Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Study of Electrolyte Conductivity in Charged Microcapillary Porous Membranes

L. Martinez[a]; A. Hernandez[a]; J. A. Ibáñez[b]; F. Tejerina[c]
[a] DEPARTAMENTO DE FISICA APLICADA II FACULTAD DE CIENCIAS, UNTVERSIDAD DE VALLADOLID, VALLADOLID, SPAIN [b] DEPARTAMENTO DE FISICA FACULTAD DE CIENCIAS, UNIVERSIDAD DE MURCIA, MURCIA, SPAIN [c] DEPARTAMENTO DE FISICA APLICADA II FACULTAD DE CIENCIAS, UNTVERSIDID DE VALLADOLID, VALLADOLID, SPAIN

To cite this Article Martinez, L. , Hernandez, A. , Ibáñez, J. A. and Tejerina, F.(1989) 'Study of Electrolyte Conductivity in Charged Microcapillary Porous Membranes', Separation Science and Technology, 24: 1, 41 — 49
To link to this Article: DOI: 10.1080/01496398908049750
URL: http://dx.doi.org/10.1080/01496398908049750

SEPARATION SCIENCE AND TECHNOLOGY, 24(1&2), pp. 41-49, 1989

Study of Electrolyte Conductivity in Charged Microcapillary Porous Membranes

L. MARTINEZ and A. HERNÁNDEZ

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

J. A. IBÁÑEZ

DEPARTAMENTO DE FISICA
FACULTAD DE CIENCIAS
UNIVERSIDAD DE MURCIA
30001 MURCIA, SPAIN

F. TEJERINA

DEPARTAMENTO DE FISICA APLICADA II
FACULTAD DE CIENCIAS
UNIVERSIDID DE VALLADOLID
47071 VALLADOLID, SPAIN

Abstract

The electrolyte conductivities of several microporous membranes, when bathed by an electrolyte solution, have been measured by the dc method. With membranes of the polycarbonate track-etched thin film type (Nuclepore), the mean pore diameter ranged from 0.015 to 0.100 μm. Concentrations of the studied electrolyte (LiCl, NaCl, and $MgCl_2$) range from 5×10^{-4} to 2×10^{-2} mol/L. The results obtained have been compared to those deduced from a space-charge model for the electrolyte transport in charged capillary pores. This allows an estimate of the charge density on the pore walls which agrees with those obtained earlier for these types of membranes and solutes from a study of other electrokinetic phenomena.

INTRODUCTION

Several ac and dc methods can be used to measure the specific conductance (or conductivity) of a membrane bathed by an electrolytic solution. Many of these standard procedures have been reviewed by Tiravanti et al. (*1*). The dc simplest one is used here (*2*). In this method the membrane is clamped between two electrolytic solutions of the same composition. One working and one probe electrode are placed at both sides of the membrane. A constant electric current is transmitted through the whole system by means of the working pair of electrodes, and the electrical potential drop between the probe electrodes is measured.

The measured potential difference is

$$\Delta V_c = R_c I_c \tag{1}$$

where I_c is the constant current and R_c is the total electrical resistance of the ensemble of the membrane and the electrolyte solutions between the probe electrodes. Therefore, the R_c resistance is the sum of the membrane resistance, R_m, and the solution resistance, R_0, which has to be determined by a black measurement without a membrane. In order to avoid any error in calculating this membrane resistance, $R_m = R_c - R_0$, the reproducibility of the cell geometry must be very good. The contributions of surface-contact resistances are the same in R_c and R_0, and therefore they cancel out. In any event, each resistance is obtained by reversing the polarity and averaging the measured pair of values.

On the other hand, the pore conductivity for a microporous membrane of porosity Π is

$$\kappa = \frac{l}{\Pi A}(R_c - R_0)^{-1} \tag{2}$$

where l is the membrane thickness and A is the membrane exposed area.

