Flow of Water Through Highly Swollen Membranes

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Synopsis

The difference between the hydraulic permeability K under a pressure gradient and the diffusive permeability P under a concentration gradient can be explained by the incipient viscous flow at high degree of swelling. This flow is opposed by the friction resistance of the macromolecules of the highly swollen membrane. It comes to an end at a critical swelling H_c when the number of permeant molecules is not more sufficient for a complete solvation of the macromolecules of the membrane. Below this swelling, K equals PV_1/RT, where V_1 is the molar volume of the permeant, and above it the difference $K - PV_1/RT$ is proportional to $H/(1 - H) - H_c/(1 - H_c)$. The proportionality factor depends on the friction coefficient of the macromolecular segments and on the average lateral chain clustering. The data on poly(glycerol methacrylate) suggest that on the average the aggregates contain two chains.

A previous study[1] on the transport of water through swollen homogeneous polymer membranes has shown that at small hydration H, i.e., at small volume fraction of water in the membrane, the hydraulic permeability K under a pressure gradient equals the generalized diffusive permeability PV_1/RT under a concentration gradient. At high H, however, K exceeds PV_1/RT by many orders of magnitude, where V_1 is the molar volume of water, R is the gas constant, and T is absolute temperature. The flux is measured in cm³/cm²sec in the hydraulic and in g/cm²sec in the diffusive experiment. The measurements were performed on membranes differing widely in chemical composition: cellulose acetate and various polymethacrylates (methyl, hydroxyethyl, hydroxypropyl, monoglycerol). The values P and K turned out to be merely dependent on hydration which, of course, is determined by the chemical composition.

The diffusive permeability was explained by the concept of the free volume per cm³,

$$v_f = (1 - H)v_{f2} + Hv_{f1} \tag{1}$$

as the weighted sum of free volume of polymer (v_{f2}) and water (v_{f1}), yielding

$$P = HD_1 e^{V_1^*/v_f} \tag{2}$$

where D_1 is the self-diffusion coefficient of water and V_1^* is a constant proportional to the cross section of water molecule. The permeability ac-

cording to eq. (2) is in good agreement with experimental data in the whole hydration range from pure water ($H = 1$) to nearly unswollen dry membrane ($H = 0$). At sufficiently high hydration it also describes well the permeability for other diffusants dissolved in water[2] if D_1 is replaced by the diffusion coefficient of the solute in water and V_1^* is modified according to the cross section of diffusant which in first approximation is proportional to $M^{2/3}$.

No explanation was attempted for the hydraulic permeability. The usual capillary model assumes, per cm² of membrane, m capillaries with an average radius r. One has

$$H = m\pi r^2 \tag{3}$$

$$K = m\pi r^4/8\eta = Hr^2/8\eta$$

which yields the average radius of the capillary as function of K/H,

$$r = (8\eta K/H)^{1/2}. \tag{4}$$

No simple way exists to predict r as function of H in such a manner to obtain the experimental K. The model assumes a constant viscosity η of the permeant.

The basic concept of a homogeneous polymer membrane, however, which yielded the simple free-volume description of diffusive permeability[1] can also be applied to the hydraulic permeability. A simple correlation can be derived which represents well the experimental data. It is based on the main assumption of the model that the polymer chains of the swollen membrane are so intimately mixed with the swelling agent (water) that no phase separation exists. The flow with a velocity of the liquid through such a membrane is rather uniformly impeded by the resistance of polymer chains. Each element of the polymer, let us say each monomer, contributes on the average the same frictional resistance fv, where the coefficient f is proportional to the viscosity of the liquid. Such a concept was introduced by Debye and Bueche[3] for the treatment of intrinsic viscosity and translational diffusion of randomly coiled macromolecules. They replaced the molecule with q monomer units by an equivalent sphere with q uniformly distributed frictional elements each having the same frictional coefficient f.

