Transport from an Aqueous Phase through Cellulosic Gels and Membranes

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Synopsis

Diffusion of some homologous series of solutes [polyhydric alcohols, oligosaccharides, poly(ethylene oxide) polymers] has been studied in cellulose gels (<20% w/w) and membranes (<60% w/w) and the same materials when acetylated. It was found that (1) The molecular weight dependence of D approximates that for the solutes in water alone; the activation energies are also identical to the value for diffusion in pure solvent. (2) The presence of the cellulose chains reduces the rate of diffusion to a degree which is approximately given by the Mackie–Meares equation. (3) Exclusion is pronounced, particularly with the acetylated membranes, and gives a high degree of molecular size discrimination by a sieving mechanism. The membranes have a very narrow range of "pore" sizes, whereas the gels have a contrastingly broad distribution.

INTRODUCTION

In spite of the unique importance of cellulosic gels and membranes in biological systems and numerous industrial processes, few broad studies have been made of the transport of low-molecular-weight solutes in such materials. Cellulosic membranes have, of course, been the subject of many studies concerned with the relative rates of permeation of ionic compounds, but a more general approach to diffusion in these systems is lacking. While NMR spin echo techniques are invaluable for examining solvent mobility (and also that of solutes fitting stringent requirements), it was considered pertinent to also use a generally applicable sorption technique described previously. This method allows simultaneous evaluation of the partitioning of the solute between solution and gel phases (exclusion) which can be an illuminating feature in understanding the transport process as molecular size changes with a given solute type. Parameters such as gel polymer concentration and character (acetylation) are examined, as well as solute molecular weight, solute character, and the influence of temperature.

This investigation forms part of a comprehensive study of molecular transport in cellulosic systems conducted together with the Swedish Forest Products Research Laboratory, Stockholm, Sweden.

EXPERIMENTAL

The gel disc to be investigated (diameter 45 mm, thickness 2.0 mm) was mounted in a Plexiglas cell of a prior description.[1] When membranes were to be studied, the cell was first filled with water. The membrane was then sandwiched between the liquid surface and the stainless mesh of the cell cover which made point contacts only with the membrane surface.

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An interval of 24 h was used for equilibration of the cell and contents against a large volume of the solvent to be used in the experiment. Since the latter were typically 12–15 h of duration, all measurements were made in a constant-temperature room (23.5°C) with the apparatus thermostated at 25.00°C; this was found to be essential to eliminate significant signal drift.

The solute concentration was 3 mg/ml at the start of each experiment, a concentration which was known to fall within the linear region of the refractive index–response relationship of the monitor. As observed previously[1] and also checked for the present systems, the diffusion and partition coefficients are essentially independent of concentration within the interval employed.

Data Acquisition

The refractive index of the solution outside the diffusion cell was monitored continuously with a Waters model 403 differential refractometer, and the resulting analog signal was converted to a digital signal via a dual-slope panel meter at a rate of 4 Hz.

The data were smoothed by integrating the results obtained within a predetermined interval (usually 300 s) and dividing by the interval length. This average value was then used as representative for the value at midinterval. In Appendix 1 it is shown that the correct placement of this average value within a 300-s interval should be 149 s after the start of the interval. This 1-s displacement has virtually no effect on the relaxation time of the exponential function appropriate to this experiment, nor does it affect the asymptotic value.

Preparation of Gels

The cellulose gels were prepared* by a carefully controlled regeneration of cellulose from viscose without use of a crosslinking agent. The cellulose membrane is Visking, from Union Carbide Inc., New Jersey.

Acetylation was made[2] on gel and membrane following equilibration in dry pyridine until water free with a 50:50 pyridine:acetic anhydride mixture (components dried over molecular sieves) at 50°C for 12 h under N_2. The degree of acetylation was 1.40:

Material	% w/w	Volume fraction polymer ϕ
Cellulose gel	15.0	0.10_6
Acetylated gel (D.S. = 1.40)	20.5	0.13_7
Cellulose membrane	41.1	0.30
Acetylated membrane (D.S. = 1.40)	58.8	0.44

The polyhydric alcohols and oligosaccharides were analytical-grade reagents (Sigma) and poly(ethylene oxides) from Merck (chromatography grade). The

* The authors are indebted to Drs. Tom Lindström and Lennart Westman, Swedish Forest Products Laboratory, Stockholm, for these materials.

molecular weights of the latter (vapor pressure osmometry) are given below:

Nominal	$\overline{M}_n$[a]	Nominal	$\overline{M}_n$[a]
PEG 200	216	1,000	959
300	300	1,500	—
400	417	4,000	4,500
600	620	5,700	—
		20,000	13,600

[a] Values from Ref. 3.

