

Transport Properties of Charged Membranes at Low Charge Densities

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Diffusion and sorption of NaCl in cellulosic membranes containing small amounts of carboxylic substituents have been investigated. Diffusion experiments were performed in a cell consisting of two well-stirred solution compartments separated by the membrane. From measurements of the cell potential between Ag,AgCl electrodes as a function of time, the diffusion flux was determined. For the interpretation of the experimental results a new theoretical approach was adopted in which the modified Nernst-Planck transport equations were integrated, employing the mean value theorem for integrals. The treatment leads to very simple explicit expressions for the cell potential and the diffusion flux. From these the diffusion coefficients for coions and counterions could be determined. In the region of high salt concentrations the diffusion behaviour in the membranes was similar to diffusion in solution, the ionic transference numbers being practically the same in both cases. At low salt concentrations a sharp decrease in the counterion diffusion coefficient was observed. This indicates an increased counterion trapping at low salt concentrations.

Electrolyte transport through charged membranes has been extensively studied. Most of this work has been carried out with membranes of high charge densities. Such membranes represent highly non-ideal systems, which complicates the interpretation of the experimental results. Also, because of the excessive Donnan exclusion of permeable electrolytes from the membrane phase, these membranes become virtually impermeable to electrolytes at low salt concentration. This limits the useful range of measurements to comparatively high concentrations of the electrolyte.

Some of these difficulties can be avoided when the

charge density is low. Measurements can then be extended into the dilute concentration range, where treatment of the experimental data is facilitated.

In the present work, cellophane and carboxymethylated cellophane membranes with varying charge densities were studied and their properties concerning diffusional transport and sorption of electrolytes were determined.

THEORY

For the interpretation of the diffusion process the classical TMS model¹⁻² is adopted, and it is used together with the modified Nernst-Planck flow equations:³

$$j_i = -10^{-3} D_i \left(\frac{dc_i}{dx} + z_i c_i \frac{F}{RT} \frac{d\psi}{dx} + c_i \frac{d \ln \gamma_i}{dx} \right) \quad (1)$$

where, for the ionic species *i*

j_i = flux (mol cm⁻² s⁻¹)

D_i = diffusion coefficient (cm² s⁻¹)

c_i = concentration (mol dm⁻³)

z_i = charge number

ψ = electrical potential

γ_i = activity coefficient.

All these quantities refer to the membrane phase, which is considered to be a homogeneous gel.

If the membrane separates two solutions of the same electrolyte of different concentrations the Nernst-Planck equations can be integrated for a stationary state, although the solutions are not explicit and numerical integration is required.³ In the present treatment a simplified approach is adopted, leading to remarkably simple explicit solutions of the transport equations. The integra-

tions are carried out "in the mean", employing the mean value theorem for integrals. The treatment should lead to accurate results, provided the concentration difference across the membrane is small.

For a single salt we may replace the index i in eqn. (1) by $+$ and $-$, referring to cations and anions, respectively. We then have

$$v_+ z_+ + v_- z_- = 0 \quad (2)$$

where v_+ and v_- are the stoichiometric coefficients of the salt.

For a stationary state, with zero electric current, we have the additional equation

$$\frac{j_+}{v_+} = \frac{j_-}{v_-} = j \quad (3)$$

where j is the constant diffusion flux for the salt.

Eliminating the electric potential in eqn. (1) we obtain with the help of (2) and (3)

$$j = -L \frac{d \ln a_{\pm}}{dx} \quad (4)$$

where

$$a_{\pm} = [c_+^{v_+} c_-^{v_-} \gamma_+^{v_+} \gamma_-^{v_-}]^{\frac{1}{v_+ + v_-}} \quad (5)$$

is the mean activity of the electrolyte and

$$L = \frac{10^{-3}(v_+ + v_-)D_+ D_- c_+ c_-}{v_+^2 D_- c_- + v_-^2 D_+ c_+} \quad (6)$$

Integrating eqn. (4) across the membrane we have

$$jd = - \int_0^d L \frac{d \ln a_{\pm}}{dx} dx \quad (7)$$

where d is the thickness of the membrane.

Observing that L is a continuous function of distance x , we can apply the mean value theorem for integrals, and obtain

$$jd = -L_{\theta} \ln \frac{\bar{a}_{\pm}''}{\bar{a}_{\pm}'} = -L_{\theta} \ln \frac{a_{\pm}''}{a_{\pm}'} \quad (8)$$

where L_{θ} is the value of L at some point θ within the membrane. The second equality in (8) implies that

we have equilibrium at the membrane interfaces (barred quantities refer to the membrane phase, unbarred to the ambient solutions; prime and double prime refer to the interfaces at $x=0$ and $x=d$, respectively).

