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Cation Transport Numbers in Polycarbonate Microporous Membranes. Effect of Unstirred Diffusion Layers

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Abstract

In this paper we obtain the apparent transport numbers across different polycarbonate microporous membranes bathed by two isothermal aqueous solutions of the same electrolyte but at different concentrations, N_1 and N_2. The effect of unstirred layers adjacent to the membrane is taken into account. Six different membranes and two electrolytes (LiCl and $MgCl_2$) were studied at 20, 30, 40, and 50°C and for N_1 and N_2 in the range 10^{-1} to 2×10^{-4} equiv/L.

INTRODUCTION

If a membrane separates two solutions of the same electrolyte which differ in concentration, then, in general, an electrical potential difference will exist between the two solutions. Isothermic–isobaric constraints are imposed on the system and external electrical fields are excluded.

In agreement with nonequilibrium thermodynamics (*1*), this potential difference E_m between the two solutions is given by

$$E_m = -\frac{RT}{F}\left(1 - \frac{\nu_+ + \nu_-}{\nu_+\nu_-}\bar{t}_+^{\text{app}}\right)\ln\frac{a_1}{a_2} \tag{1}$$

where a_1 and a_2 are the mean ionic activities in the boundaries of the membrane, $\bar{t}_{+}^{\mathrm{app}}$ is the apparent transport number of the cation through the membrane, and R, T, F, ν_{+}, and ν_{-} have their usual meanings.

In systems of the type under consideration, the rate of ionic interdiffusion between the two solutions will depend not only on the rate of diffusion of ions through the membrane itself but also on the rate of diffusion of ions up to and away from the membrane surfaces. The membranes used in this study were thin, broad pore membranes. Consequently, the bulk phases could not be stirred very vigorously. At the same time, we wanted to avoid increasing the pore end effects and pushing the solutions right through the membrane. When solutions are stirred, their compositions are not maintained uniform right up to the membrane surface, and concentration gradients develop in a layer of solution adjacent to the membrane. The theoretical treatment of diffusion processes in solutions can be greatly simplified by making use of the Nernst concept of a "diffusion layer" (*2*), the thickness of which depends on the degree of agitation in the solution. Thus, the bulk solution is assumed to be of uniform composition and to be separated from the membrane surface by a layer of completely unstirred solution (Fig. 1). The entity formed by the membrane and the two diffusion layers (with electrochemical properties similar to those of the free solution) is called the membrane system.

Thus, the potential difference E_{ms} through the membrane system, including the presence of liquid junction potentials between the solutions corresponding to the boundaries of the diffusion layers, and the membrane potential itself (*3*) is

$$E_{ms} = -\frac{RT}{F}\left[\left(1 - \frac{\nu_{+} + \nu_{-}}{\nu_{+}\nu_{-}}\, t_{+}(1)\right)\ln\frac{a_1}{a_1'} + \left(1 - \frac{\nu_{+} + \nu_{-}}{\nu_{+}\nu_{-}}\, \bar{t}_{+}^{\mathrm{app}}\right)\ln\frac{a_1'}{a_2'} + \left(1 - \frac{\nu_{+} + \nu_{-}}{\nu_{+}\nu_{-}}\, t_{+}(2)\right)\ln\frac{a_2'}{a_2}\right] \tag{2}$$

where $t_{+}(1)$ and $t_{+}(2)$ are the mean transport numbers of ions in the aqueous phases corresponding to the diffusion layers, and a_1' and a_2' are the mean ionic activities for the concentrations N_1' and N_2' in the membrane–diffusion layer interfaces (Fig. 1).

EXPERIMENTAL

This paper describes an investigation of the properties of a class of membranes with an exceptionally well-defined pore structure (*4*). These

