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True and Adsorbed Charges in Passive Membranes. Surface Charge Density and Ionic Selectivity of Several Microporous Membranes

A. Hernández[a]; J. A. Ibáñez[b]; A. F. Tejerina[c]
[a] DEPARTMENT OF THERMAL SCIENCES FACULTY OF SCIENCES, UNIVERSITY OF VALLODOLID, VALLODOLID, SPAIN [b] DEPARTMENT OF PHYSICS FACULTY OF SCIENCES, UNIVERSITY OF MURCIA, MURCIA, SPAIN [c] DEPARTMENT OF THERMAL SCIENCES FACULTY OF SCIENCES, UNIVERSITY OF VALLADOLID, VALLADOLID, SPAIN

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True and Adsorbed Charges in Passive Membranes. Surface Charge Density and Ionic Selectivity of Several Microporous Membranes

A. HERNÁNDEZ

DEPARTMENT OF THERMAL SCIENCES
FACULTY OF SCIENCES
UNIVERSITY OF VALLODOLID
47011 VALLODOLID, SPAIN

J. A. IBÁÑEZ

DEPARTMENT OF PHYSICS
FACULTY OF SCIENCES
UNIVERSITY OF MURCIA
30001 MURCIA, SPAIN

A. F. TEJERINA

DEPARTMENT OF THERMAL SCIENCES
FACULTY OF SCIENCES
UNIVERSITY OF VALLADOLID
47011 VALLADOLID, SPAIN

Abstract

In this paper we study ionic selectivity and surface charge density of several microporous membranes which are Nuclepore filters separating two NaCl solutions whose concentrations are c_1 and $c_2 > c_1$. We distinguish between adsorbed charges and those belonging to the membrane surface (true charges of the membrane). We find that ionic selectivity increases linearly with the surface density of charges due to the membrane. These surface charge densities agree with those determined by Meares et al. from electroosmotic measurements.

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INTRODUCTION

Membranes can be divided into two classes: biological membranes, including artificial model membranes, and membranes used for industrial (e.g., desalting processes) or laboratory (e.g., purification of colloidal solutions) purposes, that is to say, used in separation processes. Interest in membranes mainly derives from their different permeabilities for different species, i.e., permeselectivity or ion selectivity.

A membrane is called passive if its porous structure and charges on its surfaces are the only factors which restrict diffusion across the membrane. Microporous membranes are used in separation processes, essentially because they are impermeable to colloidal particles and big molecules while they are permeable to water and small ions. The surface charge density in biological membranes as well as in artificial ones is a factor of great importance in the ionic transport phenomena across the membranes since it controls the permeabilities of permeating ionic species and the membrane potential, φ_m, which is the difference between the electric potentials of the two liquid phases separated by the membrane. Microporous membranes are slightly selective to the ions because they have small surface charge densities.

In this paper we study the ionic selectivities of several microporous membranes which separate two solutions of an electrolyte of the 1:1 type with concentrations c_1 and $c_2 > c_1$ by means of an experimental parameter K. In this way we see that the relative ionic permeability $n_p = P_-/P_+$ and the transference numbers t_- and $t_+ = 1 - t_-$ (*1*) in the membrane system can be written as functions of K and the relative saline concentration $n_c = c_2/c_1$ (c_1 = constant). In order to determine the role of surface charge density on the ion selectivity of the membrane, we also studied the former.

The junction between two solutions separated by a membrane is accomplished by means of a so-called membrane system. This system involves the membrane and two diffusion boundary layers (*2*). Membranes also possess a Gouy-Chapman's electric double layer which adheres to each membrane interface (*3, 4*).

Each element of the membrane system makes a contribution to the membrane potential. In Fig. 1 we show the concentrations and potentials across the membrane. In this profile $(c_+)_1$, $(c_-)_1$, $(c_+)_2$, and $(c_-)_2$ represent the ionic concentrations at Interfaces 1 and 2, respectively. The corresponding saline concentrations are c_1' and c_2'. The saline concentrations at the limits between each Gouy-Chapman's double layer and the rest of the corresponding diffusion layer are $\hat{c}_1$ and $\hat{c}_2$. In the following paragraphs we denote the membrane thickness by d, the thickness of each diffusion layer by δ, and the electric double layers by Δ_1 and Δ_2.