To obtain the expression for the cell potential E , we observe that it is composed of the difference of the electrode potentials ΔE_{e1} , the diffusion potential E_d and the Donnan potential E_D . We have

$$\Delta E_{e1} = \frac{RT}{z_i F} \ln \frac{a_i''}{a_i'} \quad (9)$$

The diffusion potential is obtained by solving one of eqn. (1) for $\frac{d\psi}{dx}$ and integrating across the membrane. The Donnan potential can be obtained if equilibrium at the membrane boundaries is assumed (from the equality of electrochemical potentials in the two phases). These two potentials constitute the membrane potential E_m , which is of the form³

$$E_m = - \frac{RT}{z_i F} \left[\ln \frac{a_i''}{a_i'} - \int_0^d \frac{10^3 v_i L}{D_i c_i} \frac{d \ln a_{\pm}}{dx} dx \right] \quad (10)$$

We assume that the electrodes are reversible with respect to the anion. Eqn. (9) for anions is then combined with eqn. (10) for cations. With the help of eqn. (2) we obtain

$$E = - \frac{(v_+ + v_-)RT}{v_+ z_+ F} \left[\ln \frac{a_{\pm}''}{a_{\pm}'} - \frac{v_+^2}{v_+ + v_-} \int_0^d \frac{10^3 L}{D_+ c_+} \frac{d \ln a_{\pm}}{dx} dx \right] \quad (11)$$

Using the mean value theorem, we finally obtain

$$E = - \frac{(v_+ + v_-)RT}{v_+ z_+ F} \ln \frac{a_{\pm}''}{a_{\pm}'} \left[1 - \frac{v_+^2}{v_+ + v_-} \left(\frac{10^3 L}{D_+ \bar{c}_+} \right) \theta' \right] \quad (12)$$

where θ' refers to a point within the membrane. With the help of eqn. (6) we may rewrite (12) in the form

$$E = - \frac{(v_+ + v_-)RT}{v_+ z_+ F} \ln \frac{a_{\pm}''}{a_{\pm}'} \left[1 + \left(\frac{v_+}{v_-} \right)^2 \frac{D_- \bar{c}_-}{D_+ \bar{c}_+} \right]^{-1} \theta' \quad (13)$$

Obviously the points θ and θ' may differ. However, the difference is in general insignificant, provided the concentration gradient in the membrane is small. As a good approximation both can be referred to the midpoint in the membrane (or better, the point corresponding to the mean external salt concentration). Doing this we can combine eqns. (8) and (13) to obtain the important equation

$$\frac{j d}{E} = \frac{10^{-3} F}{RT} \frac{v_+ z_+}{v_-^2} (D_- \bar{c}_-)_\theta \quad (14)$$

From eqns. (13) and (14) we may thus obtain the quantities $(D_- \bar{c}_-)_\theta$ and $\left(\frac{D_+ \bar{c}_+}{D_- \bar{c}_-}\right)_\theta$. The ionic diffusion coefficients in the membrane can thus be determined provided we know the ionic concentrations in the membrane phase. The determination of these will now be considered.

In earlier work the Donnan law has often been directly applied to determine the distribution of the electrolyte between the membrane and solution phases. However, there is ample evidence that the simple Donnan law is not applicable to charged gels. Recent work on polyelectrolyte solutions also indicates that the counterion condensation effect^{4,5} plays a prominent role in determining the partition of the electrolyte. The problem will therefore be reconsidered and we will specifically deal with 1:1 electrolytes, studied experimentally in the present work.

The general equilibrium condition, obtained by equating the chemical potentials of the electrolyte in the gel and solution phases, is

$$\bar{\gamma}_\pm^2 \bar{c}_+ \bar{c}_- = \gamma_\pm^2 c_+ c_- \exp \left[\frac{\mu_\pm^0 - \bar{\mu}_\pm^0 + V_\pm p - \bar{V}_\pm \bar{p}}{RT} \right] \quad (15)$$

where V_\pm is the partial molar volume of the salt and p the pressure.