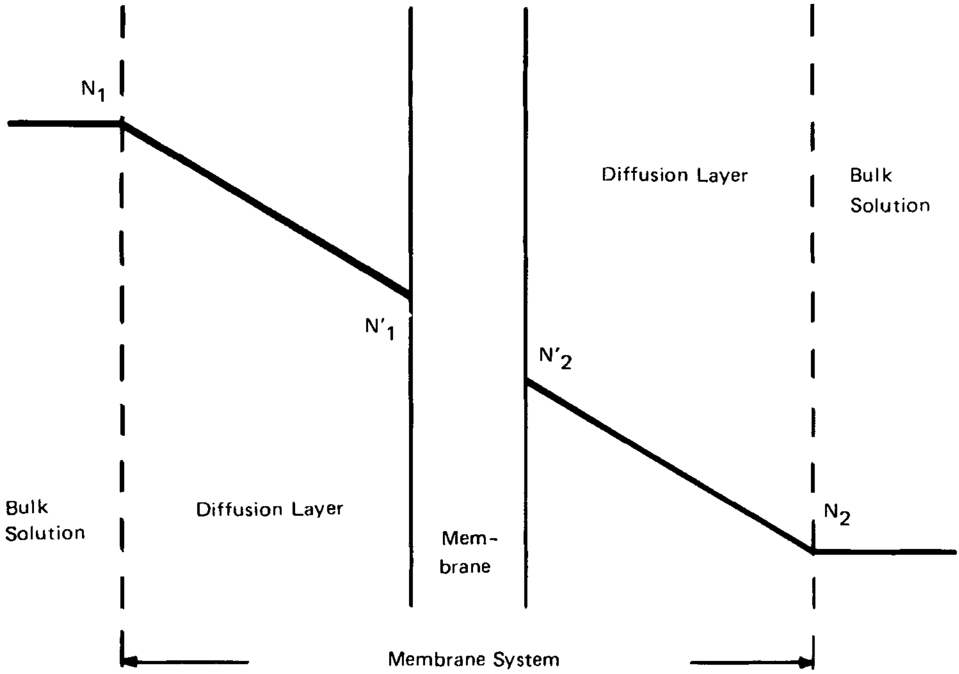

FIG. 1. Formal structure of the membrane system. The concentration profile outside the membrane is indicated.

membranes are the Nuclepore filters which consist of a sheet of polycarbonate perforated by an array of discrete and nearly parallel cylindrical pores. Filters of pore diameters 5, 2, 0.8, 0.4, 0.1, and 0.03 μm were used. They will be identified from now on as N5, N2, etc.

The water used in solutions (doubly-distilled, deionized, and degasified) had a specific conductivity of the order of 10^{-6} $\Omega^{-1}\text{cm}^{-1}$. The LiCl and $MgCl_2$ (Baker analyzed reagent) used had a purity of 99.5%.

The potential arising across the membrane system was studied by constructing a cell of the type:

Chloride selective electrode	Solution of concentration N_1	Diffusion layer	Membrane	Diffusion layer	Solution of concentration N_2	Chloride selective electrode

—— Membrane system ——

The same electrolyte was used on both sides of the membrane. The emf, E_c, of this cell was measured by using the two-compartment cell shown in a previous paper (*2*). This method allowed keeping the concentrations N_1 and N_2 constant because both solutions have agitation and renovation systems available. The concentration N_1 was fixed at 10^{-3}, 10^{-2}, and 10^{-1} equiv/L, and N_2 was varied so that $N_1/N_2 < 10$.

Chloride selective electrodes were used in the experiments, and the measured emf of the cell, E_c, therefore involved the electrodic Nernst contribution as well as the membrane system potential E_{ms}. Hence, we have

$$E_{ms} = E_c + \frac{RT}{F} \ln \frac{a_1}{a_2} \tag{3}$$

In experiments parallel to previous ones (*5*), we measured the salt flux, J_s, between solutions of concentrations N_1 and N_2. This allowed calculation of the diffusion layer thickness, δ:

$$\delta = 84 \pm 5\ \mu\text{m, when LiCl is used}$$

$$\delta = 75 \pm 5\ \mu\text{m, when MgCl}_2\text{ is used}$$

and N_1' and N_2' as

$$N_1' = N_1 - J_s \frac{\delta}{D_d(1)} \tag{4}$$

$$N_2' = N_2 + J_s \frac{\delta}{D_d(2)} \tag{5}$$

where $D_d(1)$ and $D_d(2)$ are the mean diffusion coefficients of the electrolyte in the aqueous phases corresponding to the diffusion layers.

The potential experiments as well as the salt flux experiments were carried out with both solutes, the six membranes, in the same range of concentrations (2×10^{-4} to 10^{-1} equiv/L), and at 20, 30, 40, and 50°C.

RESULTS

In a previous paper (*2*) we calculated the cation apparent transport number across the membrane system made up of the membrane itself and the two adjacent diffusion layers. Because the membrane system is similar to a composite membrane, we can assume that the transport number across the membrane system will be some average value of transport number across the membrane itself, $\bar{t}_+^{app}$, and of those across the diffusion layers, $t_+(1)$ and $t_+(2)$ (*6*).