The diffusion potential between the concentrations c_1' and c_2' is given by (5)

$$E_D(c_1',c_2') = (1 - 2t_+)\frac{RT}{F}\ln c_2'/c_1' \tag{1}$$

where we assume that t_+ is not a function of concentration. The potentials $E_D(c_1,\hat{c}_1)$, $E_D(\hat{c}_1,c_1')$, $E_D(c_2',\hat{c}_2)$, and $E_D(\hat{c}_2,c_2)$ can be expressed in the same way. Note that in Fig. 1 we assume that there is only a diffusion process inside the membrane, and so only a diffusion potential acts. The transmembrane potential is given by E_m, see Fig. 1.

We call ψ_1 and ψ_2 the surface or Gouy-Chapman potentials, and the ϕ_1 and ϕ_2 of these potentials are given by

$$\phi_1 = \psi_1 + E_D(\hat{c}_1,c_1') \tag{2}$$

$$\phi_2 = \psi_2 + E_D(c_2',\hat{c}_2) \tag{3}$$

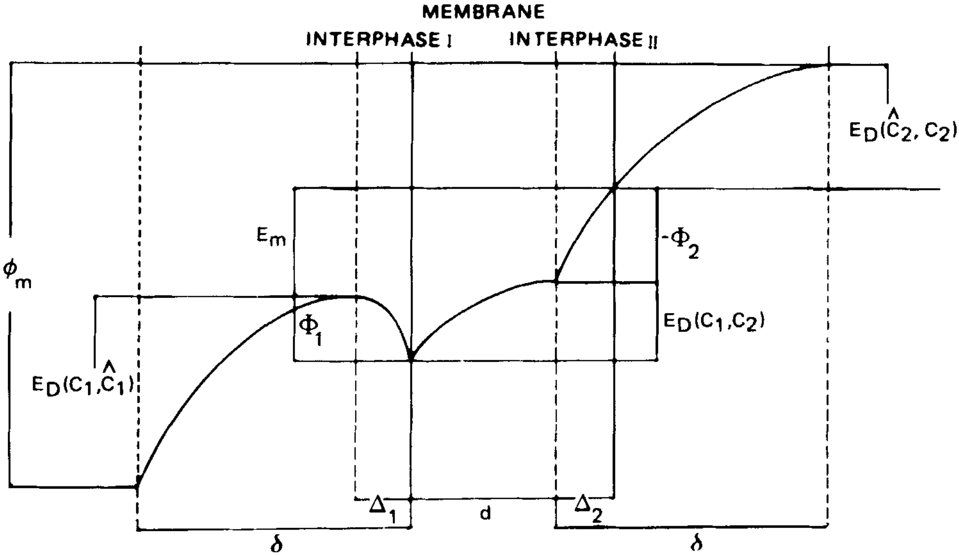

FIG. 1. Membrane potential φ_m when the presence of unstirred layers and electric double layers are considered. c_1, $\hat{c}_1$, c_1', c_2', $\hat{c}_2$, and c_2 correspond to the concentrations at the boundaries of the different elements envisaged. δ is the diffusion boundary layer thickness; Δ_1 and Δ_2 are the thicknesses of the double layers. If the contributions of $E_D(c_1,\hat{c}_1)$ and $E_D(\hat{c}_2,c_2)$ were negligible, owing to the small concentrations changes across the diffusion boundary layers, we would have $\varphi_m = E_m$.

Recently Ohki (*6*) proposed a theory to clarify the contribution of surface and diffusion potentials to the membrane potential. We have established (*7*, *8*) an alternative method which allows us to obtain the values of the Guoy-Chapman potentials ψ_1 and ψ_2 and, from ϕ_1 and ϕ_2, the effective surface charge densities. We have applied this method to several microporous membranes, and we have determined that the effective surface densities of charge depend upon the relative saline concentration $n_c = c_2/c_1$ (c_1 = constant). By employing Stern's theory of the electric double layer (*1*, *3*, *9*), we are able to distinguish between adsorbed charges and those due to the membrane. Both charges contribute to an effective charge.

EXPERIMENTAL

We have studied ionic selectivities and charges of several microporous membranes from an experimental point of view.