The accuracy of the method hinges, however, on the exact determination of the difference between the resistances R_c and R_0. Therefore, among the possible Nuclepore membranes, these of smallest porosities (less than 1%) are used. They are studied while being bathed by several electrolyte solutions (LiCl, NaCl, and $MgCl_2$) whose concentrations go from 5×10^{-4} to 2×10^{-2} mol/L.

The Nuclepore filters have well-defined cylindrical pores (*3–6*). Here, filters of diameters 0.015, 0.050, and 0.100 μm have been studied. Then the conductivity results were compared with those predicted by a space-charge model for transport through charged capillary pores in order to estimate the charge density on the pore wall.

ANALYSIS OF THE PORE TRANSPORT

Our microporous membranes are considered to consist of an array of identical circular cylindrical capillaries whose length, l (equal to the membrane thickness), is much greater than its radius, $\bar{a}$, and with a charge density of σ assumed as uniform on the pore wall. The "classical theory" for the effects of double layers on the transport of ions is due to Dresner and Osterle (*7*, *8*). Its basic equations are those of Poisson-Boltzmann and Nernst-Planck.

The total electrical potential, $\phi(r,x)$, can be written as

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

where $\psi(r,x)$ is the electrostatic potential arising from the double layer, and $E_m(x)$ is the potential which gives a nonzero electrical potential drop between the pore ends. By taking it into account, the Poisson-Boltzmann and Nernst-Planck equations are

$$\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial}{\partial \xi}\right) = \left(\frac{\bar{a}}{\lambda}\right)^2 \frac{z_+}{z_+ - z_-}\left(e^{-z_-\psi/z_+} - e^{-\psi}\right) \tag{4}$$

$$J_i(r,x) = D_i\left(\frac{\partial c_i(r,x)}{\partial x} + \frac{z_iF}{RT}c_i(r,x)\frac{\partial \phi(r,x)}{\partial x}\right), \qquad i = +, - \tag{5}$$

where r and x are the radial and axial coordinates, $J_i(r,x)$ is the flux of the i-ion, $c_i(r,x)$ is its concentration, D_i is its diffusion coefficient, ξ is the dimensionless radial coordinate ($\xi = r/\bar{a}$), λ is the Debye length, and the other symbols have their usual meanings.

The pore electrical current density

$$I = \frac{2F}{\bar{a}^2}\int_0^{\bar{a}} (z_+J_+(r,x) + z_-J_-(r,x))rdr \tag{6}$$

can be written, if Eqs. (4) and (5) are used, as

$$I = L_{11}\left(-\frac{dE_m}{dx}\right) + L_{12}\frac{RT}{F}\left(-\frac{d\ln\bar{c}}{dx}\right) \tag{7}$$

where $\bar{c}(x)$ is the equivalent bulk concentration that would be in equilibrium with the solution in the pore cross section at x, giving

$$\lambda^2(x) = \frac{\varepsilon RT}{F^2\sum_i z_i^2 \upsilon_i \bar{c}} \tag{8}$$

where ε is the dielectric constant, and L_{11}, which is the pore conductivity κ, is

$$\kappa \equiv L_{11} = \frac{2F^2}{RT}\int_0^1 \bar{c}(z_+^2\nu_+D_+e^{-\psi} + z_-^2\nu_-D_-e^{-z_-\psi/z_+})\xi d\xi \tag{9}$$

If we try to calculate κ by means of Eq. (9), the ψ potential has to be known. For that purpose, the Poisson-Boltzmann equation (Eq. 3) has been numerically solved (*9*) in terms of ξ and by taking σ and $\bar{a}/\lambda$ as given parameters.

EXPERIMENTAL

Several microporous membranes made from thin (~6 μm) sheets of polycarbonate, whose porous structure was obtained by exposure to nuclear radiation and subsequent chemical track-etching, have been studied. These membranes can be assumed to consist of cylindrical pores of equal size. Three of them, whose pore diameters are 0.1, 0.05, and 0.015 μm, were chosen and identified as the N01, N005, and N0015 membranes.