In eqn. (15) the standard chemical potentials, μ_\pm^0 and $\bar{\mu}_\pm^0$, can be chosen at will, although it should be noted that the value of the activity coefficient depends on that choice. For the solution phase we choose as usual the infinitely dilute solution as the standard state ($\gamma_\pm = 1$ for $c=0$), but for the moment we leave the standard state of the gel unspecified. The pressure difference between the gel and solution phases has been assumed to play a role for the partition of solutes, although the effect is controversial.⁶⁻⁸ In any case the pressure

difference between the gel and solution is not measurable, and the effect can be incorporated in the standard chemical potential and the activity coefficient for the gel. We can indeed write

$$\bar{V}_\pm \bar{p} = \bar{V}_\pm (\bar{p}_0 + \bar{p}_1) \quad (16)$$

where \bar{p}_0 is the pressure at the standard state and \bar{p}_1 takes into account the concentration dependence of the pressure. Obviously the former may be included in $\bar{\mu}_\pm^0$ and the latter in $\bar{\gamma}_\pm$. Thus, we may delete the pressure terms in the exponential function in eqn. (15).

To specify the ionic concentrations we denote the concentration of the simple electrolyte by c and the equivalent concentration of the fixed negative charges in the gel (charge density) by C . We then have

$$c_+ = c_- = c \quad (17)$$

$$\bar{c}_+ = \bar{c} + \alpha C \quad (18)$$

$$\bar{c}_- = \bar{c} \quad (19)$$

where α is the degree of ionization of the fixed groups. The fraction $1-\alpha$ of the counterions is thus bound by the fixed charges or "condensed".

With the aid of eqns. (17)–(19), eqn. (15) may be written in the form

$$b = \frac{c^2}{\bar{c}(\bar{c} + \alpha C)} \quad (20)$$

where

$$b = \frac{\bar{\gamma}_\pm^2}{\gamma_\pm^2} \exp \left[-\frac{\mu_\pm^0 - \bar{\mu}_\pm^0}{RT} \right] \quad (21)$$

Introducing the new variables

$$y = \frac{c^2}{\bar{c}^2} \quad (22)$$

$$x = \frac{C}{\bar{c}} \quad (23)$$

eqn. (20) takes the form

$$y = b + b\alpha x \quad (24)$$

To compress the scale on the coordinate axis, we may also write

$$\sqrt{y-b} = \sqrt{b\alpha} \sqrt{x} \quad (25)$$

This equation was found (see below) to be linear in the region of small values of the variables x and y , indicating an apparent constancy of the parameters b and α in this region. In this respect the behaviour of charged gels corresponds to that of polyelectrolyte solutions.⁹ It should be noted, however, that it is not possible unambiguously to distinguish between the effect of ion binding and the effect of changes in the activity coefficient.⁹

The derivation of the expression for the diffusion flux j from the time dependence of E is given in Appendix I.

EXPERIMENTAL

Apparatus. The diffusion cell was similar to the cell previously used in the study of Donnan equilibria.⁹ It was made of lucite and consisted of two chambers separated by the membrane. Each chamber contained a magnetic stirrer of spherical shape, kept in rotation during the measurements by a single external magnet. The cell potential was measured by Ag,AgCl electrodes using a vernier potentiometer from Cambridge Instruments. The cell was placed in a water thermostat and all measurements were performed at 25 °C. The solution volume in each chamber was $V = 5.97 \text{ cm}^3$ and the exposed membrane area $S = 0.503 \text{ cm}^2$.

Membranes. Carboxymethylation of cellophane was carried out as follows. Pieces of cellophane membrane (about 2.5 g dry weight) were extracted with water for several days. The membranes were then added piece by piece to about 300 cm³ of a 10% NaOH solution containing sodium chloroacetate. The reaction was allowed to proceed at room temperature under nitrogen atmosphere. For the membrane designated M1 the solution was 0.28 M with respect to sodium chloroacetate, and the reaction time was 22 h. For membrane M2 the corresponding figures were 0.74 M and 30 h.

The carboxyl content of the membranes was determined by titrating batches of the membranes with a standard 0.02 M NaOH solution, with phenolphthalein as indicator. Preceding this the membranes were converted to the acid form and the titration was carried out in the presence of an 0.2 M NaCl solution. The dry weight of the batch was subsequently determined by drying to constant weight at 105 °C.

Determination of sorption equilibria. Sorption equilibria with NaCl as solute were determined by a method described in detail earlier.¹⁰ The experiments were carried out in a cylindrical weighing-

bottle, which could be tightly closed with a polyethylene stopper. The total volume of the bottle was 10 cm³ and about 2 g (dry weight) of the membrane was used. After a series of measurements the pure membrane was regenerated by washing with a continuous stream of water overnight (the water was slightly alkaline, about 10⁻⁵ M NaOH, to prevent hydrolysis). To determine the mass fraction of the membrane lattice in the membrane phase, w_3 , experiments were carried out with dextran as solute, which was considered to be excluded from the membrane phase. These measurements were carried out both in salt free solutions and in the presence of NaCl. No change in the swelling of the membranes could be detected.