Membranes

The surface charge densities and ionic selectivities of several Nuclepore membranes were studied. These filters consist of a thin sheet of polycarbonate perforated by an array of discrete and nearly parallel and cylindrical pores. The pores were created by activated track etching. The membranes are available with several pore diameters. We studied six of them, which we characterize by Mab, where "ab" corresponds to the pore diameter in micrometers (manufacturer's data), e.g., M08 is a membrane whose nominal pore diameter is 0.8 μm. We used M02, M04, M06, M08, M10, and M20 membranes. The thickness of the membranes was 10 ± 1 μm (manufacturer's data).

The pore density (number of pores per surface unit, *N*) was measured by microscopic counting. The pore diameters were obtained by Teorell's "half-time" method (*10*). These data are given in Table 1.

Solutions

The solutions used were NaCl (Panreac) prepared from prefiltered, distilled, deionized, and degased water.

Concentration c_1 was kept constant at 0.0100 *M*, while c_2 ranged from 0.01 to 0.10 *M*. These NaCl concentrations are small enough to permit the

TABLE 1
Pore Diameters and Pore Densities of the Nuclepore Membranes Used. The Pore Diameters Were Measured by Teorell's "Half-Time" Method (*10*). The Pore Densities Were Measured by Microscopic Counting

Membrane	Mean pore diameter $2r$ (μm)	Pore density N (10^9 pores/m^2)
M20	1.600 ± 0.040	22.9
M10	0.822 ± 0.016	50.7
M08	0.458 ± 0.008	300.0
M06	0.434 ± 0.008	270.0
M04	0.200 ± 0.004	1000.0
M02	0.120 ± 0.002	3000.0

assumption of ideality of the solutions so concentrations, instead of activities, could be used in the transport equations (*1*).

Membrane Potentials

In order to obtain the membrane potential for several relative saline concentrations $n_c = c_2/c_1$ (c_1 = constant), we used a membrane cell whose schematic diagram is shown in Figure 2.

This membrane cell consists of a membrane holder and two electrolytic compartments, R. The R compartments contain the solutions on both sides of the membrane holder. Each compartment has an internal volume of 358 ± 3 cm^3. The exposed area of the membrane in the holder is 0.95 ± 0.02 cm^2.

The membrane potential is constant when concentrations c_1 and c_2 are kept constant during measurement. This was obtained by means of two magnetic stirrers (stirring speed of 50 rpm) and the recirculation device shown in Fig. 3.

Measurement of the membrane potentials and of the diffusion potentials was accomplished by means of two silver/silver chloride electrodes prepared by Brown's method (*11*). The electric potential difference between these electrodes was determined with a Datron 1041 microvoltmeter whose analog output was connected to a x–t Kipp-Zonen BD 8 register.

The experimental set-up was placed inside a thermostatic chamber (Fig. 2). The electrolyte reservoirs (D, Fig. 3) were placed inside a thermostatic water bath. The experiments were conducted at 298.0 ± 0.1 K.

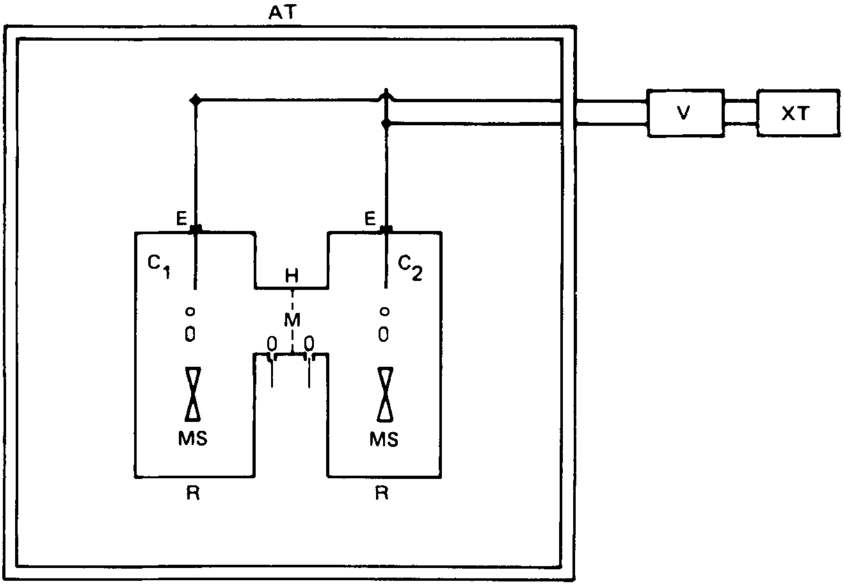

FIG. 2. Schematic diagram of the membrane cell: M is the membrane, H is the membrane holder, R is the compartment for bulk solution, MS is the magnetic stirrer, E is the electrode, O is the orifice for the insertion of the recirculation circuit (see Fig. 3), AT is the air thermostatic chamber, V is the voltmeter, and XT is the *x*–*t* register. For other details, see the text.