The salt solutions were made from sterile and degased low-conductivity water furnished by a Milli-Q system (Millipore Co., Bedford, Massachusetts) and reagent grade products (NaCl, LiCl, and $MgCl_2$). The salt concentrations went from 5×10^{-4} to 2×10^{-2} mol/L; for lower concentrations the results were not reproducible, while for higher ones the resistances were of the order of the experimental errors.

The measuring cell is schematically shown in Fig. 1. It consists of two methacrylate half-cells whose volumes are about 125 mL. Each one has several ports in order to insert a conductivity cell (for measuring the solution concentration) and a thermometer, and also for filling and emptying the cell. There are two magnetically driven paddles (500 rpm) which assure a turbulent flow inside both the half-cells in order to

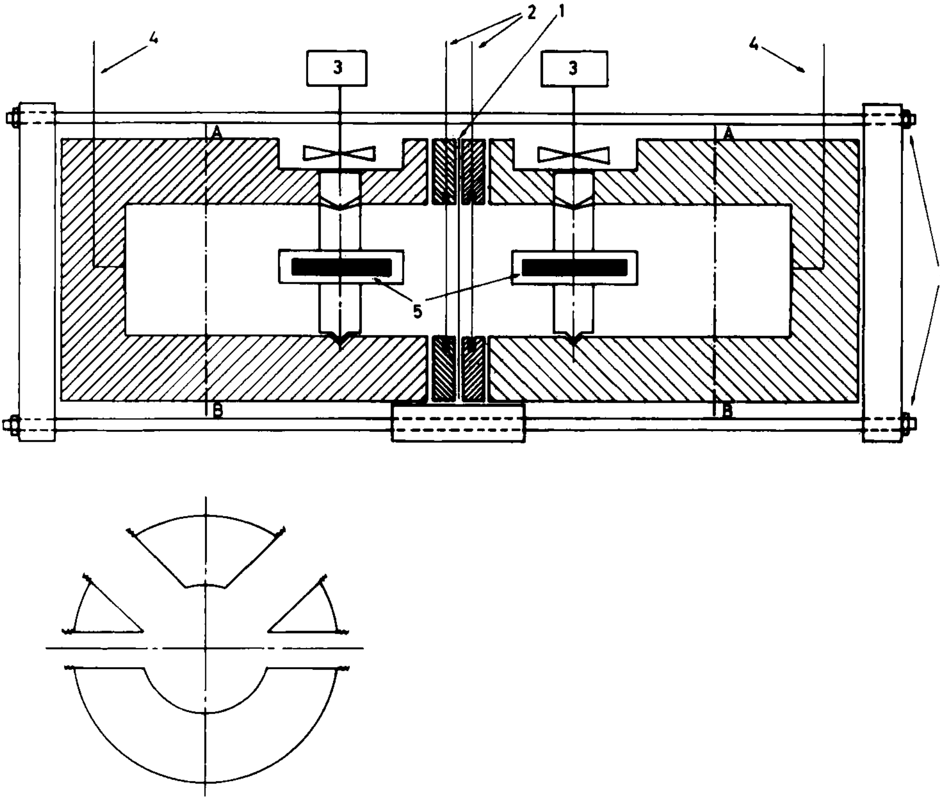

FIG. 1. Membrane cell and cross section at AB: 1) Membrane, 2) probe electrodes, 3) external stirrer motors, 4) working electrodes, 5) magnet stirrer, and 6) press closing system.

homogenize the solution. The working electrodes are a pair of Pt-plates fixed at the ends of the cell. Each probe electrode is of the Ag/AgCl type, and consists in an Ag network disk (100 cell/cm^2) prepared by Brown's method (*10*) and mounted in a methacrylate piece. These two electrode frames contain the membrane between them, and therefore form the membrane holder which is placed between the half-cells. The resulting free area of the membrane is 7.07 cm^2. The cell is closed by a press system which gives a well-reproducible geometry to the whole measuring cell.