To determine the partition coefficient $K (= \gamma_c$ in Ref. 10) the densities of the membranes had to be known. They were determined by pycnometric measurements.

Dextran concentrations were determined by a Waters' differential refractometer. The NaCl concentrations were determined potentiometrically in a cell essentially similar to the diffusion cell, but adapted to a half-micro scale. The cell potential (with the unknown solution in one chamber) was measured against reference solutions of different concentrations and the concentration corresponding to zero cell potential was obtained by interpolation. In both cases an accuracy better than 0.5% was obtained.

Materials. Cellophane, dialysis tubing from Union Carbide Corp., Chicago. Dextran, molecular weight $M_w = 110\,000$, from Pharmacia, Uppsala, Sweden. Sodium chloride, reagent grade, from E. Merck, Darmstadt. Doubly distilled water was used throughout the experiments.

RESULTS AND DISCUSSION

Measurements have been carried out with untreated cellophane (M0) and two carboxymethylated cellophane membranes (M1 and M2). Characteristic data of the membranes are listed in Table 1.

Data from the partition experiments are listed in Table 2. Plots according to eqn. (25) are shown in Figs. 1–3. Although the plots are linear at high salt concentrations (low x -values), pronounced deviations from linearity occur at low salt concentrations. It is of interest to note that the deviation from linearity is in the opposite direction to that observed with polyelectrolyte solutions.⁹ A conceivable reason for this discrepancy may be found in the fact that a gel may exhibit permanent spacial heterogeneities, whereas a solution is perfectly homogeneous (in the time average). Implications of

Table 1. Data characterizing the membranes. w_3 is the mass fraction of the membrane lattice, ρ is the density of the membrane phase, C_{av} is the experimentally determined charge density and d is the thickness of the membrane.

	M0	M1	M2
Equiv. weight of the lattice	105 000	8300	2960
w_3	0.4213	0.3872	0.2775
ρ (g cm ⁻³)	1.182	1.168	1.118
C_{av} (equiv. dm ⁻³)	0.0047	0.0545	0.1048
d (cm)	0.0135	0.016	0.021

this effect on ion exchange equilibria have previously been considered.¹¹⁻¹³ Taking this effect into account in the present treatment, we observe that the experimentally determined partition coefficient K_{av} is the volume average of the local partition coefficient K :

$$K_{av} = \frac{1}{V} \int_V K dV \quad (26)$$

where $K = \bar{c}/c$ and V is the volume of the gel.

In a charged gel K is essentially a function of the local charge density C . If this function $K(C)$ is nonlinear, K_{av} is not directly related to the average charge density C_{av} and deviations from the simple Donnan law may occur. By postulating a statistical distribution for the variation of C within the gel the integral in eqn. (26) can be evaluated and K_{av}

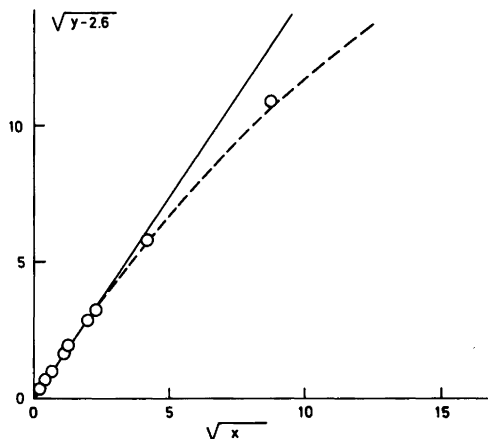


Fig. 1. NaCl sorption data plotted according to eqn. (25) for membrane M0. Broken curve represents eqn. (39) for $\phi = 0.06$.

determined. In Appendix II this is done for a two-point distribution ($C=C_0$ and $C=C_1$ for volume fractions ϕ and $1-\phi$, respectively), which represents the simplest possible model for a heterogeneous gel. The resulting expression for K_{av} , eqn. (39), has been compared with the experimental data in Figs. 1-3. By adjusting the parameter ϕ , almost quantitative agreement with experiments is obtained. The rather low values of ϕ , listed in Table 3, indicate that the postulated membrane heterogeneity is maintained on a realistic level. The membrane heterogeneity was considered to have

Table 2. Data on NaCl sorption equilibria. c is the concentration of NaCl in the external solution and K_{av} is the experimentally determined partition coefficient.