THEORY

Analysis of Data

The variation of refractive index of the external solution with time is described by the model

$$Y = A + B \exp(-Ct) \tag{1}$$

for both the gel experiments[4,1] and the membrane experiments,[5] where Y is the monitored solution refractive index and t is the time; A is the asymptotic value of the solution refractive index, B is a function of the external solution volume and the gel or membrane volume and cell volumes, as well as a partition coefficient reflecting availability of the gel or membrane volume to a given solute; and C is a term containing the diffusion coefficient. The interpretation of these numerical parameters is described separately for gel and membrane experiments below.

Although eq. (1) is nonlinear in parameters A, B, and C, a least-squares analysis of the experimental data is facilitated by a constant sampling interval. In this case, a linear model may be used, having the form

$$Y_{i+\delta} = Y_i \exp(-C\ \Delta t) + A[1 - \exp(-C\ \Delta t)]$$

described as method III in Ref. 6. In essence, it involves regressing a later portion of the data on an early portion. Data points are paired with a constant time displacement (Δt) using Y_i as the abscissa and $Y_{i+\delta}$ (displaced δ points from Y_i and a time interval Δt from it) as the ordinate. These data pairs yield a straight line with slope $\exp(-C\ \Delta t)$ and intercept $A[1 - \exp(-C\ \Delta t)]$. The constant time interval between data pairs is conveniently chosen as the estimated half-time of the process. For example, if the half-time of the process being analyzed appears to cover approximately 20 data, one would plot datum 21 vs. datum 1, datum 22 vs. datum 2, etc. The number of data used in the analysis were restricted to those lying significantly above the asymptote (those recorded within the first five half-times).

In order to avoid the influence of the higher terms in eq. (3) (see below), data recorded during the first half-time were disregarded. Consequently, the analysis typically comprised points 20 to 100 with a 20-unit interval. For the gel experiments, the standard deviation in the estimation of C (standard error of estimate) is 0.9% of C, and the corresponding 95% confidence interval is ±1.7% of C. In the case of the membrane experiments, the corresponding relative uncertainty in C is 0.2_2%, with 95% confidence limits at ±0.43% of C.

Since D is directly proportional to C, the gel and membrane diffusion coefficients are considered to lie, with 95% confidence, within ±2 and ±1%, respectively, of the true values.

Interpretation of Numerical Parameters in Gel Experiment

As shown in Ref. 1, the concentration (or any property directly proportional to the concentration) of solute in the solution external to the gel may be described as a function of time by

$$C = C_\infty \left[1 + \frac{2(1+\lambda)}{1+\lambda+\lambda^2 q_1^2} \cdot \exp\left(\frac{-q_1^2 D}{L^2} \cdot t\right)\right] \tag{2}$$

where λ is (external solution volume)/($V_i \cdot K$), V_i is gel volume times (1 − vol. fraction of polymer in gel), K is fraction of solvent volume within the gel, available to a given solute, L is gel thickness, D is diffusion coefficient, and q_1 is first root of $\tan(q) + \lambda q = 0$.

Comparison of eq. (2) with the numerical model (1) shows that

$$A = C_\infty$$

$$\frac{B}{A} = \frac{2(1+\lambda)}{1+\lambda+\lambda^2 q_1^2}$$

$$C = \frac{q_1^2 D}{L^2}$$

One first determines K, which influences both λ and q_1, from B/A and then determines D from C. The evaluation of K is easily achieved by plotting K vs. $2(1+\lambda)/(1+\lambda+\lambda^2 q_1^2)$ for K values between 0.5 and 2.0. This plot is well represented by a second-order equation:

$$K = a_0 + a_1\left(\frac{B}{A}\right) + a_2\left(\frac{B}{A}\right)^2$$

The a_0, a_1, and a_2 values were determined for the two gels used (cellulose gel and cellulose acetate gel). B/A for an experiment yields K and hence λ and q_1; one then obtains D from C. A K value greater than 1 indicates chemical affinity between gel and solute, while a K less than 1, in the absence of chemical affinity, defines the degree of accessibility of the internal volume of the gel.

Membrane Experiments

The membrane and gel experiments are similar, but there are two volumes external to the membrane: volume$_1$ enclosed within the diffusion cell by the membrane and consisting of pure solvent at the start of the experiment, and volume$_2$, which is external to the diffusion cell. Volume$_2$ alone contains probe at the start of the experimental.

