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L. Martinez[a]; A. Hernandez[a]; F. Tejerina[a]
[a] DEPARTMENTO DE FISICA APLICADA II FACULTAD DE CIENCIAS, UNIVERSIDAD DE VALLADOLID, VALLADOLID, SPAIN

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Concentration Dependence of Some Electrochemical Properties of Polycarbonate Microporous Membranes and Evaluation of Their Electrokinetic Charge

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L. MARTINEZ, A. HERNANDEZ, and F. TEJERINA

DEPARTMENTO DE FISICA APLICADA II
FACULTAD DE CIENCIAS
UNIVERSIDAD DE VALLADOLID
47071 VALLADOLID, SPAIN

Abstract

A space-charge model for electrolyte transport in charged capillary pores was employed in order to determine the pore wall charge from membrane potential measurements. These measurements have been performed at 20°C for two Nuclepore polycarbonate membranes of different pore size in LiCl and $MgCl_2$ solutions with concentrations ranging from 10^{-1} to 10^2 mol/m^3.

INTRODUCTION

Some authors (*1*, *2*) have shown that Nuclepore polycarbonate membranes possess a low fixed charge density. The aims of the present work are to obtain additional support for the existence of that fixed charge and to evaluate its effect on some electrochemical properties in two types of Nuclepore polycarbonate membranes of small pore size.

This paper is based on a membrane potential study which is one of various approaches to understanding the mechanism of membrane behavior. Various factors have been considered as governing membrane potential. Among these, the membrane fixed charge density, pore size and geometry, adsorption, ionic size, and ionic conductivity are of key importance (*3*).

In a previous paper (*4*) we showed that there are some effects of such parameters as solution concentration and temperature on the electrochemical properties of a Nuclepore membrane. Of these, the concentration of solutions bathing the membrane is the most important one if we are referring to membranes of small pore size (N01 and N003 membranes). Membranes of larger pore size show nearly the properties of a porous wall in the concentration range studied. In order to clear up the quantitative influence of concentration on the permselectivities of these two membranes, we planned new experiments for measuring membrane potentials. These measurements were performed with a constant ratio of the concentrations of the bulk solutions on both sides of the membrane ($c_1/c_2 = 2$). In this way we studied membrane potentials for two Nuclepore polycarbonate membranes of different pore size bounded by LiCl and $MgCl_2$ solutions with concentrations ranging between 10^{-1} and 10^2 mol/m^3. These results, when analyzed by a capillary model, permitted us to evaluate the adsorbed charge density on the pore walls.

TRANSPORT MODEL

This paper considers the transport properties of a membrane consisting of parallel right-circular cylindrical capillary tubes of equal radius separating ideal aqueous solutions of an electrolyte maintained at the same temperature but different solute concentrations. Ions and water molecules are allowed to pass the membrane only through the capillary portion; not the solid portion. A uniform distribution of fixed charges is assumed on the wall of each capillary as a result, for example, of ion adsorption, surface chemical reactions, or other reasons. The charge on the pore wall is assumed to be uniformly distributed, which eliminates the dependence of transport equations on angular direction inside the pore. Figure 1 illustrates the pore structure and ion distribution. The ionic flux is assumed to be one-dimensional along the pore axis, i.e., perpendicular to the plane of the membrane. An equilibrium electric double layer is assumed to be fully established inside the channel since the pore length, l (i.e., the membrane thickness), greatly exceeds the pore radius, $\bar{a}$. All this reduces the transport equations to a dependence on radial position, r, and axial position, x. Therefore, we adopted the cylindrical coordinate system (x, r) with x positive in the direction of flow and r the radial coordinate with its origin at the axis of symmetry.

