

Probing the State of Absorbed Water by Diffusion Technique

MOHAMMAD N. SARBOLOUKI, *Water Services of America, Inc.,
Milwaukee, Wisconsin 53209*

Synopsis

The diffusion coefficient of water, D_{wm} , across homogeneous cellulose acetate membranes of graded porosity ϵ (water content) are measured. At high values of porosity, D_{wm} varies monotonously as ϵ is varied. At a certain porosity ϵ_c , however, there is a sudden change in D_{wm} ; and thereafter the change becomes linear again, but with a different slope. Diffusion coefficients are interpreted, through the Stokes-Einstein relation, in terms of the overall microscopic viscosities η_{wm} of the membrane matrix. The values of η_{wm} are then correlated with the equivalent pore size r of the membranes. It is discovered that the sudden change in D_{wm} (or η_{wm}) at ϵ_c correlates with similar changes in other properties such as hydraulic permeability and selectivity of the membrane. All these observations are then attributed to the water structure inside the membranes.

INTRODUCTION

Generally speaking, a number of techniques have been used to study the state of water in systems involving water as one of their components.^{1,2} They include studies on adsorption, freezing, boiling, viscosity, solubility, DSC, and NMR.

The present work exploits the diffusion coefficient of water, D_{wm} , across water-swollen cellulose acetate (CA) membranes in order to gain information regarding the extent of structuring and the mobility of the absorbed water molecules.

THEORETICAL

The absorbed water molecules are expected to exist in two distinct states; one being the primary adsorbed molecules that are structured and have limited mobility, and the other being the more mobile, less structured secondary molecules that are mainly in contact with the primary molecules and fill the voids available in the polymer matrix, thus literally cause swelling. Depending on the nature and the extent of the water-polymer interaction, the degree of such induced structuring as well as the mobility of the water molecules would be determined. Consequently, water properties such as freezing point and ability to dissolve small, water-soluble solutes (e.g., NaCl) will be governed by the water-polymer interactions.

Thus, if for example there is practically no mobile secondary water molecule, the only possible way that a water molecule can travel across is by diffusion along the adsorption sites, which involves a great deal of interaction with the adsorbed primary water molecules as well as the polymer segments and adsorption sites. Also, one would expect that no water-soluble solute (that is, neither soluble nor interacting with the polymer) may be able to enter and travel across the membrane. If there exists, however, the smallest possible array of the secondary water molecules, it would drastically lower the friction for the traveling water molecules, and it would also allow the possible accommodation of small, water-soluble solutes into the membrane matrix (the extent of which depends on the degree of water-polymer interaction).

Therefore, one concludes that if the water content of the membrane is varied, it is expected that at a certain point there should be an excessive change in the membrane properties, such as diffusion coefficient of water, hydraulic permeability of water, and its selectivity. The following report is an attempt to verify such predictions.

EXPERIMENTAL

Membrane Preparation. Homogeneous cellulose acetate (CA) membranes of graded porosity were obtained from thoroughly mixed casting solutions of Eastman CA-39.8-3 in mixtures of various proportions of acetone-formamide, as shown in Table I. Using a Baker applicator (Gardner Instr.) set at 10 mil, they were spread onto a glass plate, and after 1 hr of evaporation (which is long enough for the complete loss of acetone³ and yet short enough so that no appreciable loss in formamide might take place and thereby prevent the formation of an inhomogeneous membrane), they were leached in distilled water for 24 hr, after which they were ready to be used.

TABLE I
Membrane Properties

Membrane no.	Casting composition CA-F-A, g	Thickness $l \times 10^3$ cm	Porosity ϵ	Diffusion coefficient $D_{wm} \times 10^6$	Hydraulic permeability $L_p, \times 10^{12}$ cm ³ /cm ² sec-barye
1	15-0-45	2.5	0.139	0.60	0.0428
2	15-1-44	3.5	0.159	0.655	0.0304
3	15-2-43	3.75	0.166	0.675	0.0367
4	15-3-42	3.5	0.176	1.072	0.0876
5	15-6-39	5	0.292	1.5	0.845
6	15-9-36	5.2	0.393	2.5	8.3
7	15-12-33	6.7	0.446	3.6	21.6
8	15-15-30	7	0.52	4.6	68.6
9	15-18-33	7.5	0.565	4.75	113

Thickness Measurement. Membrane thicknesses (while wet), l , were obtained by using a micrometric thickness-measurement device (Peacock) with a precision of $\pm 10^{-3}$ cm. The thicknesses at five points at least were measured, and the average is reported in Table I.