Once the membrane and electrolyte solution to be studied were in the cell, it was dipped into a water thermostat (23.0 ± 0.1°C). We waited for about 12 h for it to reach equilibrium.

The resistances were measured with and without the membrane by means of an electronic voltmeter (HP 3456 A) with a 4-wire configuration. A constant dc current furnished by an internal source (50 μA in all experiments) was transmitted through the Pt electrodes, and the electrical potential difference between the Ag/AgCl electrodes was measured, the resistence being directly displayed by the voltmeter.

The asymmetrical potential of the Ag/AgCl electrodes and other possible contributions coming from unavoided concentration gradients were corrected by the above-mentioned reverse-polarity method. The stirring was expected to be vigorous enough to prevent any charge polarization phenomena at the membrane–solution interfaces (*11*, *12*). Actually, these polarization effects turned out to be negligible. In fact, a parallel time evolution was observed for the resistances with and without a membrane once the current step was switched on. Following the model of Tiravanti (*13*), this implies that the polarization effects are not relevant and the transitories obtained came from the nonzero response times of the measuring devices.

RESULTS AND DISCUSSION

The pore conductivities of each membrane in equilibrium with an electrolyte solution can be obtained from Eq. (2) if R_m, R_c, and $l/\Pi A$ are known. The resistances R_m and R_0 were measured by following the outlined method. The thicknesses of the membranes were measured by a interferometric method, as described early (*14*). Finally, Π was evaluated by taking into account that for high concentrations,

$$R_m\kappa_b = R'_m\kappa'_b \tag{10}$$

where R_m and R'_m are two membrane resistances corresponding to two concentrated solutions whose bulk conductivities are κ_b and κ'_b. Equation (10) was experimentally tested for all our membranes when the electrolyte concentrations exceeded 10^{-2} mol/L. For these concentrations the enhancement of the pore conductivity is negligible, probably because the charge density on the pore wall is very low (*15*). Then, from Eqs. (2) and (10),

$$\frac{l}{\Pi A} = R_m\kappa_b \tag{11}$$

where κ_b is given by

$$\kappa_b = \frac{F^2\bar{c}}{RT}(z_+^2\nu_+D_+ + z_-^2\nu_-D_-) \tag{12}$$

which is the limit of Eq. (9) when ψ goes to zero.

In Fig. 2 the experimental pore conductivities are plotted versus $\bar{a}/\lambda$ for the membranes and electrolytes studied. In this figure, each solid line has been calculated by means of the outlined "classical theory" for the transport through capillary pores with a constant charge density, σ, on its wall; the dashed lines refer to the bulk conductivity. Note that for a given σ, the theoretical curves approach a constant value for κ as $\bar{a}/\lambda$ goes to zero. This is so because, when the electrolyte concentration is low ($\bar{a}/\lambda \rightarrow 0$), the overall pore electroneutrality implies a balance between the counterions and the pore wall charge. This is better observed for the N0015 membrane (membrane with the smallest pore size) and high charge densities. On the other hand, for a given σ, the corresponding enhancement of the pore conductivity decreases, as expected, when the electrolyte concentration (i.e., $\bar{a}/\lambda$) increases.

From these experimental results on pore conductivities, it can be concluded that:

(1) The magnitude of the pore conductivity when the membrane was bathed in different chloride solutions follows the order $Mg^{2+} > Na^+ > Li^+$, which is the reverse order of the hydrated sizes of these ions.

(2) From a qualitative point of view, any of our membranes behaves in a similar way, whichever of the three studied electrolyte solutions bathes them. The charge on the pore wall is always very small, and decreases when the solution concentration decreases.