The main aim of this paper is to study the cation transport number across the membrane itself, without the mask of the cation transport numbers across the diffusion layers. This is found by use of Eqs. (2)-(5) from the experimental results of N_1, N_2, E_c, J_s, and δ.

For these equations, the values of a_1, a_1', a_2, a_2', $D_d(1)$, $D_d(2)$, $t_+(1)$, and $t_+(2)$, all referred to free diffusion, were taken from the literature (*7*).

The apparent transport numbers for the different membranes at the different concentrations and temperatures under study are given in Figs. 2 and 3.

Measurements with N5 and N2 membranes yielded values of $\bar{t}_+^{app}$ close to the free diffusion values for all concentrations of bounding solutions and temperatures. For all the other membranes, $\bar{t}_+^{app}$ is higher than the free diffusion values of cation transport when the pore radius and the concentrations of the solutions decrease. This can be interpreted as a consequence of the adsorption of chloride ions in the solution on the pore walls. Thus, a diffused electrical double layer is formed (*8*), from which the anions are excluded. As importance as this layer inside the total volume of the pore is, even higher is $\bar{t}_+^{app}$ with regard to the cation transport for free diffusion.

Previous papers dealing with Nuclepore membranes have shown that there is some charge (probably due to adsorption of ions from solution) on the pore walls (*9*) when these membranes are bathed by electrolyte solutions. Our results point out that the electrokinetic effects of this charge depend greatly on the pore size, and become more important for membranes with smaller pores (especially the N003 membrane) recently put on the market.

Finally, the presence of the diffusion layers and the results obtained for $\bar{t}_+^{app}$ permit the results obtained to be analyzed qualitatively for the potential additivity principle.

The additivity principle [proposed by Meares et al. (*10*)] is easily obtained by use of Eq. (1):

$$E_m(a_1,a_2) = E_m(a_1,a_3) + E_m(a_3,a_4) + \cdots \qquad (6)$$

which, bearing in mind the use of reversible electrodes for E_c measurements, becomes