The transport characteristics of the membrane are given by the behavior of a single pore which is, therefore, analyzed. We also admit that there is equilibrium between the bulk solution just outside the pore and the solution just inside the pore at the respective pore ends. If there are two diffusion layers adhering on both sides of the membrane, equilibrium exists between the pore contents just inside the pore at $x = 0$

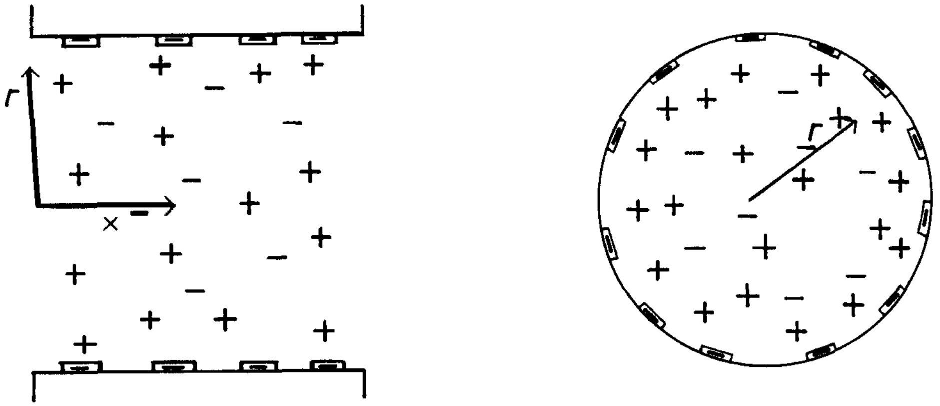

FIG. 1. End and side view of the model pore.

and $x = l$ and the solution at the membrane-diffusion layers interfaces. Henceforth, c_1 and c_2 will refer to the concentrations of the solutions separated by the membrane, and c_1' and c_2' to the concentrations in the membrane-diffusion layers interfaces.

The bulk solutions contain a single and completely dissociated electrolyte whose ions have charge numbers z_+ and z_-. Inside the pore, the activity coefficient of the electrolyte is assumed to be unity at all concentrations, and for a single ion diffusion coefficients D_i are assigned their free diffusion values, corresponding to the mean value of the concentration at the pore ends. Pore solution properties, such as the dielectric constant, ε, and the coefficient of viscosity, η, are assumed to equal the pure solvent values.

The basic equations of the model, due to Dresner (*5*) and Osterle and coworkers (*6–8*), are the Poisson and the Nernst-Planck equations:

$$\nabla^2\Phi(r,x) = -\frac{F}{\varepsilon}\sum_i z_i c_i(r,x), \qquad i = +,- \tag{1}$$

$$J_i(r,x) = -D_i\left[\nabla c_i(r,x) + \frac{z_i F}{RT} c_i(r,x)\nabla\Phi(r,x)\right], \qquad i = +,- \tag{2}$$

where c_i is the concentration, J_i is the flux of component i at some point (r,x) inside the pore, F is the Faraday constant, and R is the gas constant. The potential Φ includes the externally applied potential E_m and the dimensionless channel double-layer potential ψ:

$$\Phi(r,x) = \frac{RT}{F}\psi(r,x) + E_m(x) \tag{3}$$

The integration of the radial-flux Eq. (2) lead to the radial ion concentration distribution, which is of the Boltzmann type, as a function of the r-dependent part, ψ, of the potential:

$$c_i(r,x) = c_i^\circ(x) \exp(-z_i F\psi(r,x)/RT) \tag{4}$$

When $\psi = 0$, then $\Phi = E_m$ and $c_i = c_i^\circ = \nu_i\bar{c}$, which defines $\bar{c}$, ν_i being the stoichiometric coefficient. This occurs in the phases at either end of the tubes and, if the tubes are sufficiently large, also along their center lines.

Substituting Eqs. (3) and (4) into Eq. (1), we obtain the Poisson-Boltzman equation, which can be written if the length of the tube is much greater than the radius:

$$\frac{1}{\xi}\frac{\partial}{\partial\xi}\left(\xi\frac{\partial\psi}{\partial\xi}\right) = \left(\frac{\bar{a}}{\lambda}\right)^2 \frac{1}{z_+ - z_-}\left[e^{-z_- \psi} - e^{-z_+\psi}\right] \tag{5}$$

with λ the Debye length:

$$\lambda^2(x) = \frac{\varepsilon RT}{F^2 \sum_i z_i^2 c_i^\circ(x)} \tag{6}$$

and where $\bar{a}$ is the pore radius and ξ the normalized radial distance:

$$\xi = r/\bar{a} \tag{7}$$

At the pore wall the surface charge density σ is equal to the radial potential gradient at the wall by Gauss's law:

$$\frac{\partial\psi}{\partial\xi} = \frac{F}{\varepsilon RT}\bar{a}\sigma \tag{8}$$