The relevant equations have been derived by Spacek and Kubin:[5]

$$\frac{C_2 - C_1}{C_0} = \sum_{i=1}^{\infty} 4\alpha[q_i^2 + \alpha(2+\alpha)]^{-1} \exp\left(\frac{-q_i^2 D t}{L^2}\right) \tag{3}$$

where α is $(\alpha_1 + \alpha_2)/2$, α_1 is $V_{mem}K/V_1$, $\alpha_2 = V_{mem}K/V_2$, V_{mem} is membrane

volume, V_1 is volume$_1$ (see above), V_2 is volume$_2$, K is fraction of membrane volume available to a given solute, L is membrane thickness, D is diffusion coefficient, and q_i is the *ith* root of tan $(q) - 2\alpha \cdot q/(q^2 - \alpha^2) = 0$. (4)

Equations (3) and (4) utilize the mean α and are accurate descriptions of the transport behavior for $\alpha_2/\alpha_1 = 1$. An error of approximately 5–6% is introduced when α_2/α_1 increases to 2. In this investigation, the ratio was 1.17.

One cannot conveniently measure C_1, but introduction of the expression for mass balance into eq. (3) yields

$$C_2 = C_\infty \left[1 + \alpha_2 \left(\frac{1}{\alpha_1} + \frac{1}{2}\right) \sum_{i=1}^{\infty} \frac{4\alpha}{(q_i^2 + \alpha\,(2 + \alpha))} \exp\left(-\frac{q_i^2 Dt}{L^2}\right)\right] \tag{5}$$

In the summation in eq. (5), terms beyond the first are negligible shortly after the start of the experiment, and eq. (5) reduces to

$$C_2 = C_\infty \left\{1 + \frac{\alpha_2 \left(\frac{1}{\alpha_1} + \frac{1}{2}\right) 4\alpha}{q_1^2 + \alpha(2 + \alpha)} \exp\left(-\frac{q_1^2 Dt}{L^2}\right)\right\} \tag{6}$$

Comparing eq. (6) with the numerical model (1), one finds

$$A = C_\infty$$

$$\frac{B}{A} = \alpha_2 \left(\frac{1}{\alpha_1} + \frac{1}{2}\right) 4\alpha[q_1^2 + \alpha(2 + \alpha)]^{-1}$$

$$C = \frac{q_1^2 D}{L^2}$$

allowing, in principle, evaluations of K, q, and D. However, owing to the very small volume of the membrane in comparison with V_1 and V_2, a small change in B/A corresponds to a large change in K, and the uncertainty in B/A leads to a large scattering in the estimated K (and q_1). The following empirical relationships were thus used to obtain K from the experimental parameter C:

$$\lg K = \lg\left(\frac{C}{D_0}\right) + 4.44 \qquad \text{(cellulose membrane)} \tag{7a}$$

$$\lg K = \lg\left(\frac{C}{D_0}\right) + 4.58 \qquad \text{(acetylated cellulose membrane).} \tag{7b}$$

The constants of eqs. (7a) and (7b) were evaluated as follows: q_1^2 in $C = q_1^2 \cdot (D/L^2)$ is replaced by a function of K obtained through solution of eq. (4) for selected values of K:

$$K = 31.0 \times q_1^2$$

Assuming only that the exponent a in $D = kM^a$ is a constant for a particular homologous series–solvent system, as has been experimentally verified for a series of gels,[1] linear plots of lg (C/D_0) vs. M yield the constant terms. The latter are determined as the abscissae at the molecular weight of water since K equals unity by definition for the solvent itself.

RESULTS AND DISCUSSION

Molecular Weight Dependence of Diffusion

Figure 1 illustrates the dependence of the diffusion coefficient on molecular weight for the homologous series of polyhydric alcohols in the various systems. The slope in each case is indistinguishable from that characterizing free diffusion in water alone. Similar results were obtained for the oligosaccharides (Fig. 3) and poly(ethylene oxide) polymers (Fig. 4). The inference here, as observed previously for polyacrylamide gels,[1] is that the frictional interactions derive only from the solute–solvent pair, the presence of polymer chains simply serving to impose a more tortuous, and thus longer, path for the diffusing particle. It may be pointed out here that the parallelism in Figures 1, 3, and 4 is maintained as solute size increases within a given series due to the effect of the progressive increase in exclusion being taken into account by the equilibrium partition coefficient K. If K were assigned a value of unity throughout a series, the diffusion coefficient, as calculated from eq. (2), respectively eq. (6) (theory section), would fall off rapidly with increasing size, particularly with the membranes for which molecular exclusion is pronounced. K enters eqs. (2) and (6) in the definition of the effective volume ratio λ for the gel and α for membrane, where KV_i (respectively KV_{mem}) is the volume available to a given solute within the gel or membrane. Alternatively, since the thickness dimension L is fixed, this corresponds to an available cross-sectional area within the gel/membrane perpendicular to the concentration gradient.