The flow through a highly hydrated membrane under a pressure gradient can be considered as the sum of fluxes due to diffusion J_d and viscous flow J_f,

$$J = J_d + J_f = (K_d + K_f)\Delta p/\Delta x. \tag{5}$$

As already mentioned, the coefficient K_d of the diffusion flow is closely connected with the permeability P under a concentration gradient. One hence obtains for the viscous flow permeability

$$K_f = K - K_d = K - PV_1/RT. \tag{6}$$

The viscous resistance $1/K_f$ is caused by the frictional resistance of all chain elements of the membrane (n/cm^3).

The driving force F overcoming the resistance to flow through 1 cm³ of the membrane reads

$$F = \frac{\Delta p}{\Delta x} = nfv = J_f/K_f \qquad (7)$$

and the flux due to viscous flow,

$$J_f = Hv. \qquad (8)$$

since n is given by

$$n = (1 - H)\rho_m N/M_0, \qquad (9)$$

where M_0 is the molecular weight of the repeating unit, N is Avogadro's number, and ρ_m is the density of the dry membrane; K_f is given by

$$K_f = \frac{M_0}{f\rho_m N} \cdot \frac{1}{x}, \qquad (10)$$

with the hydration parameter

$$x = (1 - H)/H \qquad (11)$$

measuring the ratio polymer/water in the membrane. Equation (10) yields infinite flow permeability for pure water, $H = 1$, and vanishing flow permeability for a nearly dry membrane, $H \to 0$.

This relation must be modified at lower hydration when there are not sufficient permeant molecules for complete solvation of the membrane macromolecules and still less for a viscous flow between them. In this case the molecules of the permeant are severely impeded in their mobility.[4] One can assume that this effect brings the viscous flow of permeant to zero at a critical hydration H_c which corresponds to the point where $K_f = 0$, and $K = K_d = PV_1/RT$. With this modification, eq. (10) becomes

$$K_f = \frac{M_0}{f\rho_m N} \left(\frac{1}{x} - \frac{1}{x_c}\right), \qquad (12)$$

yielding $K_f = \infty$ at $H = 1$ ($x = 0$) and $K_f = 0$ at $H = H_c = 1/(1 + x_c)$.

The data presented in ref. 1 are replotted as $K_f = K - PV_1/RT$ versus $1/x$ in Figure 1. In agreement with eq. (12), they are located on a straight line with a slope $M_0/f\rho_m N$ and an abscissa intercept $x = x_c$. From this plot $1/x_c$ was estimated as 0.75 and $M_0/f\rho_m N = 2.88 \times 10^{-7}$ cm²/sec atm = 2.94×10^{-13} cm³sec/g.

The calculated values of K_f asymptotically approach infinity as x goes to zero. In a plot of the calculated log K_f versus x (Fig. 2), this is noticeable for values of x smaller than 0.1. In the range of x values from 0.1 to 1.1, the curve can be well approximated by a straight line. Beyond that range it rapidly goes to minus infinity as x approaches x_c. The existence of the linear section seems to be the explanation of the fact that an apparently linear dependence of log K on x was found for a certain range of small x.[1]
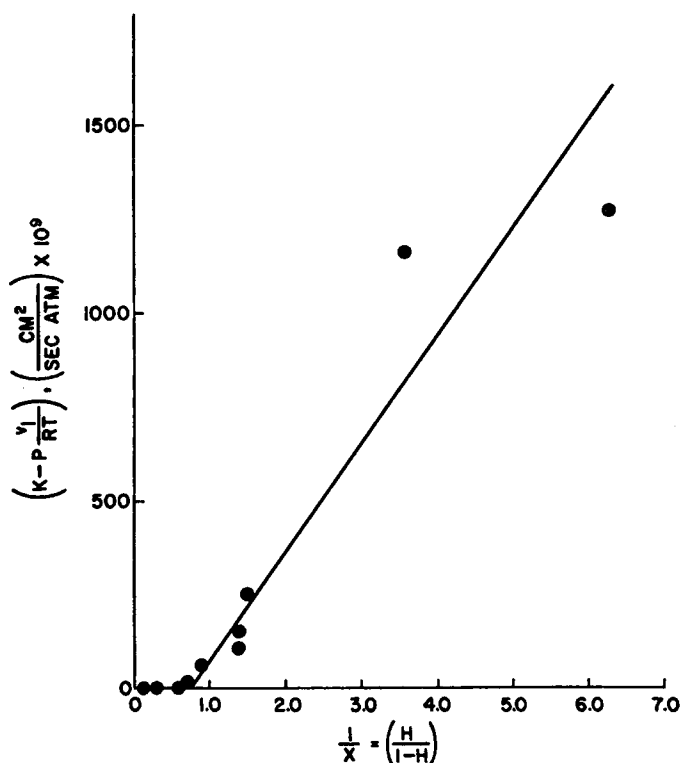
Fig. 1. Viscous permeability $K_f = K - PV_1/RT$ of different polymethacrylate and cellulose acetate membranes[1] vs. $1/x = H/(1 - H)$. Full line corresponds to eq. (12).