$$E_c(a_1,a_2) = E_c(a_1,a_3) + E_c(a_3,a_4) + \cdots \qquad (7)$$

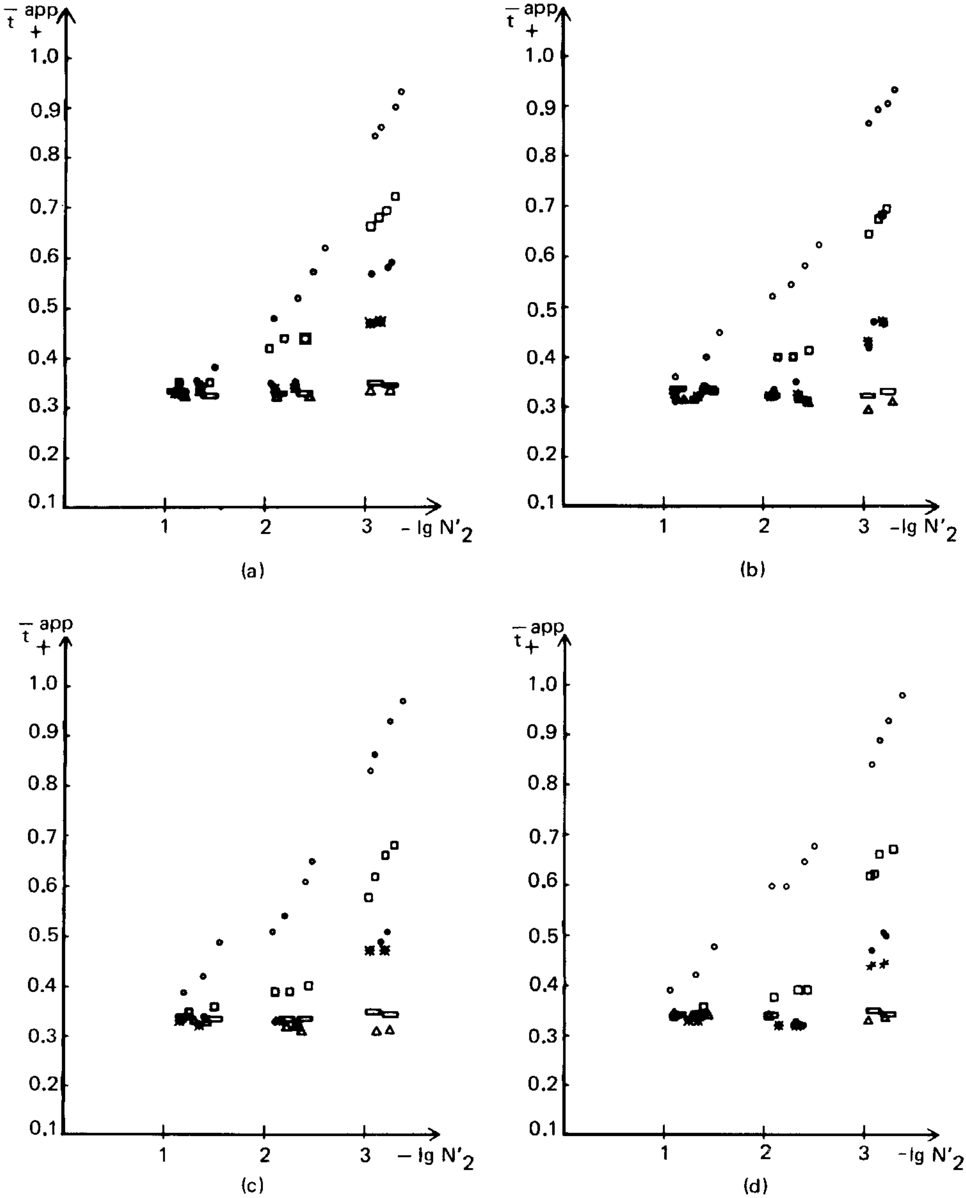

FIG. 2. Apparent transport number $\bar{t}_+^{app}$ vs $-\lg N_2'$ for different membranes. Solute: LiCl. (a) $T = 20°C$, (b) $T = 30°C$, (c) $T = 40°C$, (d) $T = 50°C$. Symbols: (△) N5, (▭) N2, (*) N08, (●) N04, (□) N01, (○) N003.