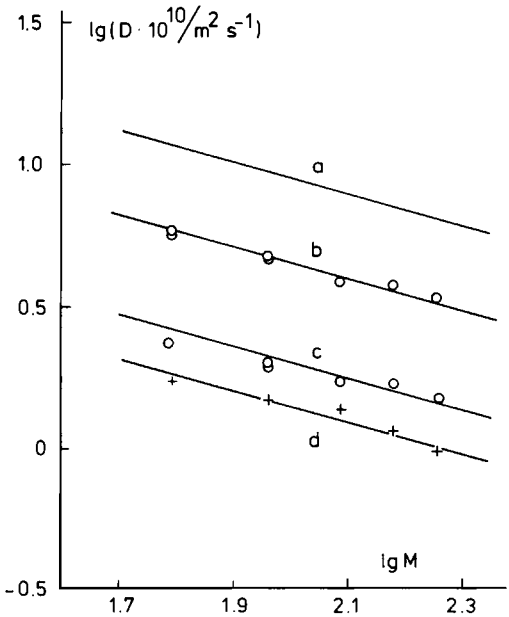

Fig. 1. Molecular weight dependence of the diffusion coefficient for polyhydric alcohols (ethylene glycol through mannitol): (a) free diffusion in water; (b) cellulose gel; (c) cellulose membrane; (d) acetylated cellulose membrane.

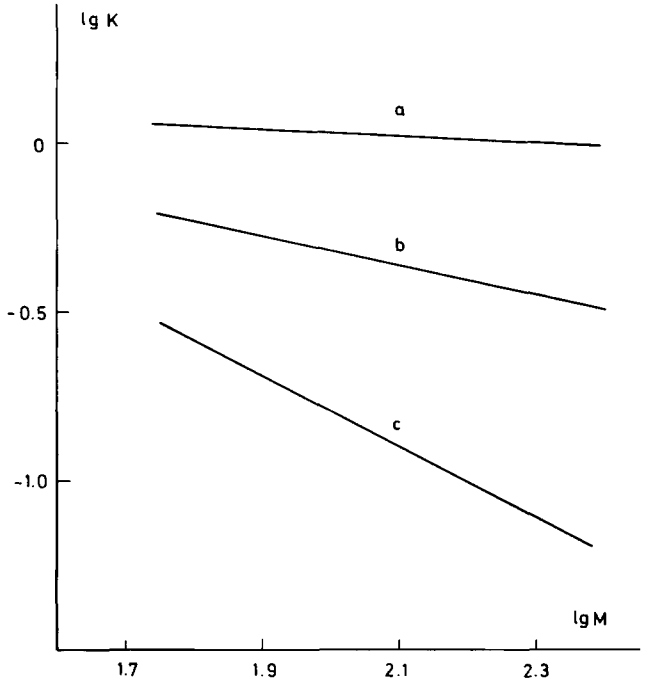

Fig. 2. Partition coefficient K as function of molecular weight for polyhydric alcohols on: (a) cellulose gel, (b) cellulose membrane, and (c) acetylated cellulose membrane.

The Ratio D/D_0

According to various obstruction theories, such as those of Wang,[7] Mackie and Meares,[8] and Prager,[9] the ratio D/D_0 is a constant for a particular gel or membrane composition. The expression of Mackie and Meares[8] has been found to fit the experimental data well:

$$\frac{D}{D_0} = \left(\frac{1-\phi}{1+\phi}\right)^2 \tag{8}$$

so that, if there are no specific interactions between polymer and a given solute, this ratio is defined only by a simple function of the polymer content. This appears to be the case for a variety of solutes diffusing in the acetylated gel and membrane (Fig. 5). The broken line is drawn according to eq. (8). With the nonacetylated cellulose gel/membrane, the experimental points fall below this line (Fig. 6), indicating that, while the solute interactions with the gel are small, they are not negligible. Using the same solutes, a similar effect was observed[1] with polyacrylamide gels, although the interactions are there more pronounced.

The "nonselectivity" of the cellulosic materials for these solutes, varying substantially in polarity, is noteworthy and indicates that a straightforward "sieving" mechanism is operative. Furthermore, the function of cellulose acetate membranes as desalination barriers clearly does not derive from a reduction in the diffusion coefficient by virtue of specific interactions between the acetate moieties and the ionic species, but rather is a consequence of a sterically determined exclusion. The diffusion coefficients for water in the gels/membranes