With the experimental technique outlined, we found that the membrane potential (when c_2 ranges from 0.01 to 0.10 and $c_1 = 0.0100$ *M*) is given by

$$\varphi_m = m \ln c_2/c_1 = \mathrm{m} \ln n_c \tag{4}$$

where *m* is an experimental parameter that depends on the membrane solute and temperature.

Diffusion Potentials

If a capillary saline bridge is used instead of the membrane holder to join the R compartments, the diffusion potential, $E_D(c_1,c_2)$, is a function of the relative saline concentration $n_c = c_2/c_1$ (c_1 = constant) and thus (*12*)

$$E_D(c_1,c_2) = 7.07 \ln n_c \tag{5}$$

with a correlation coefficient of 0.9998 and a fitting quality of 99.9%.

Comparison of Eqs. (5) and (1) leads us to conclude that $(1 - 2t_+)RT/F = 7.07$.

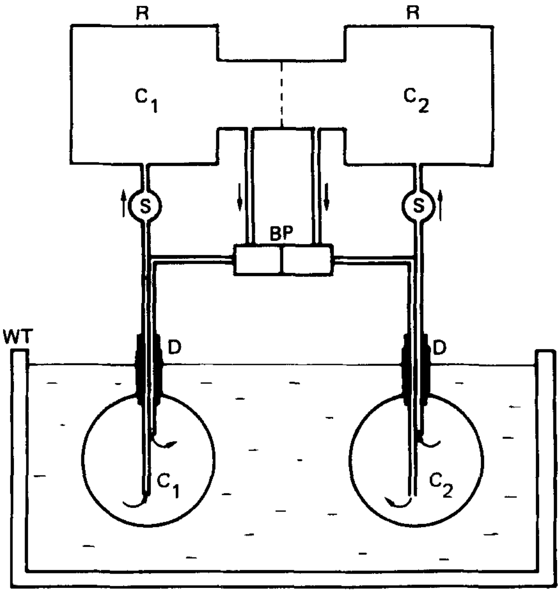

FIG. 3. Recirculation device: R is the compartment for the bulk solution, D is the electrolyte reservoir (1 L capacity), S is the thermostatic glass coil, BP is the peristaltic pump, and WT is the water thermostatic bath.

Saline Fluxes

In order to measure the saline fluxes, we used the experimental device outlined above with the recirculation device turned off, the stirring stopped, and the electrodes out of the cell.

The saline flux corresponding to the initial concentrations c_1 and c_2 was determined from a study of the mean saline fluxes at different time intervals and by extrapolation to zero time. The mean saline fluxes over a given time are obtained from the concentration change in the dilute solution (initial concentration c_1). This concentration change was determined from Eq. (5) by measuring the diffusion potential between the dilute solution and a reference solution (0.0100 *M*).

The saline flux, J, is given by (*2*)

$$J = P_{SM}(c_2 - c_1) \tag{6}$$

where P_{SM} is the saline permeability across the membrane system. This equation allow us to determine P_{SM} from J.

Finally, from the so-called law of elemental permeabilities (*13*),

$$\frac{1}{P_{SM}} = \frac{2\delta}{D} + \frac{d}{\pi M}\,\frac{1}{r^2N} \tag{7}$$

where D is the diffusion coefficient of the solute in the aqueous phase, M is the diffusion coefficient of the electrolyte inside the membrane, and r is the pore radius.

From Eq. (7) it follows that $1/P_{SM}$ versus $1/r^2N$ yields a straight line whose ordinate intercept is $2\delta/D$ and whose slope is $d/\pi M$. For those membranes studied at 298.0 ± 0.1 K and stirred at 50 rpm, $\delta/D = 255 \pm 20$ s/cm and $M = (18.1 \pm 0.5) \times 10^6$ cm^2/s. Given that $D =$ 1,512 ± 0.002) 10^{-5} cm^2/s (*14*) at the temperature used, the diffusion layer thickness is $\delta = 39 \pm 2$ μm.