Porosity. Porosity ϵ was determined by carefully weighing the blotted wet and the vacuum oven dried (115°C) pieces of the membrane (at least four pieces). The porosities were calculated as follows

$$\begin{aligned} \text{Porosity } \epsilon &= \frac{\text{cm}^3 \text{ of water}}{\text{cm}^3 \text{ of the membrane}} \\ \epsilon &= \frac{(\text{wet weight-dry weight})}{(\text{wet weight-dry weight}) + \frac{\text{dry weight}}{1.3}} \end{aligned} \quad (1)$$

where 1.3 refers to the CA density. The values of ϵ are represented in Table I.

Diffusion Coefficient. To measure D_{wm} , the membrane was mounted in a diffusion cell consisting of two identical compartments (150 cm³ each), with a partition area of 10 cm². Both compartments were filled with distilled water, and stirrers were set at maximum speed. At time zero, 1 ml of one compartment was replaced with 1 ml THO (Packard, $2.55 \times 10^6 \pm 1$ dpm/g) via a precision micropipet with disposable head. Right after the introduction of THO, 0.5-ml samples were withdrawn from both sides simultaneously. Seven of such samplings were performed at regular intervals of about 1 hr (partition area was always under water in both sides throughout the experiment). Samples were mixed with 5 ml of a "scintillation cocktail" as prescribed by the Beckman Liquid Scintillation Counter Model LS-250: 5 g PPO (2,5-diphenyloxazole), 100 g naphthalone, and dioxane to 1000 ml (all the ingredients were scintillation grade obtained from Packard Instr. Co.). The counter was set at 50 min counting and 0.2% error, and the background count was corrected for.

Assuming a quasi-steady-state diffusion condition and by applying Fick's first law, the diffusion coefficient was determined from the slope of

$$\log \left(1 - \frac{2A_2^t}{A_1^0} \right) = - \frac{2\epsilon D_{wm} S}{2.3Vl} t + B \quad (2)$$

where D_{wm} = diffusion coefficient of water across the membrane (cm²/sec); A_1^0 = the radioactivity (cpm) of the hot side at time zero; A_2^t = instantaneous radioactivity of the cold side at time t ; S = partition area (10 cm²); V = compartment's volume (150 cm³); l = membrane thickness (cm); t = time (sec); ϵ = porosity; and B = constant. At least two pieces of each membrane were tested and the results are summarized in Table I.

Hydraulic Permeability. To measure L_p , three pieces of each membrane were mounted in three identical stainless steel high-pressure cells (effective area 9.4 cm²) and permeation rates of distilled water were measured at 100

psi (6.81 atm) pressure. In the case of the densest membrane (no. 1), the applied pressure was 500 psi in order to overcome its very slow throughput rate. The values of hydraulic permeabilities thus determined are shown in column 5 of Table I.

RESULTS AND DISCUSSION

Figure 1 illustrates the relationship between D_{wm} and ϵ . A clearly sharp change in the magnitude of D_{wm} occurs at about $\epsilon = 0.175$ and is accompanied by a change in the slope of the plot. A similar change in the slope has also been reported by Yasuda et al.,⁴ however at $\epsilon = 0.3$, when studying a number of hydrophilic polymers. The difference in the values of ϵ in these two reports might be attributed to the difference in the systems being studied.