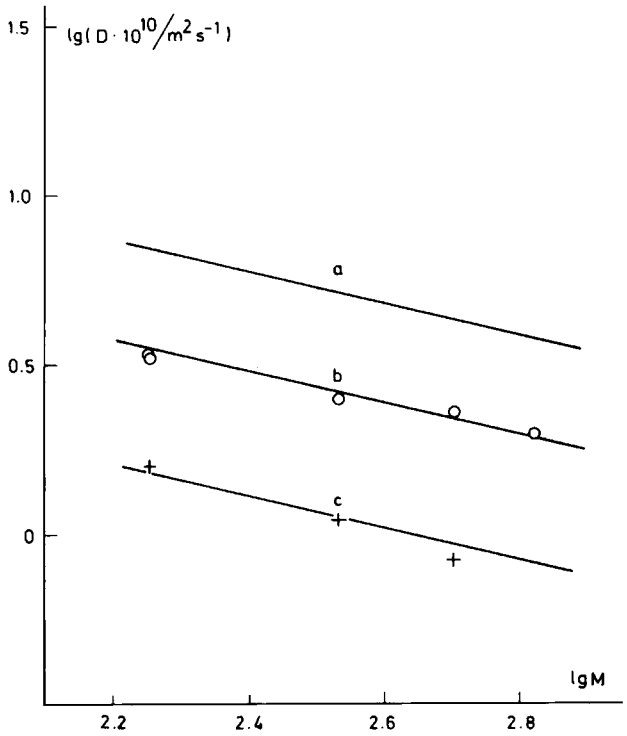

Fig. 3. Molecular weight dependence of diffusion for polyethylene oxide polymers: (a) free diffusion; (b) cellulose gel; (c) cellulose membrane.

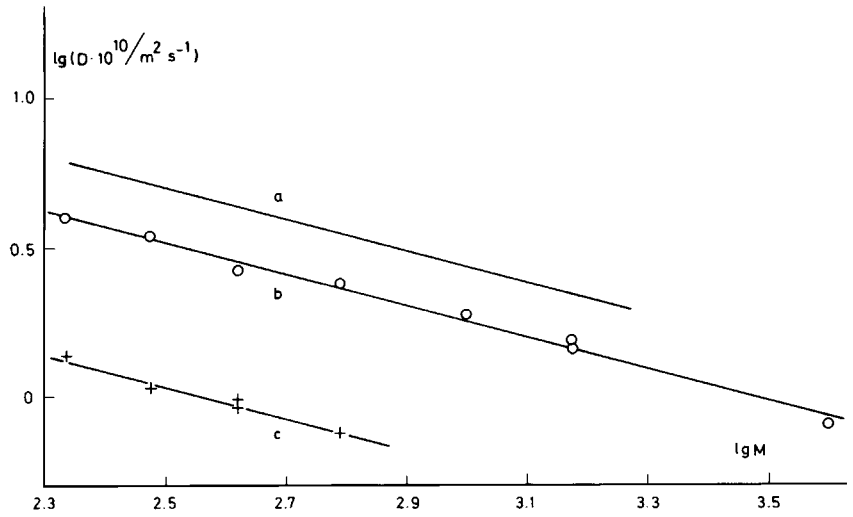

Fig. 4. Molecular weight dependence of diffusion for oligosaccharides (glucose through stachyose): (a) free diffusion; (b) cellulose gel; (c) cellulose membrane.

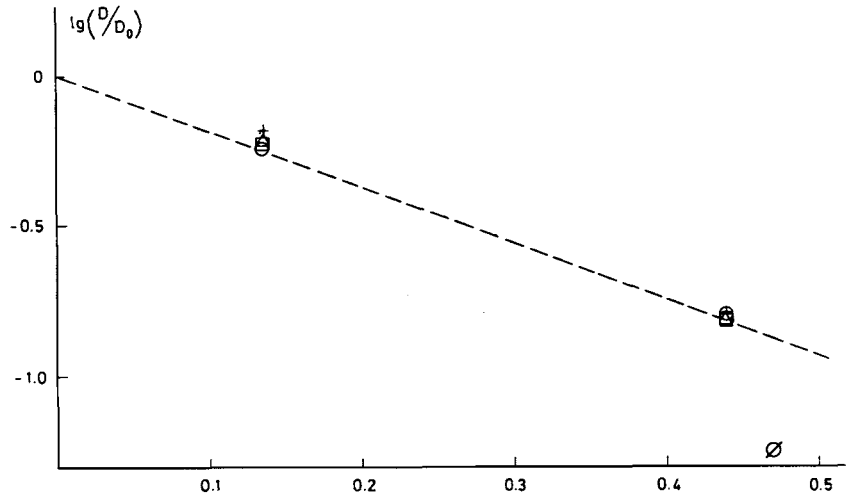

Fig. 5. Diffusion ratio (D/D_0) as function of polymer volume fraction for PEG 200 (+), mannitol (△), glucose (□), and LiCl (○) in the acetylated cellulose gel ($\phi = 0.14$) and the acetylated cellulose membrane ($\phi = 0.44$). Broken line is according to eq. (8).

listed in Table I for comparison purposes have been obtained using the D/D_0 ratio corresponding to the material in question. NMR spin echo measurements[10] show that the water mobility is reduced by the same factor.