At the pore center, the potential gradient is zero due to symmetry,

$$\frac{\partial\psi}{\partial\xi} = 0, \qquad \xi = 0 \tag{9}$$

The dimensionless electrostatic potential ψ depends explicitly on ξ with

$\bar{a}/\lambda$ and σ as parameters, and derives its dependence on x from the fact that λ is a function of $\bar{c}(x)$. Given these parameters, Eq. (5) has been solved numerically for ψ versus ξ using a mathematical algorithm, which will be the object of a future publication.

On the other hand, the average flux in the pore, $\langle J_{ix} \rangle$, is found by integrating the local ionic flux in the pore axial direction, J_{ix}, over the pore cross section; i.e., for example:

$$\langle J_{ix} \rangle = \frac{2}{\bar{a}^2} \int_0^{\bar{a}} J_{ix}(r,x)rdr \tag{10}$$

where J_{ix} is given by Eq. (2). The current density I, of interest here, is defined as

$$I = \frac{2F}{\bar{a}^2} \int_0^{\bar{a}} (z_+J_{+x}(r,x) + z_-J_{-x}(r,x))rdr \tag{11}$$

can be expressed, taking into account the former relations as

$$I = L_{11}\left[- \frac{dE_m}{dx} \right] + L_{12}RT\left[- \frac{d}{dx} \ln \bar{c} \right] \tag{12}$$

where

$$L_{11} = \frac{2F^2}{RT}\bar{c} \int_0^1 (D_+z_+^2\nu_+e^{-z+\psi} + D_-z_-^2\nu_-e^{z-\psi})\xi d\xi \tag{13}$$

$$L_{12} = \frac{2F}{RT} \bar{c}\int_0^1 (D_+z_+\nu_+e^{-z+\psi} + D_-z_-\nu_-e^{-z-\psi})\xi d\xi \tag{14}$$

where we see that L_{11} and L_{12} are functions of definite integrals involving $\psi(\xi;\ \bar{a}/\lambda,\sigma)$; since λ is a function of $\bar{c}(x)$, these coefficients are implicit functions of x, which causes some computational problems when different electrolyte concentrations c_1' and c_2' exist in the solution on either side of the pore. In this case, Eq. (5) must be solved, given the electrolyte and the surface charge density in the pore for the range of $\bar{a}/\lambda$ from the high concentration side of the pore to the low concentration side. If this is done, the cation transport number inside the membrane, $\bar{t}_+$, which is directly related with the membrane potential, E_m, by

$$\bar{t}_+ \equiv \frac{\nu_+\nu_-}{(\nu_+ + \nu_-)}\left(1 - \frac{F}{RT}\,\frac{E_m}{\ln c_1'/c_2'}\right) \tag{15}$$

where the different symbols have their usual meanings, can be evaluated by numerical integration. In fact, when the steady state is reached (the assumption of steady state inside the pore is valid provided that the time constant of the membrane is much smaller than the time scale characterizing changes in the bulk solutions (9)), it will be

$$I = 0 \tag{16}$$

and placing Eq. (16) into Eq. (12), we get

$$\frac{E_m}{(RT/F)\Delta \ln \bar{c}} = \frac{F}{\Delta \ln \bar{c}} \int_1^2 \frac{L_{21}}{L_{22}}\, d \ln \bar{c} \tag{17}$$

where 1 and 2 refer to the pore limits and $\Delta \ln \bar{c} = \ln c_2' - \ln c_1'$.

From the experimental values of the membrane potential and given c_1' and c_2', the value of $E_m/(RT/F)\ \Delta \ln \bar{c}$ has been calculated. Otherwise, using Eqs. (14) and (15), we can evaluate $\int_1^2 (L_{21}/L_{22})\, d \ln \bar{c}$, if σ is taken as a parameter. The value of σ which fits Eq. (17) will be accepted as the electrokinetic mean charge on the pore surfaces.

EXPERIMENTAL

We have performed potential and salt flux measurements through Nuclepore polycarbonate membranes separating two solutions of the same electrolyte (LiCl or $MgCl_2$) but at different concentrations c_1 and c_2. We used the same experimental device described in a previous paper (*10*).