(3) It is known from earlier work on membrane potentials and saline fluxes (*9*) that the space-charge model of electrolyte transport through capillary pores fits well with the characteristics of the Nucelpore membranes. This now confirmed by the pore conductivity results. In fact, if we fit the experimental conductivities with those theoretically predicted, we obtain surface charge densities σ which agree with those calculated by us from the membrane potentials and saline fluxes as well as with the values given by other methods and authors (*5*).

(4) Enhancement of the pore conductivity, i.e., the pore wall charge effect, is relevant only for small $\bar{a}/\lambda$ (always less than 4). Therefore, given that the concentration range studied is the same for all

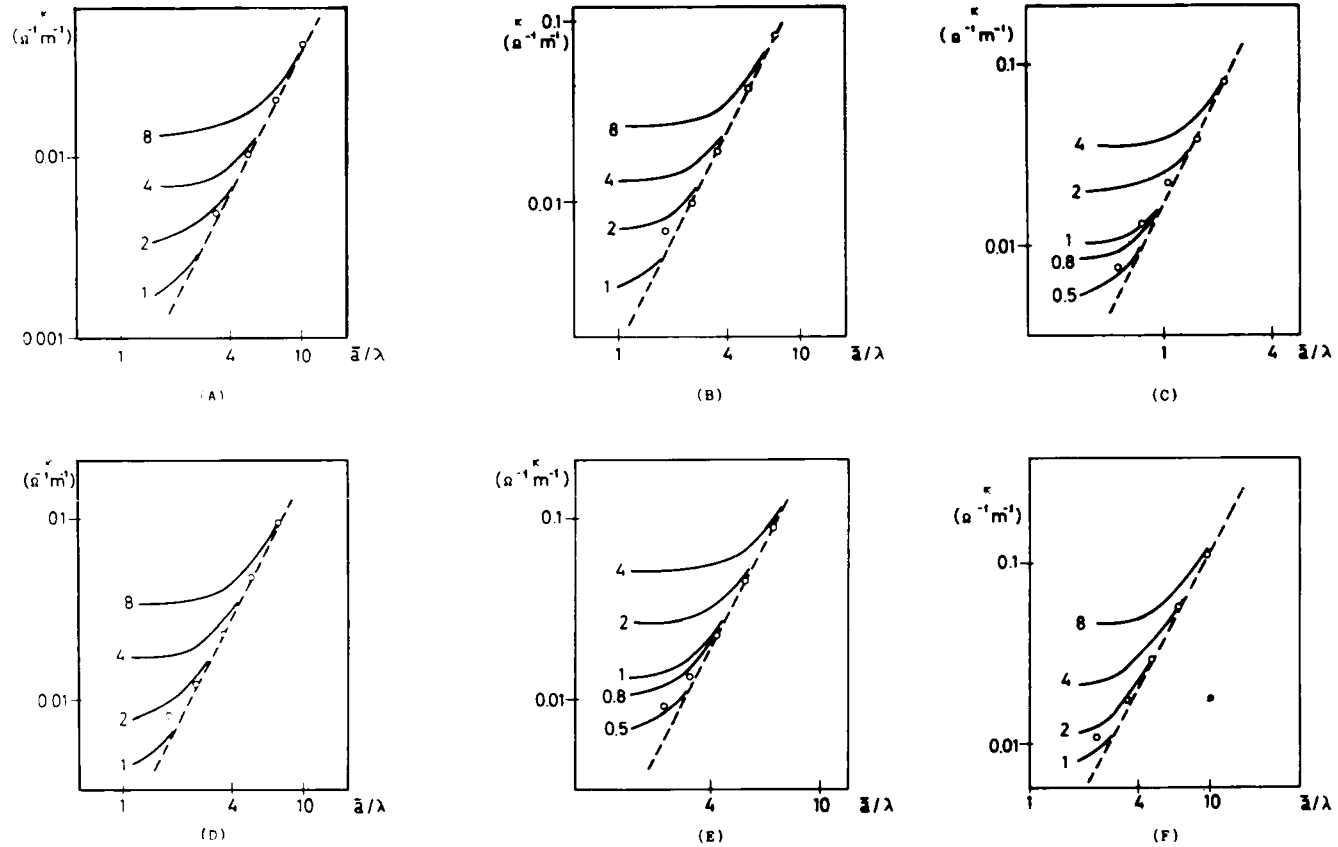

FIG. 2. Pore conductivities for several membranes and aqueous electrolyte solutions versus $\bar{a}/\lambda$: (A) N01 and LiCl, (B) N005 and LiCl, (C) N0015 and LiCl, (D) N005 and NaCl, (E) N0015 and NaCl, and (F) N005 and $MgCl_2$. Solid curves are theoretical predictions for various values (shown besides the corresponding curves) multiplied by $\sigma \times 10^3$ (C/m^2). Dashed lines are the bulk conductivities.

membranes, this effect is more relevant for membrane having the smallest pore size (N0015).

(5) Other electrokinetic parameters, such as the membrane potential (*9*), depend more strongly than the pore conductivity on the concentration. This make them better for the estimation of σ, especially when $\bar{a}/\lambda > 4$.

REFERENCES

1. G. Tiravanti and R. Passino, "A New Direct Current Method for Resistance Measurements of Ionic Membranes and Its Application to Composite Membranes," *J. Membr. Sci., 13,* 349 (1983).

2. F. Helfferich, *Ion Exchange,* McGraw-Hill, New York, 1962.