Molecular Exclusion

In the definition of λ, eq. (2), the water content (V_i) replaces the volume of the gel phase employed previously.[1] Here, K takes a maximum values of unity (with no adsorption) for the smallest solutes (and water itself by definition) having accessibility to the whole internal volume of the gel phase. The values of K, obtained as described in the theory section, are listed in Table I. From

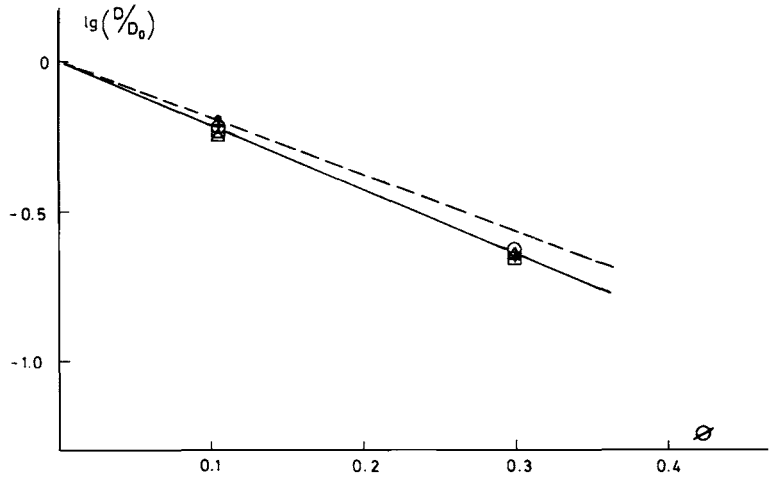

Fig. 6. Diffusion ratio (D/D_0) as function of polymer volume fraction for PEG 200 (+), mannitol (△), glucose (□), and LiCl (○) in the cellulose gel ($\phi = 0.11$) and the cellulose membrane ($\phi = 0.30$). Broken line is according to eq. (8).

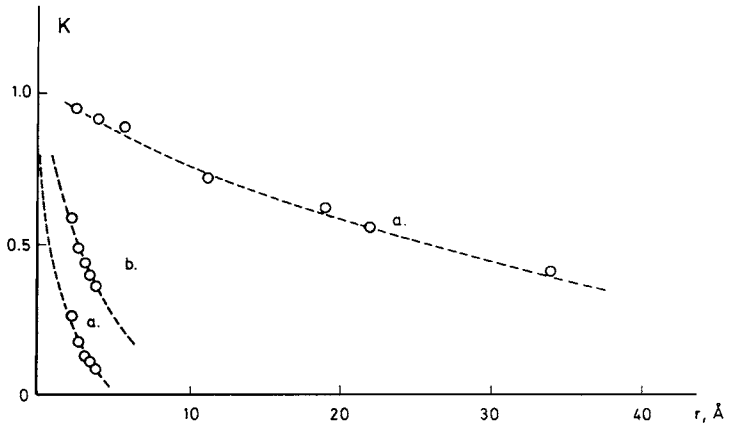

Fig. 7. Partition coefficient K as function of the Stokes' radius of the solute for (a) cellulose gel (polyethylene oxides), (b) cellulose membrane (polyhydric alcohols), and (c) acetylated cellulose membrane (polyhydric alcohols).

the latter, it is seen that the cellulose gel contains a very wide spectrum of "pore" sizes, about 38% of the internal volume being accessible to particles of 34 Å radius (the latter dimension is the Stokes' radius from the free diffusion coefficient) (Table II). The structural arrangement of the network strands in regenerated cellulose is complex since "crystallites" are considered to form on regeneration. If this is the case, there will be a heterogeneous distribution of segments and consequently a broader spectrum of "hole" sizes than would be the case with the corresponding homogeneous distribution.

Nevertheless, the partition coefficients show that essentially all of the water

TABLE I
Summary of Diffusion and Partition Coefficients in the Various Systems at 25°C (Solvent–Water)