But the somewhat similar dependence of $\log K$ and $\log P$ on x in this range does not reflect a similar influence of hydration on the two types of transport through the membrane. If x goes to zero, P approaches the self-diffusion constant D_0 of water while K_f, and consequently K, approach infinity.

According to eq. (12), at high $x > x_c$ the viscous flux disappears completely so that $K = K_d = PV_1/RT$, in good agreement with observation (Fig. 1). In a semilogarithmic plot of K_f versus x, the experimental data show a more gradual decrease, with a complete vanishing above $x \sim$ 10. Such a situation seems nearly self-evident because the blocking of the viscous flow certainly is not abrupt but gradually proceeds with decreasing hydration.

The value $M_0/f\rho_m N$ can be used for the calculation of the friction coefficient of the monomer unit of the membrane. If one assumes that each monomer is a sphere freely suspended in water without any hydrodynamic interaction from other monomers, one deduces for the hydrodynamic radius $a_h = f/6\pi\eta$ of the monomer unit the value $2 \times 10^{-3} M_0$ (Å). With $M_0 = 145$, one obtains $a_h = 0.3$ Å, which is much too small. Since the polymer chain is much more like a cylinder than a string of widely separated spherical beads with no hydrodynamic interaction, it makes more sense to calculate
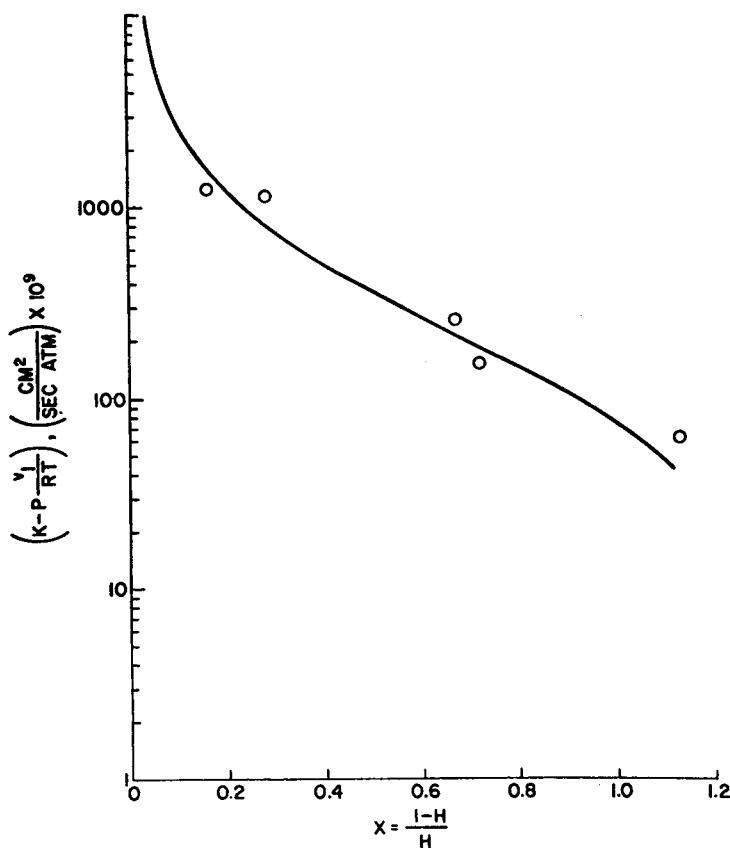
Fig. 2. Semilogarithmic plot of K_t vs. $x = (1 - H)/H$ for the same data as in Fig. 1. Full line corresponds to eq. (12).