The membranes utilized are track-etched polycarbonate membranes characterized by their exceptionally well-defined pore structure. They consist of a sheet of polycarbonate perforated by an array of discrete and nearly parallel cylindrical pores (*11*). Filters of pore diameters 10^{-7} and 3×10^{-8} m were used. They will be identified from now on as N01 and N003, respectively.

The concentrations c_1 and c_2 range from 10^{-1} to 10^2 mol/m^3. In the potential measures the concentration ratio c_1/c_2 was kept at about 2 by means of a renovation flow, nearly 16×10^{-7} m/s, of the solutions. When the cell potential E_c was constant, this value was taken as the cell potential at that concentration ratio.

In parallel experiments we measured the salt flux J_s through the membrane when it separated two solutions of concentrations c_1 and c_2. This allowed us (*4*) to calculate the permeability of the membrane system (membrane plus the two adjacent diffusion layers), the diffusion layer thickness, and the concentrations c_1' and c_2' in the membrane–diffusion layers interfaces.

In all the experiments the stirring speed of the solutions was 200 rpm and the temperature was 293 K.

These results allow the determination of E_m from E_c. In Tables 1 and 2 the E_m results are shown. The cation transport number through the membrane, $\bar{t}_+$, is determined from E_m as

$$E_m = -\frac{RT}{F}\left(1 - \frac{\nu_+ + \nu_-}{\nu_+\nu_-}\,\bar{t}_+^{\mathrm{app}}\right)\ln\frac{a_1'}{a_2'} \qquad (18)$$

where a_1' and a_2' are the mean ionic activities for the concentrations c_1' and c_2', respectively. The assumption of $a_1'/a_2' = c_1'/c_2'$ introduces a small error (*12*) because $c_1' < 10^2$ mol/m^3 and in all experiments $c_1'/c_2' < 2$. In addition, $\bar{t}_+^{\mathrm{app}} = \bar{t}_+$ also introduces only a small error (*13*) because we deal with very dilute solutions.

TABLE 1
Data and Results on N01 and N003 Membranes in LiCl Solutions
(P_{sm} = membrane system permeability)

Membrane	c_1 (mol/m^3)	c_2 (mol/m^3)	$P_{sm} \times 10^6$ (m/s)	c_1' (mol/m^3)	c_2' (mol/m^3)	E_m (mV)	$-\sigma$ (C/m^2)
N01	1.00	0.505	4.4	0.85	0.655	+2.19	0.0031
	2.01	1.00	4.3	1.70	1.31	+0.34	0.0033
	4.01	2.02	4.3	3.40	2.63	−0.52	0.0044
	8.02	4.00	4.3	6.77	5.24	−1.36	0.0046
	16.0	8.06	4.2	13.5	10.5	−1.66	0.0061
	31.9	16.0	4.0	26.9	21.0	−1.95	0.0065
	63.5	32.0	3.9	54.3	41.3	−2.32	0.0085
N003	1.01	0.500	2.1	0.932	0.575	+10.46	0.0027
	2.01	1.01	2.3	1.84	1.18	+6.96	0.0029
	3.98	2.00	2.5	3.64	2.34	+3.78	0.0034
	6.87	3.38	2.7	6.29	3.96	+1.41	0.0038
	13.7	6.83	2.6	12.4	8.12	−0.39	0.0051
	27.2	13.7	2.5	24.6	16.2	−1.86	0.0060
	57.2	28.9	2.5	51.8	34.3	−2.69	0.0075

TABLE 2
Data and Results on N01 and N003 Membranes in $MgCl_2$ Solutions
(P_{sm} = membrane system permeability)