Diffusant	Cellulose gel		Cellulose membrane		Acetylated membrane	
	$D \times 10^{10}$, m²/s	K	$D \times 10^{10}$, m²/s	K	$D \times 10^{10}$, m²/s	K
Ethylene glycol	6.6_3	1.0_7	2.3_6	0.5_9	1.7_5	0.2_7
Glycerol	5.2_8	1.0_6	2.0_3	0.5_0	1.4_8	0.1_8
Erythitol	4.6_0	1.0_5	1.7_3	0.4_4	1.3_8	0.1_4
Arabitol	4.2_8	1.0_3	1.7_0	0.4_0	1.1_5	0.1_1
Mannitol	3.8_9	1.0_2	1.5_2	0.3_7	0.9_8	0.0_9
Glucose	3.6_6	1.0_7	1.5_9	0.3_7	1.0_4	0.1_0
Cellobiose	2.7_6	1.0_7	1.1_1	0.2_9	—	—
Raffinose	2.5_4	0.9_6	0.8_4	0.2_4	—	—
Stachyose	2.1_8	0.9_5	0.8_6	0.2_1	—	—
LiCl	7.7_3	1.0_7	2.8_5	0.5_3	2.0_7	0.1_6
PEG 200	3.8_1	0.9_2	1.3_7	0.3_5	0.99	0.1_2
300	3.1_8	0.9_3	1.0_6	0.3_0	—	—
400	2.9_1	0.8_9	0.9_8	0.2_2	—	—
600	2.6_7	0.9_8	0.7_6	0.1_5	—	—
1000	2.0_8	1.0_4				
1500	1.5_6	0.7_1				
4000	0.7_9	0.6_2				
5700	1.1_4	0.5_5				
20000	0.6_1	0.4_1				
Water	~14.0	1	~5.3	1	~3.9	1

TABLE II
Diffusion Coefficients in the Pure Solvent and Hydrodynamic Radii Evaluated from Them

Diffusant	$D_0 \times 10^{10}$, m²/s	r, Å
PEG 200	6.22[a]	3.9
300	5.04[a]	4.9
400	4.31[a]	5.7
600	3.45[a]	7.1
1000	2.74[a]	9.0
1500	2.20[b]	11.2
4000	1.29[a]	19.0
5700	1.12[b]	21.9
20000	0.73[a]	34.0
Glucose	6.75[c]	3.6
Cellobiose	5.16[c]	4.8
Raffinose	4.19[c]	5.9
Stachyose	3.75[c]	6.6
Ethylene glycol	11.52[d]	2.1
Glycerol	9.40[d]	2.6
Erythritol	8.06[d]	3.0
Arabitol	7.13[d]	3.4
Mannitol	6.43[d]	3.8

[a] From Ref. 3.
[b] Interpolated values.
[c] From Ref. 11.
[d] From Ref. 12.

within the gels is accessible to the smallest solutes. Figure 7 illustrates the degree of accessibility as a function of the hydrodynamic radius of the solute estimated from the free diffusion coefficient.

In the acetylated membrane, the bulky acetate groups serve to effectively block a large proportion of the openings in a hypothetical "pore" system, which is nonetheless a convenient means of explaining selectivity on the basis of molecular size. About 16% of the water-filled volume is accessible to LiCl having a Stokes' radius only twice that of the water molecule. This illustrates the extremely

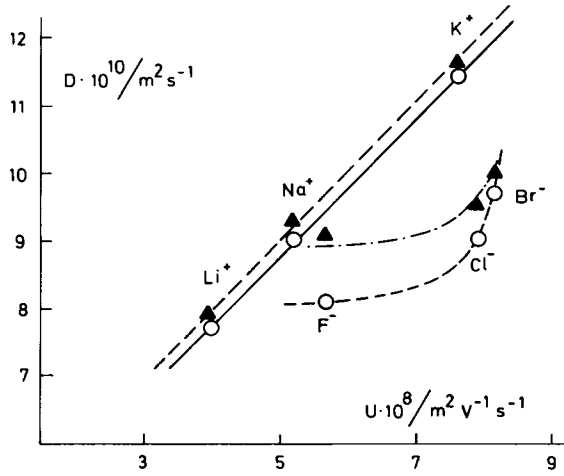

Fig. 8. Diffusion coefficients for the alkali metal chlorides and sodium halides as function of the ionic mobility at 25°C. (○) Cellulose gel, (●), acetylated gel.

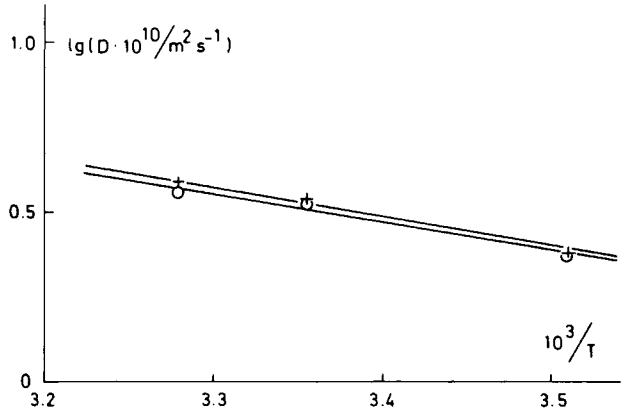

Fig. 9. Arrhenius plot for the diffusion of PEG 200 (+) and mannitol (O) on the cellulose gel. Lines are drawn with a slope corresponding to the temperature dependence of the inverse viscosity of water.