3. F. Martínez-Villa, J. I. Arribas, and F. Tejerina, "Quantitative Microscopical Study of Surface Characteristic Parameters in Track-Etched Membranes," *J. Membr. Sci., 36,* 19 (1988).

4. W. M. Deen, M. P. Bohrer, and N. B. Epstein, "Effects of Molecular Size and Configuration on Diffusion in Microporous Membranes," *AIChE J., 27,* 952 (1981).

5. P. Meares and K. R. Page, "Rapid Force-Flux Transitions in Highly Porous Membranes," *Philos. Trans. R. Soc., 272,* 1 (1972).

6. W. John, S. Hering, and G. Sasaki, "Characteristics of Nuclepore Filters with Large Pore Size. I. Physical Properties," *Atmos. Environ., 17,* 115 (1983).

7. L. Dresner, "Electrokinetic Phenomena in Charged Microcapillaries," *J. Phys. Chem., 67,* 1635 (1963).

8. R. J. Gross and J. F. Osterle, "Membrane Transport Characteristics of Ultrafine Capillaries," *J. Chem. Phys., 49,* 228 (1968).

9. L. Martínez, A. Hernández, and F. Tejerina, "Diffusive Salt Permeation Properties of Charged Membranes at Low Charge Densities. Experimental Verification of a Space Charge Model," *Sep. Sci. Technol., 23,* 243 (1988).

10. A. S. Brown, "A Type of Silver Chloride Electrode Suitable for Use in Dilute Solutions," *J. Am. Chem. Soc., 56,* 646 (1934).

11. W. H. Koh and J. L. Anderson, "Electroosmosis and Electrolyte Conductance in Charged Microcapillaries," *AIChE J., 21,* 1176 (1975).

12. H. Strathmann, "Membrane Separation Processes," *J. Membr. Sci., 9,* 121 (1981).

13. G. Tiravanti, "The Direct Current Method for Measuring Charged Membrane Conductance," *Ibid., 9,* 229 (1981).

14. L. Martínez, A. Hernández, and A. F. Tejerina, "Diffusion Coefficients across Polycarbonate Microporous Membranes," *Nuovo Cimento, 9,* 174 (1987).

15. G. B. Westerman-Clark and J. L. Anderson, "Experimental Verification of the Space-Charge Model for Electrokinetics in Charged Microporous Membranes," *J. Electrochem. Soc., 130,* 839 (1983).

Received by editor January 13, 1988