M0		M1		M2	
c 10 ³ mol dm ⁻³	K_{av}	c 10 ³ mol dm ⁻³	K_{av}	c 10 ³ mol dm ⁻³	K_{av}
0.6760	0.091	0.7563	0.030	0.5706	0.028
1.600	0.167	1.438	0.050	0.7310	0.020
3.082	0.276	3.808	0.087	2.514	0.046
3.962	0.303	6.990	0.152	4.150	0.072
6.715	0.399	10.13	0.168	4.632	0.085
7.960	0.431	21.02	0.259	8.714	0.131
8.437	0.443	24.85	0.312	14.43	0.176
19.36	0.525	43.25	0.409	22.10	0.237
43.06	0.567	47.04	0.445	23.87	0.228
69.60	0.603	123.1	0.532	28.25	0.264
92.90	0.593	198.5	0.569	49.46	0.365
124.0	0.604			72.98	0.420
				141.6	0.513

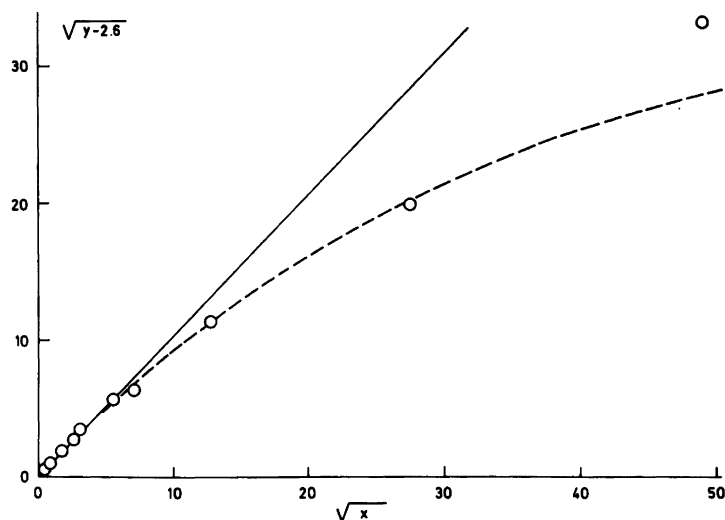


Fig. 2. NaCl sorption data plotted according to eqn. (25) for membrane M1. Broken curve represents eqn. (39) for $\phi = 0.04$.

no further effects on the transport properties of the membrane.

The diffusion experiments were carried out with NaCl solutions having the initial concentrations $c' = c$ and $c'' = \frac{2}{3}c$. The mean concentration in the membrane \bar{c}_θ was computed from the mean external concentration $\langle c \rangle = \frac{1}{2}(c' + c'')$ by eqn. (39), using the ϕ -value of the membrane concerned.

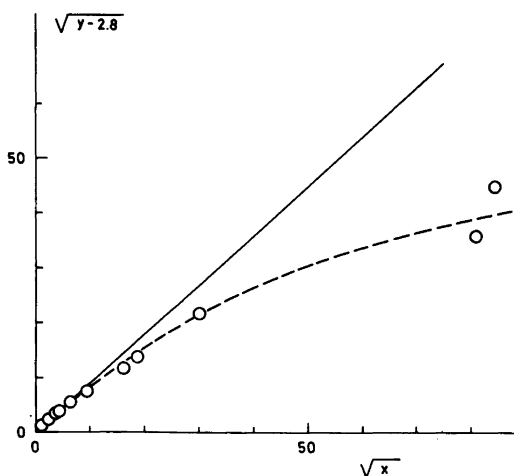


Fig. 3. NaCl sorption data plotted according to eqn. (25) for membrane M2. Broken curve represents eqn. (39) for $\phi = 0.03$.

The activity coefficients were computed by the equation¹⁴

$$\log \gamma_{\pm} = -\frac{0.5091 \sqrt{c}}{1 + 1.315 \sqrt{c}} + 0.0521 c \quad (27)$$

The experimental data and the computed diffusion coefficients for the different membranes are listed in Tables 4–6.

The ratio D_+/D_- was obtained by dividing $(D_+ \bar{c}_+ / D_- \bar{c}_-)_\theta$ with the ratio of the stoichiometric concentrations:

$$\left(\frac{\bar{c}_+}{\bar{c}_-}\right)_\theta = 1 + \frac{C}{\bar{c}_\theta} \quad (28)$$

The D_+/D_- -values for the different membranes are very similar and are represented in a common plot in Fig. 4. It is interesting to note that at low salt concentrations the ratio D_+/D_- decreases

Table 3. Parameters characterizing NaCl sorption equilibria. b and α refer to eqn. (24), ϕ to eqn. (39).