To gain an insight into the physical meaning of what is happening at $\epsilon = 0.175$, an attempt was made to determine the equivalent pore size of

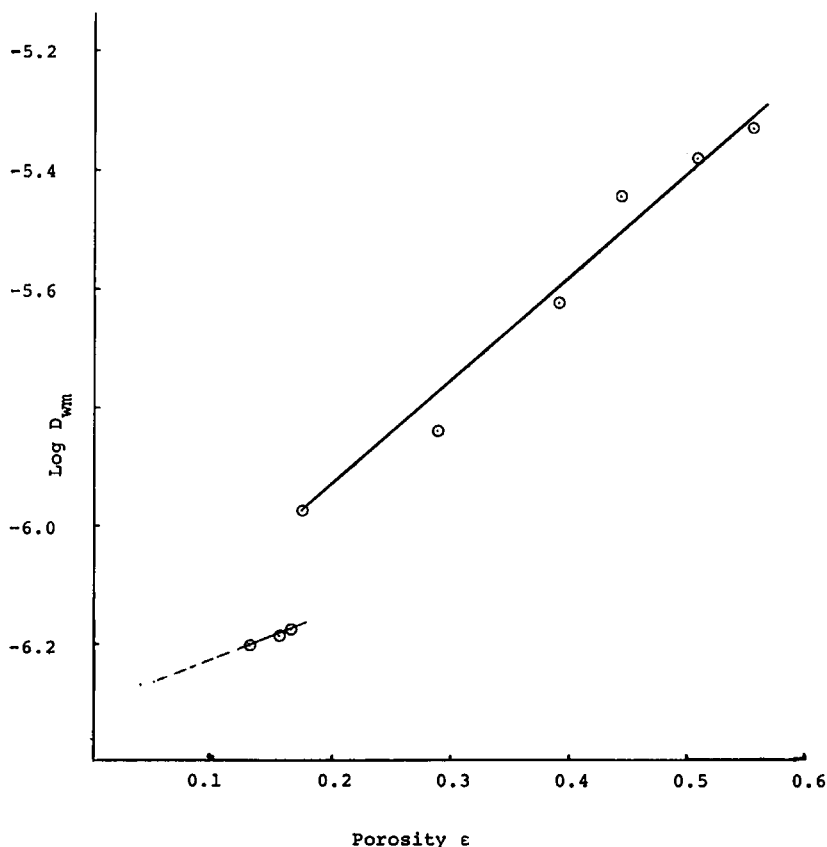


Fig. 1. Diffusion coefficient of water across the membrane, D_{wm} , vs. membrane porosity ϵ .

these membranes. Among many equally valid pore size formulas available, the one derived by Ussing⁵ and Pappenheimer⁶ was applied:

$$r = \sqrt{\frac{8L_p\eta_w^0}{(A_p/l)}} \tag{3}$$

where L_p = hydraulic permeability; η_w^0 = viscosity coefficient of pure water, and (A_p/l) is related to D_{wm} (or rather to the diffusive permeability) and is evaluated from the slope of eq (2),⁶⁻⁸
or

$$r = 3.6 \sqrt{g} (A^0) \tag{4}$$

where g is the ratio of hydraulic permeability to the diffusive permeability (both expressed in the same units).⁹

Also, in order to determine the extent of friction that a diffusing water molecule experiences, the overall microscopic viscosities of the membrane matrices were calculated from the Stokes-Einstein relationship as follows:

$$D = \frac{kT}{6\pi\eta a}$$

$$D\eta = \frac{kT}{6\pi a} \text{ constant (at constant } T\text{).}$$

Thus,

$$D_w^0\eta_w^0 = D_{wm}\eta_{wm} = \frac{kT}{6\pi a_w} = \text{constant}$$

or

$$\eta_{wm} = \frac{D_w^0\eta_w^0}{D_{wm}} \tag{5}$$

Table II shows the values of the overall microscopic viscosities and those of equivalent pore sizes of the membranes. By way of comparison, Kest-