the hydrodynamic radius of such an equivalent cylinder. The hydrodynamic resistance of a cylinder or elongated spheroid depends on the length to diameter ratio p. If one has μ monomers in a straight section of the macromolecule of the membrane, the ratio p equals $\mu h/2r$, where $h = 2.5$ Å is the length of the vinyl monomer unit and $2r$ is its diameter which can be estimated from the density of the material. Under the assumption of closest packing of cylinders, one obtains for poly(glycerol methacrylate) with $M_0 = 145$ a value 5 Å for the cylinder radius. The true value is certainly a little smaller. The hydrodynamic resistance coefficient per length h of such a cylinder turns out to be

$$6\pi\eta\left(\frac{3\mu h r^2}{4}\right)^{1/3} \frac{\varphi(p)}{\mu} = 6\pi\eta h\varphi(p)(16p^2/3)^{-1/3} \tag{13}$$

where $\varphi(p)$ is a tabulated function[6] increasing rather slowly with p. If one puts $f(p)/6\pi\eta = 2 \times 10^{-3} M_0$ (Å) $= a_h = 0.3$ Å, one obtains

$$p^{2/3}/\varphi(p) = 0.572h/a_h = 4.8 \tag{14}$$

yielding for p a value close to 60 and 600 Å for the length of the straight section of the macromolecule. Both values seem to be too high. That means that neither isolated monomers without hydrodynamic interaction nor individual cylindrical macromolecules are a good model for the highly hydrated polymer membrane.

A more reasonable value is obtained if one assumes that the macromolecular chains are not completely separated but occur in bundles,[5] so that the friction unit has a significantly higher molecular weight than the monomer. If on the average ν chains are sticking together, the cylinder radius increases by a factor $\nu^{1/2}$, the mass per unit length, and hence a_h by ν and the ratio p reduces by $\nu^{-1/2}$. By taking $\nu = 2$, one obtains $p^{2/3}/\varphi(p) = 2.4$ yielding a value for p of about 5 and for the length of straight section about 35 Å which is equivalent to 14 monomer units on one chain. This seems to be a reasonable estimate for the model of the homogeneously swollen membrane considering that the experimental figures are very rough averages over the wide variety of samples investigated.

One can conclude that the model presented in ref. 1 with a relatively small amount of lateral chain clustering ($\nu = 2$) explains adequately the transport of water in a homogeneous polymer membrane both under hydraulic and diffusive conditions. It is expected that the general relationship, eq. (12), found for water in hydrated polymer membrane can be extended to more general liquid permeants in swollen polymer membranes.

References

1. H. Yasuda, C. E. Lamaze, and A. Peterlin, *J. Polym. Sci. A-2*, **9**, 1117 (1971).

2. H. Yasuda, A. Peterlin, C. K. Colton, K. A. Smith, and E. W. Merrill, *Makromol. Chem.*, **126**, 177 (1969).

3. P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

4. H. Yasuda, B. Crist, H. G. Olf, C. E. Lamaze, and A. Peterlin, *Water Structure at the Water Polymer Interface*, H. H. G. Jellineck, Ed., Plenum Press, 1972.

5. R. L. Coalson, A. Day, and R. H. Marchessault, *Holzforsch.*, **22**, 190 (1968).

6. T. Svedberg and K. D. Pedersen, *Ultrazentrifuge*, D. Steinkopff Verlag, Leipzig, 1940, p. 39.