THEORY

In the following paragraphs we study the ionic selectivity and the effective surface charge density of our microporous membranes from a theoretical point of view. We also distinguish between the adsorbed and inherent charges of the membrane, and relate the latter to ionic selectivity.

Concentrations

With known saline concentrations c_1 and c_2, we have to calculate c_1', c_2', $\hat{c}_1$, and $\hat{c}_2$ in order to obtain the ϕ_1 and ϕ_2 potentials and, from them, the surface charge densities.

With respect to c_1' and c_2', we have established (*10*) that

$$c_j' = c_j \pm P_{SM}(c_2 - c_1)\delta/D, \qquad j = 1, 2 \tag{8}$$

("+" for $j = 1$ and "−" for $j = 2$).

On the other hand, if a linear variation with distance is accepted for the saline concentration in the diffusion layers, we have

$$\frac{\hat{c}_j - c_j'}{\Delta_j} = \frac{c_j - c_j'}{\delta} \quad \text{or} \quad \hat{c}_j = c_j' - \Delta_j(c_j' - c_j)/\delta, \qquad j = 1, 2 \tag{9}$$

where Δ_j, the Debye-Hückel length (*1*), is

$$\Lambda_j = (8\pi N_a e^2 c'_j/\varepsilon kT)^{-1/2} \qquad (j = 1, 2)$$

with N_a the Avogadro constant, ε the dielectric constant of water, k Boltzmann's constant, and e the electron charge.

Experimental Parameter for Ionic Selectivity

We define an experimental parameter K as

$$K = mF/RT \tag{10}$$

where m corresponds to Eq. (4). By the introduction of this parameter, the relative ionic permeability $n_p = P_-/P_+$ reduces to (*15*)

$$n_p = \frac{n_c^{K+1} - 1}{n_c - n_c^k} \tag{11}$$

while the transference numbers are given by

$$t_+ = \frac{n_c - n_c^K}{n_c - n_c^K + n_c^{K+1} - 1} \tag{12}$$

$$t_- = \frac{n_c^{K+1} - 1}{n_c - n_c^K + n_c^K - 1} \tag{13}$$

In the case of passive transport with only the concentration gradient as the driving force, only values of K such as $|K| \leqq 1$ are possible (*15*). In Table 2 the values of K for membranes M02–M20 are shown.

Charges on the Membrane Surfaces

To obtain the surface charge densities of the membranes, we studied the ϕ_1 and ϕ_2 potentials.

From the Hodgkin-Katz's theory (*16*) it follows that

$$E_m = \frac{RT}{F} \ln \frac{(c_+)_2 + (c_-)_1 n_p}{(c_+)_1 + (c_-)_2 n_p} \tag{14}$$

TABLE 2

Values of the Parameter of Ionic Selectivity K for Several Nuclepore Membranes. In All Cases $c_1 = 0.01\ M$ and the Experiments Were Conducted at 298.0 ± 0.1 K. Rate of Stirring: 50 rpm

Membranes	M02	M04	M06	M08	M10	M20
K	0.30 ± 0.04	0.32 ± 0.07	0.29 ± 0.07	0.33 ± 0.05	0.20 ± 0.06	0.30 ± 0.04

If we consider that the ions of the double layers are discrete charges distributed according to Boltzmann's law, the following expressions for the ionic concentrations at the surfaces of the membrane are obtained:

$$(c_+)_j = \hat{c}_j e^{-e\phi_j/kT}, \qquad j = 1, 2 \tag{15}$$

$$(c_-)_j = \hat{c}_j e^{+e\phi_j/kT}, \qquad j = 1, 2 \tag{16}$$

From Eqs. (14), (15), and (16), we obtain

$$E_m = \phi_1 - \phi_2 + \frac{RT}{F} \ln \frac{\hat{c}_1 n_p + \hat{c}_2 x}{\hat{c}_2 n_p + \hat{c}_1 x} \tag{17}$$

with

$$x = e^{-(\phi_1 + \phi_2)e/kT} \tag{18}$$

On the other hand, from Fig. 2 it follows that

$$E_m = \phi_1 - \phi_2 + E_D(c_1', c_2') \tag{19}$$

$$\varphi_m = \phi_1 - \phi_2 + E_D(c_1, \hat{c}_1) + E_D(\hat{c}_2, c_2) + E_D(c_1', c_2') \tag{20}$$

and from Eqs. (17) and (19)

$$E_D(c_1', c_2') = \frac{RT}{F} \ln \frac{\hat{c}_1 n_p + \hat{c}_2 x}{\hat{c}_2 n_p + \hat{c}_1 x} \tag{21}$$