sensitive sieving resolution possible with these materials. It corresponds to a low "solubility" of the electrolyte in such membranes and thus accounts for the effectivity of desalination when acetate membranes are so employed. The diffusion of the alkali metal halides in the gels is proportional to the cation mobility but has a less simple correlation with that of the anion (Fig. 8). Since the ionic mobility is simply related to the hydrodynamic radius, the cation behavior is that expected due to the strong variation in solvation numbers of the alkali metal ions. Since the K^+ and Cl^- ions are known to have similar Stokes' radii, it is clear that the anions are retarded during diffusion in the gel. It is inviting to suggest that the "pores" are marginally δ^- due to polarization of water molecules. In this case, the cations will be relatively unaffected whereas the anions will tend to be repelled, and increasingly so as the Stokes' radius of the anion decreases.

Figure 9 shows the temperature dependence for PEG 200 and mannitol on the cellulose gel. The slope corresponds to the temperature dependence of the inverse viscosity of water. A similar finding was made[10] using NMR spin echo

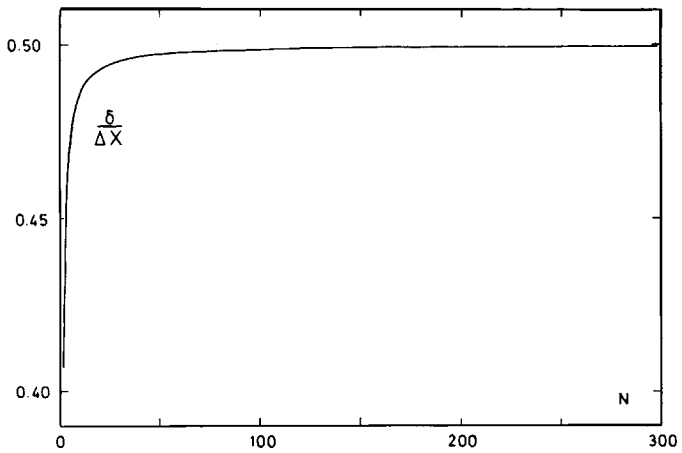

Fig. 10. See text.

measurements to examine the temperature dependence of the self-diffusion of water in the gel. The implication is that the frictional characteristics are defined by the diffusant–solvent pair. In these cellulosic systems, the presence of polymer segments serves only to lengthen the effective path length in diffusion by a constant factor which is determined by the polymer concentration.

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APPENDIX

The area under the exponential function ($Y = A + B \exp(-CX)$, between X and $X + \Delta X$ is

$$\text{area} = \int_X^{X+\Delta X} A + B \exp(-CX)\, dX$$

$$= A\,\Delta X + B \exp(-CX) \left[\frac{1 - \exp(-C\,\Delta X)}{C}\right]$$

The "mean ordinate" in this interval we define as area/ΔX,

$$\overline{Y} = A + B \exp(-CX) \left\{\frac{1 - \exp(-C\Delta X)}{C\Delta X}\right\} \tag{1}$$

The X value corresponding exactly to this mean ordinate is displaced δ from the beginning of the interval

$$\overline{Y} = A + B \exp[-C(X + \delta)] = A + B \exp(-CX) \exp(-C\delta) \tag{2}$$

Combining the equations, we find

$$\exp(-C\delta) = \frac{1 - \exp(-C\Delta X)}{C\Delta X}$$

$$C\delta = \ln\left\{\frac{C\Delta X}{1 - \exp(-C\Delta X)}\right\}$$

$$\frac{\delta}{\Delta X} = \frac{1}{C\Delta X} \ln \frac{C\Delta X}{1 - \exp(-C\Delta X)} \tag{3}$$

C may be expressed in terms of the half-time $t_{1/2}$:

$$C = \frac{\ln 2}{t_{1/2}}$$

If we make N measurements within the five half-life effective duration of the experiment, then

$$N\,\Delta X = 5t_{1/2} = \frac{5 \ln 2}{C} \text{ or } C\,\Delta X = \frac{5 \ln 2}{N} \tag{4}$$

Inserting eq. (4) in (3), we obtain

$$\frac{\delta}{\Delta X} = \frac{N}{5 \ln 2} \ln \frac{5 \ln 2}{N\left\{1 - \exp\left(-\frac{5 \ln 2}{N}\right)\right\}} \tag{5}$$

A plot of this function vs. N is seen in Figure 10, from which it is readily seen that the proper placement of the mean Y very rapidly approaches the midpoint of the interval, as the number of points accumulated within the five half-time duration increases.

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