	M0	M1	M2
b	2.6	2.6	2.8
α	0.85	0.392	0.286
ϕ	0.06	0.04	0.03

Table 4. Diffusion data for membrane M0.

$\langle c \rangle 10^3$ mol dm ⁻³	$\bar{c}_\theta 10^3$ mol dm ⁻³	E mV	$j 10^9$ mol cm ⁻² s ⁻¹	$D_- 10^6$ cm ² s ⁻¹	$\left(\frac{D_+ \bar{c}_+}{D_- \bar{c}_-}\right)_\theta$	$\frac{D_+}{D_-}$	$D 10^6$ cm ² s ⁻¹
0.2080	0.0114	19.72	0.0017	2.62	20.87	0.051	0.25
0.6934	0.0663	19.23	0.0099	2.69	14.72	0.205	0.92
1.387	0.2091	18.54	0.0331	2.96	9.82	0.418	1.75
2.312	0.498	16.88	0.0704	2.90	4.91	0.470	1.85
3.467	0.973	15.49	0.129	2.97	3.27	0.561	2.13
6.934	2.769	12.65	0.285	2.82	1.715	0.636	2.19
9.245	4.094	11.44	0.390	2.89	1.347	0.627	2.23
13.87	6.847	10.42	0.573	2.79	1.111	0.659	2.22
30.82	17.23	9.16	1.281	2.81	0.886	0.696	2.31
46.23	26.17	8.45	2.02	3.17	0.775	0.657	2.51
92.45	55.37	7.67	4.05	3.31	0.667	0.615	2.52
214.2	130.9	7.71	10.1	3.48	0.672	0.649	2.74

Table 5. Diffusion data for membrane M1.

$\langle c \rangle 10^3$ mol dm ⁻³	$\bar{c}_\theta 10^3$ mol dm ⁻³	E mV	$j 10^9$ mol cm ⁻² s ⁻¹	$D_- 10^6$ cm ² s ⁻¹	$\left(\frac{D_+ \bar{c}_+}{D_- \bar{c}_-}\right)_\theta$	$\frac{D_+}{D_-}$	$D 10^6$ cm ² s ⁻¹
1.563	0.0792	20.06	0.0100	2.59	58.48	0.085	0.41
3.365	0.270	19.85	0.042	3.22	51.77	0.255	1.31
6.250	0.784	19.14	0.124	3.40	20.83	0.295	1.55
13.46	3.004	18.16	0.432	3.26	11.03	0.576	2.38
20.83	6.200	16.56	0.817	3.27	5.363	0.548	2.32
31.25	11.54	15.21	1.413	3.31	3.547	0.620	2.53
46.62	20.21	13.65	2.40	3.58	2.393	0.647	2.81
69.93	34.03	12.16	3.77	3.74	1.718	0.660	2.97
93.75	48.47	11.10	5.20	3.97	1.375	0.647	3.12
187.5	106.1	9.68	10.8	4.31	1.022	0.675	3.47
349.7	206.5	8.47	22.1	5.21	0.774	0.612	3.96

Table 6. Diffusion data for membrane M2.

$\langle c \rangle 10^3$ mol dm ⁻³	$\bar{c}_\theta 10^3$ mol dm ⁻³	E mV	$j 10^9$ mol cm ⁻² s ⁻¹	$D_- 10^6$ cm ² s ⁻¹	$\left(\frac{D_+ \bar{c}_+}{D_- \bar{c}_-}\right)_\theta$	$\frac{D_+}{D_-}$	$D 10^6$ cm ² s ⁻¹
0.9161	0.0265	19.91	0.0029	2.97	34.0	0.0086	0.05
3.615	0.2132	19.80	0.0374	4.78	47.4	0.096	0.84
5.497	0.4376	19.72	0.0835	5.22	51.9	0.216	1.85
14.46	2.456	19.05	0.427	4.92	26.0	0.595	3.67
18.32	3.725	18.28	0.693	5.49	12.93	0.444	3.38
28.92	8.043	17.38	1.330	5.13	8.10	0.577	3.75
40.72	13.74	16.22	2.33	5.64	5.10	0.591	4.19
82.45	36.65	13.80	5.83	6.22	2.558	0.663	4.96
164.9	84.85	11.55	13.4	7.38	1.522	0.681	5.98
274.8	150.1	10.33	24.8	8.63	1.155	0.680	6.99