From the experimental values of φ_m, $RT(1 - 2t_+)/F$ (Eq. 1); n_p (Eqs. 4, 8, and 9); c_1, c_2, c_1', c_2' (Eq. 8); $\hat{c}_1$ and $\hat{c}_2$ (Eq. 9); and Eqs. (18), (20), and (21), we can calculate ϕ_1 and ϕ_2.

The surface charge density is found from the ϕ_1 and ϕ_2 potentials (*1, 3, 9*) by

$$\sigma_j = (kT/2\pi e\Delta_j) \sinh (e\phi_j/2kT), \qquad j = 1, 2 \tag{22}$$

The surface charge densities obtained for Nuclepore membranes M02–M20 are shown in Figs. 4 to 9. In these figures we can see that σ_1 and σ_2 are negative and depend upon the relative saline concentration $n_c = c_2/c_1$ (c_1 = constant). This dependence indicates that the surface charge densities, as well as the fixed charges on the membrane surfaces, include some term

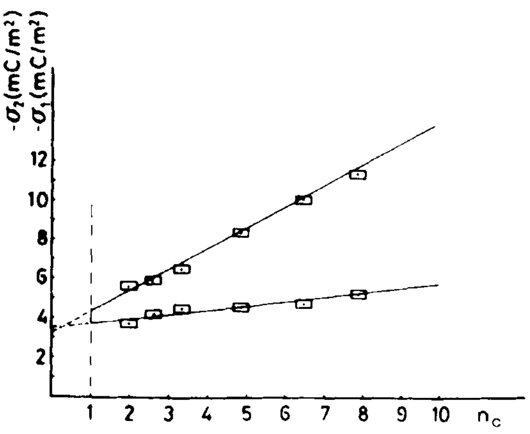

FIG. 4. Surface charge densities σ_1 and σ_2 as functions of $n_c = c_2/c_1$ (c_1 = constant). The fitted straight lines have a correlation factor greater than 0.99. Membrane M02.

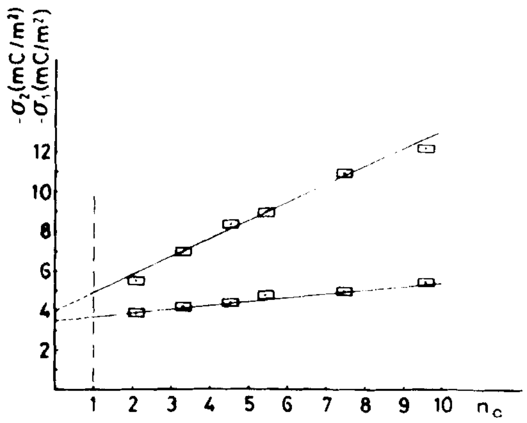

FIG. 5. Surface charge densities σ_1 and σ_2 as functions of $n_c = c_2/c_1$ (c_1 = constant). The fitted straight lines have a correlation factor greater than 0.99. Membrane M04.

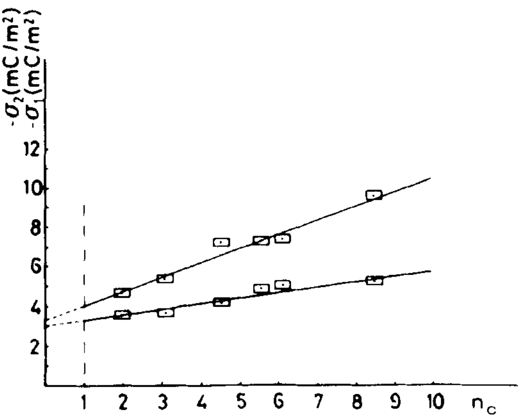

FIG. 6. Surface charge densities σ_1 and σ_2 as functions of $n_c = c_2/c_1$ (c_1 = constant). The fitted straight lines have a correlation factor greater than 0.99. Membrane M06.