TABLE II
Viscosity vs. Pore Size

Membrane no.	η_{wm} , cp	Pore size r , Å	Normalized hydraulic permeability $L_p l, \times 10^{15}$ cm ⁴ /cm ² sec·barye
1	36.2	4.52	0.117
2	33.2	4.21	0.1065
3	32.1	4.63	0.1375
4	20.2	6.01	0.3065
5	14.5	12	4.22
6	8.7	27.2	43.15
7	6	38.9	144.5
8	4.8	65.2	480
9	4.6	74.1	849

ing¹⁰ reports a value of 35 cp for water flow across skin (dense) layer of the asymmetric CA membranes. These data are depicted in Figure 2. It is clear that there is a tremendous drop in the viscosity at a pore size of $\approx 3-8 \text{ \AA}$. Considering the fact that the radius of the water molecules is about 1.5 \AA , it may be concluded that two (or possibly three) arrays of water molecules form the primary water layers along the pore wall; and if the pore becomes larger, so that a third or more layers could be accommodated, then an aqueous channel with mobile water layers will be formed and the friction against the travelling molecule will be greatly reduced.

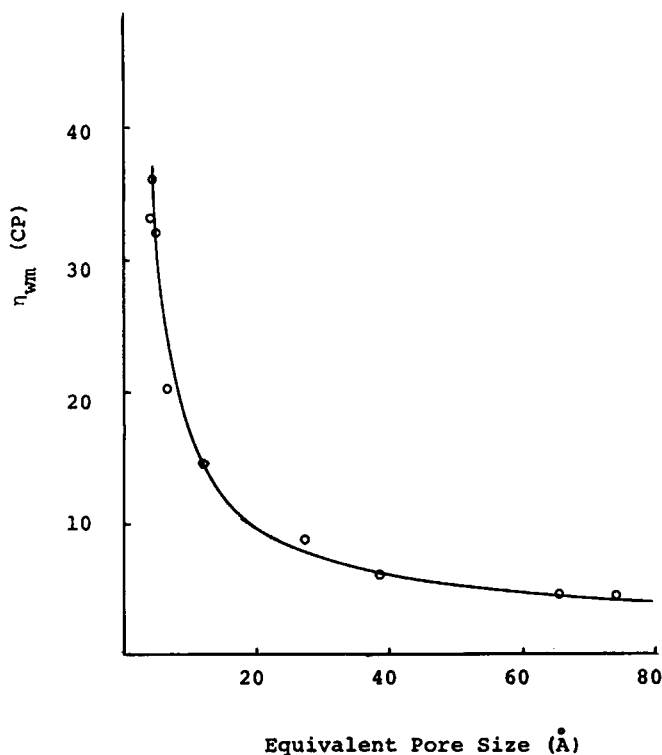


Fig. 2. Relationship between overall microscopic viscosity of the membrane matrix η_{wm} and membrane equivalent pore size r .

This conclusion is supported by the relationship that exists between the normalized hydraulic permeability and the pore size as shown in Figure 3.

Theoretically speaking, when the ratio of hydraulic permeability equals the diffusive permeability, i.e., $g = 1$, then diffusion is the only possible flow mechanism, in response to any kind of driving force, and under this condition the pore size predicted by eq. (4) is $r_c = 3.6 \text{ \AA}$. A value of $3-4.5 \text{ \AA}$ has been also predicted by others.^{11,12}

Studies on selectivity of these membranes¹³ in reverse osmosis experiments reveal that the salt rejection drops drastically at a pore size larger