Membrane	c_1 (mol/m^3)	c_2 (mol/m^3)	$P_{sm} \times 10^6$ (m/s)	c_1' (mol/m^3)	c_2' (mol/m^3)	E_m (mV)	$-\sigma$ (C/m^2)
N01	0.535	0.266	4.4	0.454	0.346	+0.23	0.0032
	1.08	5.40	4.4	0.92	0.70	−0.79	0.0038
	2.15	1.08	4.3	1.82	1.41	−1.24	0.0052
	4.31	2.15	4.2	3.62	2.83	−1.53	0.0080
	8.70	4.30	4.1	7.40	5.56	−2.02	0.0140
	17.3	8.60	4.0	14.6	11.2	−2.11	0.023
	34.2	17.3	3.8	28.9	22.4	−2.16	0.044
	69.0	34.2	3.7	58.0	44.9	−2.50	0.064
N003	0.540	0.267	1.8	0.51	0.298	+4.38	0.0026
	1.09	0.540	1.8	1.03	0.60	+1.36	0.0023
	2.20	1.09	1.7	2.07	1.21	−0.78	0.0027
	4.46	2.20	1.7	4.18	2.46	−2.38	0.0034
	9.0	4.45	1.6	8.4	4.99	−3.22	0.0052
	17.9	9.0	1.6	16.8	10.1	−3.77	0.0082
	35.1	17.7	1.5	32.8	19.9	−4.22	0.0013
	67.0	34.1	1.5	63.0	38.2	−4.69	0.021

The membrane permselectivity $\bar{P}_s$, a measure (better than $\bar{t}_+$) of the membrane selectivity for counterions over the coions, is then calculated from the relation

$$\bar{P}_s = \frac{\bar{t}_+ - t_+}{1 - t_+} \tag{19}$$

given by Winger et al. (*14*), where t_+ is considered the cation transport number in a free solution of an average concentration $(c_1' + c_2')/2$.

The $\bar{t}_+$ and $\bar{P}_s$ results for the two membranes at different concentrations and for the two solutes are given in Figs. 2 and 3. From these results it is concluded that the selectivity of the membrane for cations increases as the pore radius and solutions concentrations decrease.

RESULTS ON CHARGE DENSITY AND DISCUSSION

In order to justify the results on $\bar{t}_+$ and $\bar{P}_s$, a transport model has to be postulated. Concretely, they have to be explained by the adsorption of chloride ions on the pore walls, given the non-ionogenic character of our polymeric membranes. Thus, following the assumed model, a diffuse

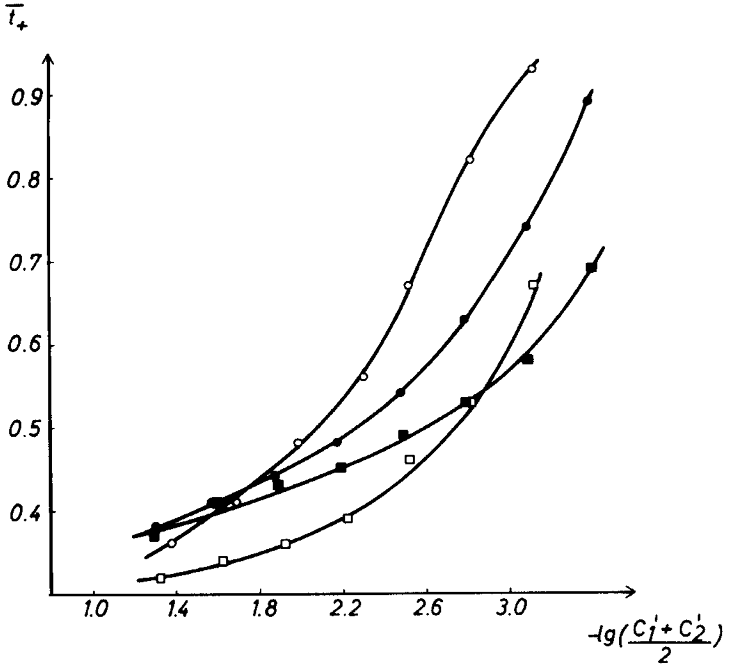

FIG. 2. $\bar{t}_+$ versus log $[(c_1' + c_2')/2]$ for the two membranes in solutions of the two electrolytes. (□) N01 in LiCl; (○) N003 in LiCl; (■) N01 in MgCl$_2$; (●) N003 in MgCl$_2$.