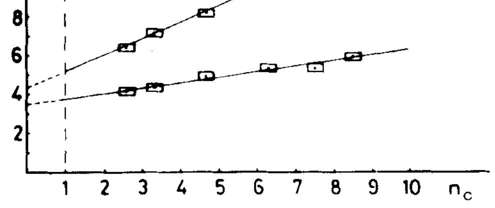

FIG. 7. Surface charge densities σ_1 and σ_2 as functions of $n_c = c_2/c_1$ (c_1 = constant). The fitted straight lines have a correlation factor greater than 0.99. Membrane M08.

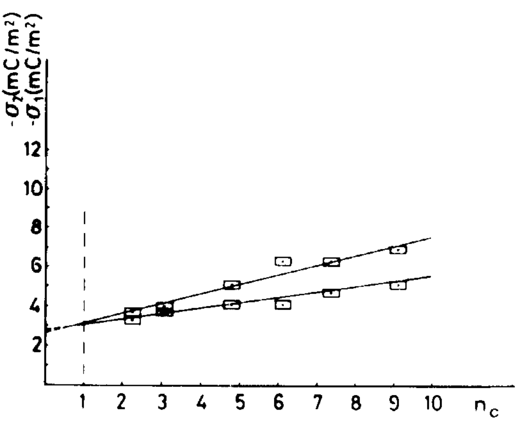

FIG. 8. Surface charge densities σ_1 and σ_2 as functions of $n = c_2/c_1$ (c_1 = constant). The fitted straight lines have a correlation factor greater than 0.99. Membrane M10.

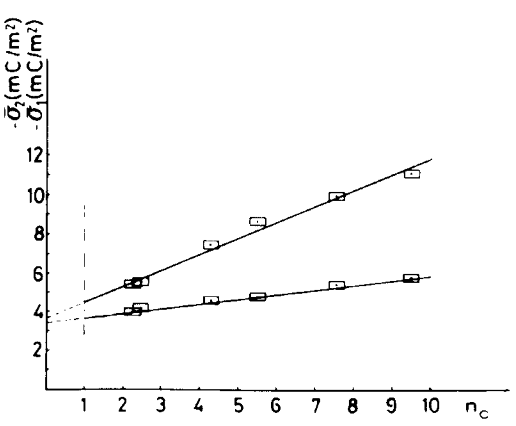

FIG. 9. Surface charge densities σ_1 and σ_2 as functions of $n_c = c_2/c_1$ (c_1 = constant). The fitted straight lines have a correlation factor greater than 0.99. Membrane M20.

TABLE 3

Values of α_{min} and α_{max} (see text) from the Crystallographic Radius, the Primary Solvation Numbers of the Na^+ Ion, and the Radius of a Molecule of Water (*1*). In the Calculation of α_{max} It Is Assumed That Half the Number of Water Molecules Hydrating Each Na^+ Cation are Placed on Each Side of It

Crystallographic radius of Na^+, r_{Na^+}	Primary number of solvation of Na^+ n_{min}	Primary number of solvation of Na^+ n_{max}	Radius of a molecule of water, r_{H_2O}	$\alpha_{n_{min}} = 2r_{H_2O} + 2r_{Na^+} + n_{min}r_{H_2O}$
0.95 Å	2	4	1.38 Å	6.04 Å

$\alpha_{max} = 2r_{H_2O} + 2r_{Na^+} + n_{max}r_{H_2O}$	$\alpha_{min} = 2r_{Na^+}$
7.42 Å	1.9 Å

changing with n_c. That is, σ_1 and σ_2 are effective surface charge densities; they are not the surface density of charges due to the membrane.

Helmholtz-Perrin's theory (*1, 3, 9*), which assumes the existence of a layer of ions in contact with the surfaces of the membrane, has to be taken into account. Stern's theory (*1, 3, 9*) considers the above-mentioned adsorbed layer of ions and Gouy-Chapman's double layer. This is equivalent to applying Gouy-Chapman's model to ions with a finite size instead of point charges, and it implies that the centers of the ions cannot be at a distance less than a critical distance α from the membrane surface. That is, the Gouy-Chapman diffuse double layer starts at a distance α from the membrane.

