

## Permeation Rate Constants for Water and Salt Flux Through Synthetic Membranes

W. E. SKIENS and H. I. MAHON, *The Dow Chemical Company, Western Division, Pittsburg, California*

Ultrafiltration through synthetic membranes has been studied by a number of workers as a technique for the separation of salt and water in saline solutions.<sup>1-6</sup> A selective flux of water through a membrane is generated by an applied hydrostatic pressure difference. This pressure must exceed the osmotic pressure of the solution to which it is applied for "reverse osmosis" to occur. The permeate, depleted in solute, emerges from the low-pressure side.

The membranes used are frequently divided into two groups, ion-selective and ion-restraining. The ion-selective membranes are composed of polyelectrolytes. The passage of either cations or anions through them is prevented by the bound electrolyte groups. Ion-restraining membranes normally contain hydrophilic groups. The passage of ions is restrained by an undefined mechanism.

In the ultrafiltration of salt solutions the selectivity for water is most often expressed as the salt rejection:

$$\text{Salt rejection, \%} = \frac{\text{charge concn.} - \text{permeate concn.}}{\text{charge concn.}} \times 100$$

The relationship of salt rejection and pressure has been studied with a number of different membranes that exhibit a permselectivity for water over sodium chloride. Figure 1 is a reproduction of some of these data together with a similar curve from our work. Reid and Spencer's<sup>1</sup> data, shown in the top curve, were obtained with a composite membrane consisting of a mixture of a methyl vinyl ether-maleic anhydride copolymer and polyvinyl alcohol (PVM/MA-PVA). This polymer mixture was solution-cast on a cellophane film backing. Breton<sup>2</sup> used cellulose acetate membranes, and his data are shown in the middle curve. The data from our laboratory, shown in the bottom curve, were obtained with cellulose triacetate membranes.

The curves in Figure 1 show a characteristic increase of salt rejection with pressure. For example, Breton's data show an increase in salt rejection from 66 to 95% with a pressure increase from 10 to 56 atm. Breton proposed that the increased salt rejection was related to compression of

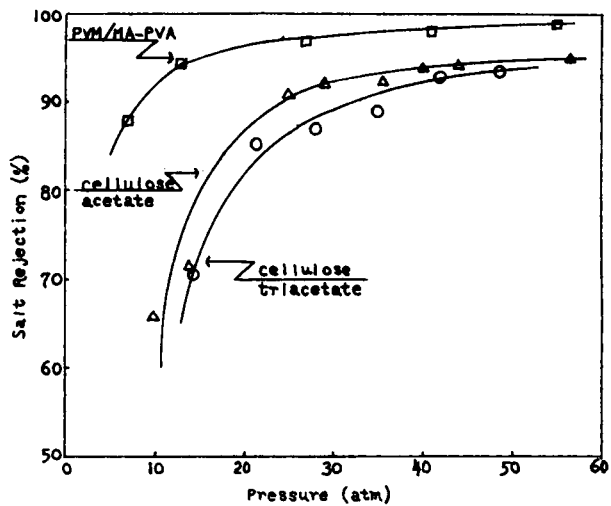


Fig. 1. Salt rejection as a function of pressure for PVM/MA-PVA, cellulose acetate, and cellulose triacetate membranes.

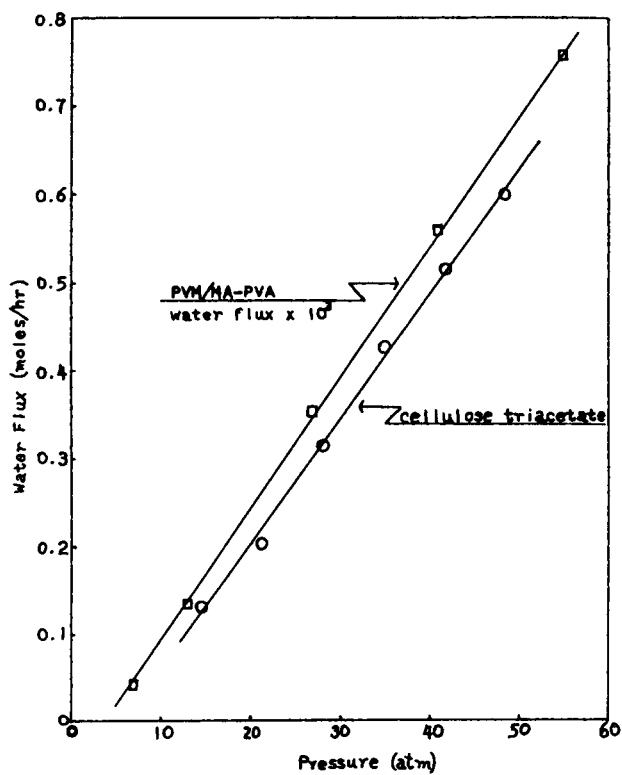


Fig. 2. Water flux as a function of pressure for PVM/MA-PVA and cellulose triacetate membranes.