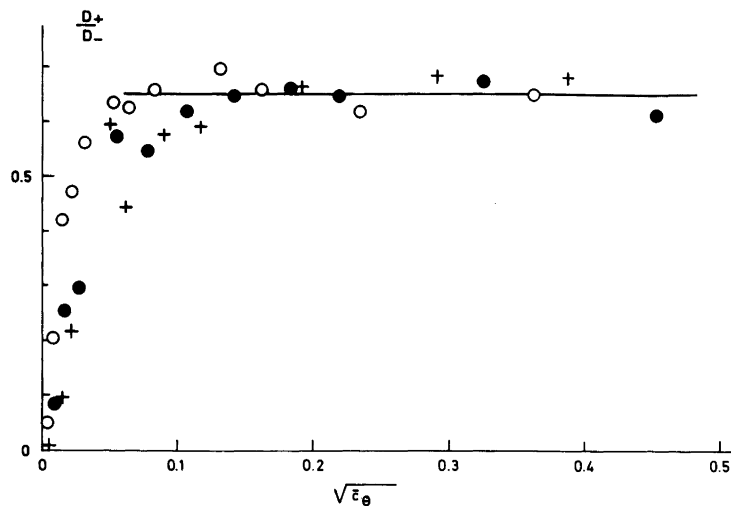


Fig. 4. Dependence of D_+/D_- on the mean concentration in the membrane. Open circles for M0, filled circles for M1 and crosses for M2.

sharply, indicating a decrease in the mobility of the counterions in this region. The reason for this is probably an increased electrostatic trapping of the counterions to the locations of the fixed charges. At higher concentrations this ratio is constant, indicating that no counterion binding occurs in this region. From this plateau region we obtain the average value $D_+/D_- = 0.65$, common for all membranes. This corresponds to a cation transference number $t_+ = 0.394$, which is very close to the t_+ -value for NaCl in aqueous solution¹⁵ ($t_+^0 = 0.3963$).

It is of interest to compare these findings with the counterion condensation effect, considered in connection with partition equilibria. In the latter case the parameter α , representing the degree of ionization, was practically independent of salt concentration and decreased with increasing charge density of the membrane. Obviously the transport properties are not consistent with a model where the condensed counterions (the fraction $1 - \alpha$) are firmly bound to the fixed charges in the region of high salt concentrations. Either the condensed counterions are completely mobile, or the parameter α should

* For a 1:1 electrolyte the cation transference number is $t_+ = D_+ \bar{c}_+ / (D_+ \bar{c}_+ + D_- \bar{c}_-)$. According to eqn. (28) this relation reduces to $t_+ = \frac{D_+}{D_-} / (1 + \frac{D_+}{D_-})$ at high salt concentrations.

be interpreted as an effect of the activity coefficient. Theoretical considerations favour the latter interpretation, since in all membranes the charge density parameter ζ is lower than unity, which is the critical limit for condensation.^{4,5}

In Fig. 5 the coion diffusion coefficient D_- is represented as a function of salt concentration in the membrane. The diffusion coefficient is seen to increase with increasing salt concentration. This is contrary to the behaviour in solution and may possibly be due to heterogeneities in the membrane, analogous to the effect considered in connection with partition equilibria. The diffusion coefficient, D_- , also increases with increasing charge density. This is most probably due to an increased swelling of the membranes.

The ionic diffusion coefficients may be combined to yield the diffusion coefficient of the salt:¹⁶

$$D = \frac{2D_+D_-}{D_+ + D_-} \quad (29)$$

D -values computed by this equation are listed in Tables 4–6. The diffusion coefficients are seen to decrease at low salt concentrations because of increased counterion trapping. It should be noted that this effect is additional to the decrease in diffusion flux caused by increasing salt exclusion at low salt concentrations. The latter effect is inherently