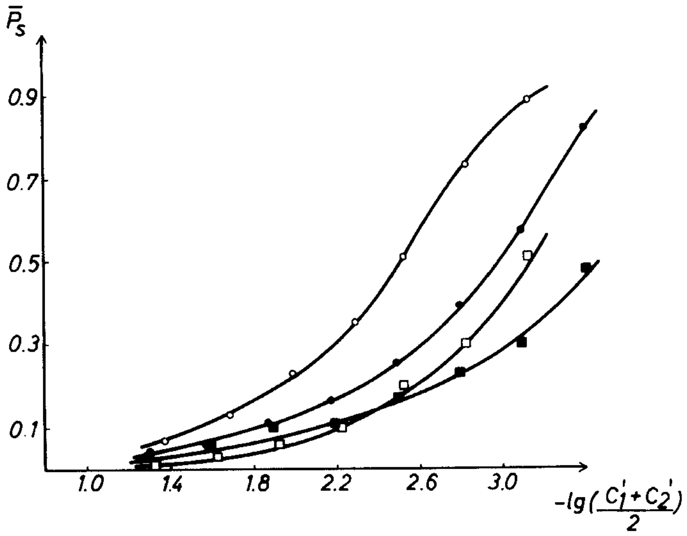

FIG. 3. $\bar{P}_s$ versus log $[(c_1' + c_2')/2]$ for the two membranes in solutions of the two electrolytes. (□) N01 in LiCl; (○) N003 in LiCl; (■) N01 in MgCl$_2$; (●) N003 in MgCl$_2$.

electrical double layer *(15, 16)* is formed, see Fig. 1, where the anions are excluded. As great as is the importance of this layer inside the pore volume, greater is the density of the adsorbed charge, and even greater is $\bar{P}_s$. Figure 4 shows the dependence of $\bar{P}_s$ on the parameter $\bar{a}/\lambda$ (a measure of the relevance of the double layer as related to the pore volume) for each membrane and solute; here λ is the Debye length for the mean concentration $(c_1' + c_2')/2$.

The results agree qualitatively with the model predictions: there is a decrease of $\bar{P}_s$ when the concentration increases. Small differences between the two solutes imply that some difference in the density of adsorbed charge exists, i.e., the charge density is a function of the solute and membrane. We obtained this charge density on the pore wall by fitting the experimental data to the model predictions as given in Eq. (15). The results so obtained are shown in Tables 1 and 2.

The results on the charge density indicate that (1) the wall charge is not constant for each membrane and electrolyte, but depends on the electrolyte concentration. This seems to confirm that the charge comes from cation adsorption from the solution. (2) Differences in the charge density for the different membranes and solutes are like those obtained by other authors (*1*) with other Nuclepore polycarbonate membranes and solutes, and from other types of experiments.

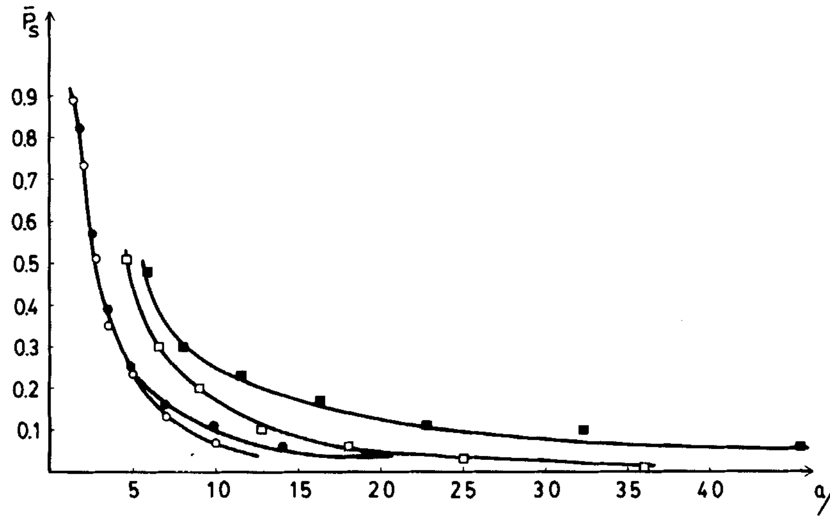

FIG. 4. $\bar{P}_s$ versus $\bar{a}/\lambda$ for the two membranes in solutions of the two electrolytes. (□) N01 in LiCl; (○) N003 in LiCl; (■) N01 in MgCl$_2$; (●) N003 in MgCl$_2$.

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