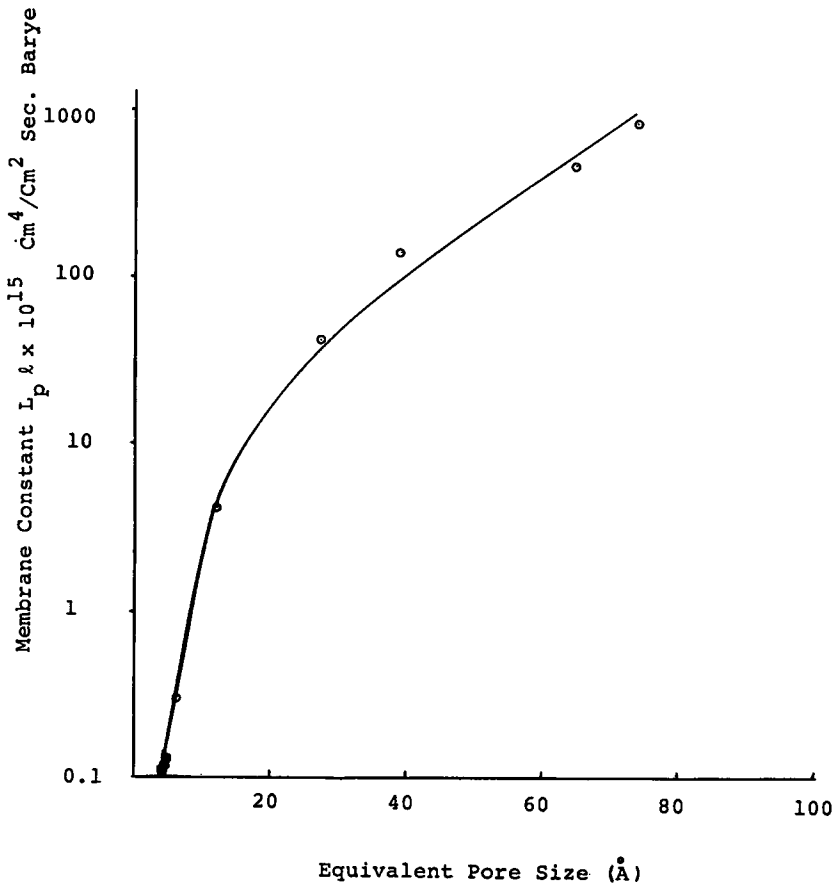


Fig. 3. Normalized hydraulic permeability (membrane constant) vs. equivalent pore size r .

than $\approx 5 \text{ \AA}$, and an almost complete rejection is attained at $r \approx 3 \text{ \AA}$, which again supports the conclusions reached above.

CONCLUSIONS

It was demonstrated that diffusion technique is an easy and useful way of probing the state of the water in polymer-water systems.

It was illustrated that excessive changes in diffusion coefficient which is due to changes in the water structure is accompanied by similar changes in other properties such as hydraulic permeability and selectivity of the membranes. Therefore, it is a useful technique in studying such systems under flow conditions.

The critical pore size of 3–4.5 \AA , as predicted by several authors, where the flow mechanism becomes truly diffusive was experimentally confirmed.

The author wishes to express his sincere thanks to his advisor, Prof. I. F. Miller, for helping him through this work.

This work is part of the doctoral dissertation by the author at the Chemistry Department of the Polytechnic Institute of Brooklyn, New York, June 1972.

References

1. H. A. G. Jellinek, *Water Structure at the Water-Polymer Interface*, Plenum Press, New York, 1972.
2. G. N. Ling, *Int. J. Neurosci.*, **1**, 129 (1970).
3. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **14**, 1983 (1970).
4. H. Yasuda, C. E. Lamaze, and A. Peterlin, *J. Polym. Sci. A2*, **9**, 1117 (1971).
5. V. Koefoed-Johnson and H. H. Ussing, *Acta Physiol. Scand.*, **28**, 60 (1953).
6. J. R. Pappenheimer, E. J. Renkin, and L. M. Borrero, *Amer. J. Physiol.*, **167**, 13 (1951).
7. E. J. Renkin, *J. Gen. Physiol.*, **38**, 225 (1954).
8. N. Lakshminarayanaiah, *J. Appl. Polym. Sci.*, **11**, 1737 (1967).
9. O. Kedem and A. Katchalsky, *J. Gen. Physiol.*, **45**, 143 (1961).
10. R. E. Kesting, *Synthetic Polymer Membranes*, McGraw Hill, New York, 1971, p. 258.
11. L. B. Ticknor, *J. Chem. Phys.*, **162**, 1843 (1958).
12. H. C. Longuet-Higgins and G. Austin, *Biophys. J.*, **6**, 217 (1966).
13. M. N. Sarbolouki and I. F. Miller, *Desalination*, Elsevier, 1973.

Received November 1, 1972

Revised December 12, 1972