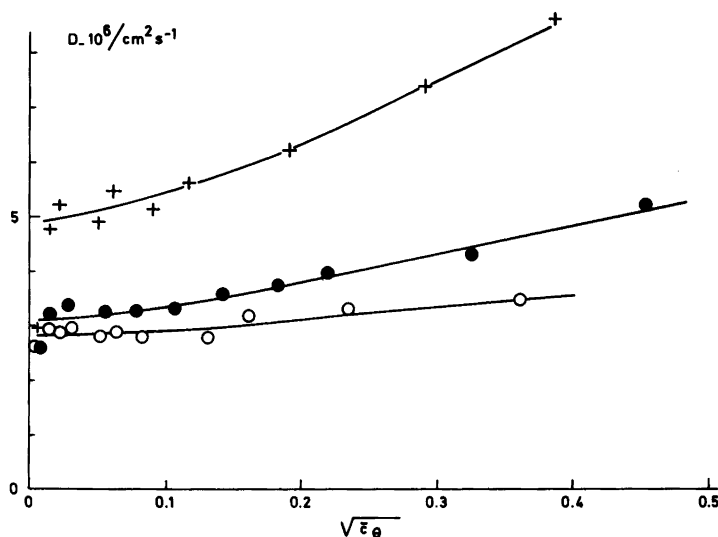


Fig. 5. Dependence of the coion diffusion coefficient on the mean concentration in the membrane. Open circles for M0, filled circles for M1 and crosses for M2.

taken into account when dividing eqn. (14) by \bar{c}_θ .

It should further be noted that cellophane, which is normally considered to be uncharged, clearly behaves as a charged membrane at sufficiently low salt concentrations. As such it becomes almost impermeable to salt at low concentrations. This is of practical importance as it implies that it is virtually impossible to remove all traces of salt from a solution by dialysis through cellophane membranes.

APPENDIX I

To determine the diffusion flux from the time dependence of the cell potential we take the time derivative of eqn. (13). For a 1:1 electrolyte we obtain

$$\frac{dE}{dt} = -2 \frac{RT}{F} \left[1 + \frac{D_- \bar{c}_-}{D_+ \bar{c}_+} \right]_{\theta'}^{-1} \left[\frac{1}{c''} \frac{dc''}{dt} - \frac{1}{c'} \frac{dc'}{dt} + \frac{d}{dt} \left(\ln \frac{\gamma_{\pm}''}{\gamma_{\pm}'} \right) \right] \quad (30)$$

Using eqn. (27) for the activity coefficient we obtain

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$$\frac{d \ln \gamma_{\pm}}{dt} = \Phi(c) \frac{dc}{dt} \quad (31)$$

where

$$\Phi(c) = - \ln 10 \left[\frac{0.5091}{2(1 + 1.315 \sqrt{c})^2 \sqrt{c}} - 0.0521 \right] \quad (32)$$

For a symmetric diffusion cell we have the mass balance equation

$$\frac{dc''}{dt} = - \frac{dc'}{dt} = 10^3 \frac{S}{V} j \quad (33)$$

where S (cm^2) and V (cm^3) are the membrane area and the solution volume in one half-cell, respectively.

Substituting from eqns. (31)–(33) into (30), and dividing by E , eqn. (13), we finally obtain

$$\frac{d \ln E}{dt} = \frac{10^3 S j}{V \ln (a_{\pm}''/a_{\pm}')} \left[\frac{1}{c'} + \frac{1}{c''} + \Phi(c') + \Phi(c'') \right] \quad (34)$$

Thus, from the initial slope of a plot of $\ln E$ v. t the diffusion flux j can be determined, since all other quantities in the right member of (34) are known.

APPENDIX II

From the definition of K and eqns. (22)–(24) we obtain

$$K^{-2} = y = b + b\alpha \frac{C}{Kc} \quad (35)$$

Solving for K we obtain

$$K = -\frac{\alpha C}{2c} + \sqrt{\left(\frac{\alpha C}{2c}\right)^2 + \frac{1}{b}} \quad (36)$$

If, for the volume fraction ϕ of the gel $C = C_0$, and $C = C_1$ for the rest, we have

$$C_{av} = \phi C_0 + (1 - \phi) C_1 \quad (37)$$

and

$$K_{av} = \phi K_0 + (1 - \phi) K_1 \quad (38)$$

K_0 and K_1 are obtained from eqn. (36) using appropriate values of the parameters b and α .

For simplicity we put $C_0 = 0$. Then, to obtain K_0 from (36), only b_0 has to be known. As the parameter b does not vary appreciably with C , we may use for b_0 the value obtained for untreated cellophane ($b_0 = 2.6$). In the region of charge density C_1 , b_1 and α_1 are assumed to be equal to the values determined for the homogeneous model (obtained from the linear part of the plot for the particular membrane). From eqns. (36)–(38) we thus obtain

$$K_{av} = \frac{\phi}{\sqrt{b_0}} + (1 - \phi) \left[-\frac{\alpha_1 C_{av}}{2c(1 - \phi)} + \sqrt{\left(\frac{\alpha_1 C_{av}}{2c(1 - \phi)}\right)^2 + \frac{1}{b_1}} \right] \quad (39)$$

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