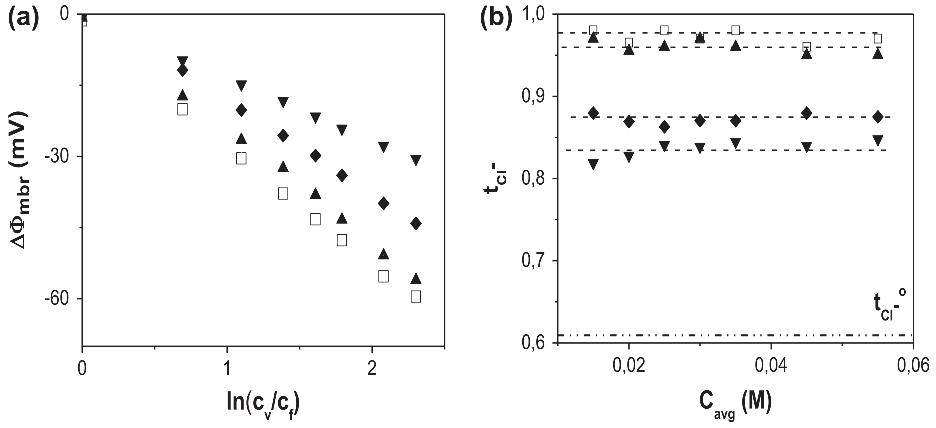

Fig. 1. (a) Membrane potential vs. NaCl concentration ratio at both membrane sides for the studied membranes; (b) variation of anion transport number in the membranes as a function of the average concentration $C_{\mathrm{avg}} = (C_f + C_v)/2$. (□) Ionics (+), (▲) Ionics(+)/HCl, (▼) Ionics(+)/NaOH, (♦) Ionics(+)/PP.

Table 1
Average anion transport number, $\langle t_{\mathrm{Cl}^-} \rangle$, anion permselectivity, $S(\mathrm{Cl}^-)$ and average contact angle, $\langle \varphi \rangle$, for the studied membranes

	$\langle t_{\mathrm{Cl}^-} \rangle$	$S(\mathrm{Cl}^-)$ (%)	$\langle \varphi \rangle$ (°)
Ionics(+)	0.975 ± 0.024	93.5 ± 2.3	57 ± 2
Ionics(+)/HCl	0.952 ± 0.031	87.5 ± 2.8	73 ± 3
Ionics(+)/NaOH	0.832 ± 0.058	56.4 ± 3.9	0
Ionics(+)/PP	0.867 ± 0.049	65.5 ± 3.7	100 ± 3

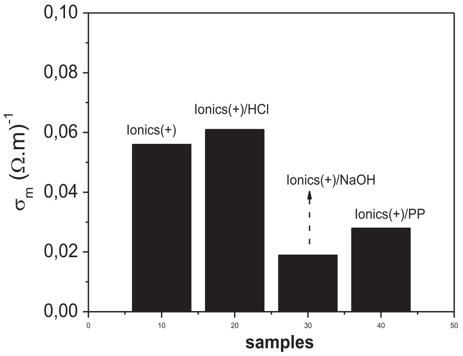

Fig. 2. Conductivity values for the studied samples determined from electrical resistance values by using Eq. (3).

permselectivity values for the studied membranes are indicated in Table 1, where the significant effect of 0.1 M NaOH solution to the barrier behaviour of the membrane to cation Na^+ can clearly be observed; in this case also the error interval corresponds to standard deviation.

Membrane conductivity (σ_m) can also give information on the effect of chemical treatments on the membrane performance. For that reason, the electrical resistance of the studied membranes (R_m) was measured and (σ_m) values were determined by the following expression:

$$\sigma_m = \Delta x_m / (S \cdot R_m) \tag{3}$$

where Δx_m and S represent the membrane thickness and cross section, respectively. Conductivity values obtained for the different membranes are indicated in Fig. 2. These results also show the slight effect of HCl treatment on conductivity values as well as the significant reduction due to both wastewater and 0.1 M NaOH solutions, in agreement with that already obtained from membrane potential results.

To establish possible membrane surface modification of the samples due to their contact with acid/basic solutions, contact angle measurements were performed. Average values of the initial contact angle, determined for the studied samples from six measurements performed on both surfaces of each membrane, are also indicated in Table 1, where differences among the studied samples can be observed. Fig. 3 shows a comparison of the water drop at $t = 0$ for the different samples. These results show that treatment with HCl and wastewater solutions seems to increase the hydrophobic character of the samples (although solid deposition could also be included in the case of Ionics(+)/PP), but the immersion of the Ionics(+) membrane during 1 month in a 0.1 M NaOH solution apparently destroys the surface of the fabric where the charged polymer is sandwiched [3]. In the case of the Ionics(+)/PP sample, the possible deposition on the membrane surface of solid particles from the working wastewaters might introduce other elements which could also contribute to membrane surface modification.

4. Conclusions

Changes in the electrical behaviour of a commercial anion-exchange membrane as a result of its contact during 1 month with 0.1 M acidic/basic solution (HCl and NaOH, respectively), as well as for a sample in contact with the wastewater from a working pilot plant, have been established by measuring membrane potential and electrical resistance with NaCl solutions. These results show a significant reduction of both Cl^- transport number and conductivity for the samples treated with the NaOH solution when compared with the untreated membrane, which is even higher than that obtained for the membrane treated with the electrodialysis plant working solution, while the contact

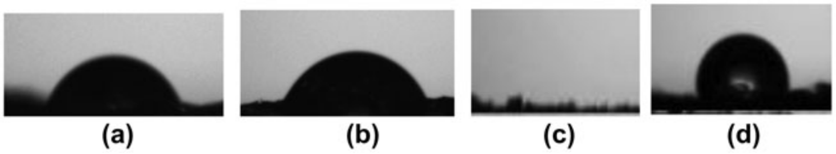

Fig. 3. Photographs of the water drop on the surface of membranes: (a) Ionics(+), (b) Ionics(+)/HCl, (c) Ionics(+)/NaOH, and (d) Ionics(+)/PP.

with the HCl solution does not seem to affect the membrane transport parameters. Moreover, changes in the membrane surface were also determined from contact angle measurements, and the results obtained with this "ex-situ" technique shows the effect of basic solution on the integrity of the membrane, which might partially cause the changes also found from the typical membrane electrochemical characterization measurements.

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