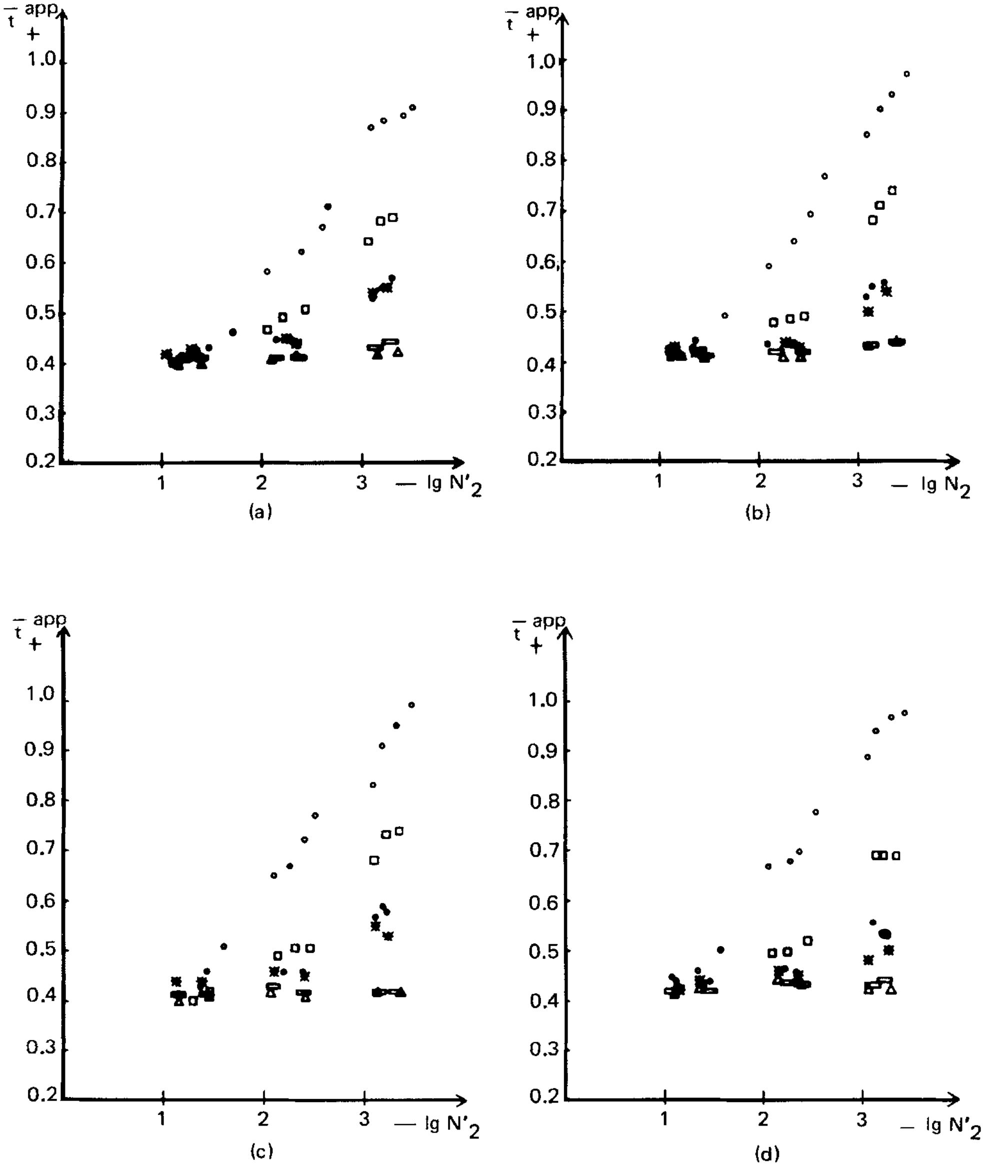

FIG. 3. Cation apparent transport number $\bar{t}_+^{app}$ vs $-\lg N_2'$ for different membranes. Solute: $MgCl_2$. (a) $T = 20$°C, (b) $T = 30$°C, (c) $T = 40$°C, (d) $T = 50$°C. Symbols: (△) N5, (▭) N2, (*) N08, (●) N04, (□) N01, (○) N003.

where $a_1 > a_3 > a_4 > \cdots > a_2$. $E_c(a_1,a_2)$ is the cell potential when the membrane system separates two solutions at mean ionic activities a_1 and a_2, etc.

The results reported in Table 1 show the validity of Eq. (7) for the N5 and N2 membranes. According to Eq. (1), that is because the transport properties are homogeneous throughout the membrane system, i.e., those of the membrane are equal to those of the diffusion layers, and therefore equal to those of the free diffusion, as shown in the $\bar{t}_+^{\text{app}}$ results for these two membranes.

For the N01 and N003 membranes, Eq. (7) is not valid. In effect, as inferred from $\bar{t}_+^{\text{app}}$ results given above, the cation transport numbers inside these membranes are higher than the cation transport numbers for free diffusion (or inside the diffusion layers).

TABLE 1
Test of the Additivity Principle for E_c Values (in mV): Solute LiCl

$$\Delta_r = \frac{E_c(N_1,N_3) + E_c(N_3,N_4) + E_c(N_4,N_2) - E_c(N_1,N_2)}{E_c(N_1,N_2)}, \qquad N_1 > N_3 > N_4 > N_2$$

Membrane N5 $T = 20°\text{C}$	$E_c(0.00202,0.00100) = 11.3$ $E_c(0.00460,0.00202) = 13.2$ $E_c(0.0100,0.00460) = 12.3$	$E_c(0.0100,0.00100) = 36.8$	$\Delta_r = 0.00$
Membrane N2 $T = 20°\text{C}$	$E_c(0.00200,0.00100) = 11.3$ $E_c(0.00460,0.00200) = 13.3$ $E_c(0.0100,0.00460) = 12.3$	$E_c(0.0100,0.00100) = 36.8$	$\Delta_r = 0.00$
Membrane N08 $T = 20°\text{C}$	$E_c(0.00190,0.00100) = 11.3$ $E_c(0.00460,0.00200) = 13.3$ $E_c(0.0100,0.00470) = 11.9$	$E_c(0.0100,0.00100) = 37.1$	$\Delta_r = 0.02$
Membrane N04 $T = 20°\text{C}$	$E_c(0.00200,0.00100) = 11.3$ $E_c(0.00460,0.00200) = 13.9$ $E_c(0.00100,0.00460) = 12.3$	$E_c(0.0100,0.00100) = 37.0$	$\Delta_r = 0.02$
Membrane N01 $T = 20°\text{C}$	$E_c(0.00230,0.00100) = 16.5$ $E_c(0.0100,0.00230) = 25.2$	$E_c(0.0100,0.00100) = 39.1$	$\Delta_r = 0.06$
Membrane N003 $T = 30°\text{C}$	$E_c(0.00200,0.00100) = 21.9$ $E_c(0.00467,0.00200) = 22.5$ $E_c(0.0100,0.00467) = 16.8$	$E_c(0.0100,0.00100) = 56.0$	$\Delta_r = 0.09$

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