We can consider the interior of the adsorbed layer as a combination of two configurations (*1*): in one of them, at some distance from the membrane, there is a layer of dipoles (water molecules hydrating the membrane) and at a greater distance a layer of solvated counterions (cations, because the membrane is negatively charged); in the other configuration there are no dipoles and the cations are in direct contact with the membrane. From these assumptions and for NaCl solutions, it is found that α must be between 1.9 and 7.42 Å (*1*), see Table 3. Given that Δ_j is equal to the corresponding Debye-Hückel length, for our membranes we obtain

$$\Delta_{1,\mathrm{min}} = 20.3 \pm 0.1 \text{ Å}, \qquad \Delta_{2,\mathrm{min}} = 10.5 \pm 0.1 \text{ Å} \quad (\text{M20 and } n_c = 9.3 \pm 0.1) \tag{23}$$

$$\Delta_{1,\mathrm{max}} = 28.8 \pm 0.1 \text{ Å}, \qquad \Delta_{2,\mathrm{max}} = 22.2 \pm 0.1 \text{ Å} \quad (\text{M02 and } n_c = 2.0 \pm 0.1) \tag{24}$$

From Eqs. (23) and (24) we obtain the mean quantities:

$$\bar{\Delta}_j/\bar{\alpha}\ 4.22 \qquad \text{and} \qquad \delta/\bar{\Delta}_j = 1984.73 \tag{25}$$

Observe that Δ_j is approximately four times α, while δ is approximately two thousand times Δ_j.

If $\sigma_{j\alpha}$ ($j = 1, 2$) represents the contribution to the effective surface charge density due to the charges retained at a distance smaller than α from the j-surface of the membrane, and σ_{js} is the surface charge density due to the membrane surface (true surface charge density of the membrane), we have

$$\sigma_{js} = \sigma_j - \sigma_{j\alpha} \tag{26}$$

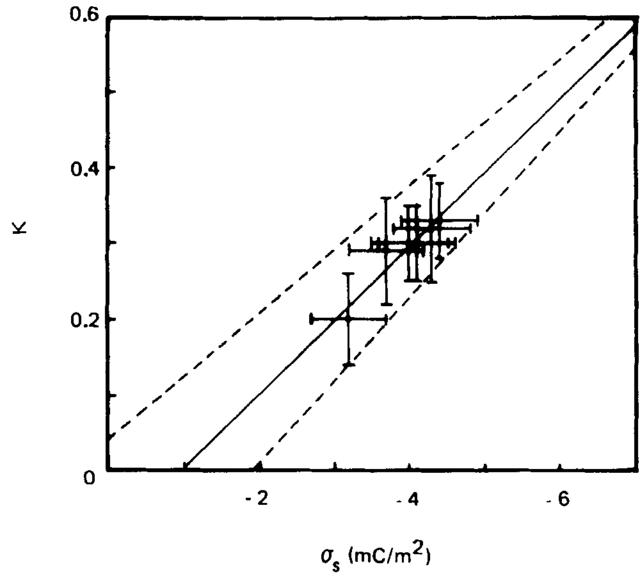

FIG. 10. Surface density of charges due to the membrane surface (true charges of the membrane) versus the ionic selectivities given by the experimental parameters K for the membranes M10, M06, M20, M02, M04, and M08 (with K and $-\sigma_s$ increasing).

The σ_{ja} contributions depend on the concentration, so when $n_c = 1$ these contributions are equal on both sides of the membrane and cancel out. In Figs. 4 to 9 it can be seen that

$$(\sigma_1)_{n_c \to 1} = (\sigma_2)_{n_c \to 1} \tag{27}$$

within the error range. Thus the surface density of charges due to the membrane surface (true charges of the membrane) is

$$\sigma_s = \left(\frac{\sigma_1 + \sigma_2}{2} \right)_{n_c \to 1} \tag{28}$$

Figure 10 illustrates σ_s as a function of the ionic selectivity given by the experimental parameter K. Note that $K = 0$ when $\sigma_s = 0$, and K is linear with σ_s. The values of the surface charge density due to the membrane are, for each membrane, of the same order as the mean value given by Meares for all Nuclepore membranes. This value was obtained from electroosmotic measurements (*17*). We distinguish between the membranes and also between adsorbed charges and those which are actual charges of the membrane surface.

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