the membrane and consequent changes in the membrane-water structure. He proposed the following theory:

"Those ions and molecules that cannot enter into hydrogen bonding with the membrane are transferred by hole-type diffusion. The rate of diffusion appears to be governed by a water-cellulose acetate structure. The reaction between water and cellulose acetate polymers to form bound water is induced by compressing the membrane. As pressure is applied on the membrane, more bound water is produced, which causes the rate of hole-type diffusion to decrease."

"On the other hand, those ions and molecules that can associate with the membrane through hydrogen bonding actually combine with the membrane and are transported through it by alignment-type diffusion. The formation of the water-cellulose acetate structure does not appreciably diminish the diffusion rate of water through the membrane."

Breton has proposed that the flux of water (hydrogen-bonding molecules) increases linearly with pressure, and this is demonstrated by the data shown in Figure 2 for PVM/MA-PVA and cellulose triacetate membranes. Breton has also proposed that the flux of salt ions (nonhydrogen-bonding) is increasingly restrained by changes in the membrane structure with pressure. An increase of membrane resistance to salt permeation with pressure can be implied when the data are presented as salt rejection versus pressure, as in Figure 1. In this paper the data will be treated as separate water and salt fluxes rather than salt rejection. The data are presented in this manner to show that the flux changes with pressure can be related to activity difference driving forces by kinetic equations, without postulating changes in membrane structure.

### Kinetics of Membrane Processes

Laidler and Schuler,<sup>7</sup> in their paper "Kinetics of membrane processes," derive flux equations for membranes permeable to both solvent and solute. The equations involve certain general assumptions regarding the mechanism of transport. It was assumed that eventually a steady-state flux was established through the membrane at a constant pressure and that the flux was the result of three kinetic processes: (1) adsorption at the interface (rate constant,  $k_1$ ), (2) desorption at the interface (rate constant,  $k_{-1}$ ), (3) diffusion through the membrane (diffusion constant,  $D_N$ ). In order to simplify the resulting equations it was also assumed that the rate-determining step was diffusion through the membrane. This assumption can be inferred if the flow rate is proportional to the concentration difference across the membrane and inversely proportional to the thickness of the membrane.

The following equations were derived for the solvent and solute fluxes through a membrane:

$$dn_1/dt = Q_1 A c_i / d' [N_1^\alpha f_1^{1-\alpha} - N_1^\beta f_1^{\circ\beta} \exp \{P \bar{V}_1 / RT\}] \quad (1)$$

$$dn_2/dt = Q_2 A c_i / d' [N_2^\alpha f_2^{\circ\alpha} - N_2^\beta f_2^{\circ\beta} \exp \{P \bar{V}_2 / RT\}] \quad (2)$$

where:

- 1 = solvent species
- 2 = solute species
- $\alpha$  = low-pressure chamber
- $\beta$  = high-pressure chamber
- $dn/dt$  = flux, moles/hr.
- $Q$  = combined rate constant  $(k_1/k_{-1}) D_N$ , cm.<sup>2</sup>/hr.
- $A$  = cross-sectional area of membrane, cm.<sup>2</sup>
- $c_i$  = concentration of all species present, moles/cm.<sup>3</sup>
- $d'$  = thickness of membrane, cm.
- $N$  = mole fraction
- $f^\circ$  = activity coefficient at atmospheric pressure
- $P$  = total applied hydrostatic pressure, atm.
- $\bar{V}$  = partial molar volume, cc./mole
- $R$  = gas constant, cc. atm./°K. mole
- $T$  = absolute temperature, °K.

The sign of the flux is negative for flow from the high-pressure chamber  $\beta$  to the low-pressure chamber  $\alpha$ . Permeation rate constants have been defined as

$$K_1 = Q_1 A c_i / d', \text{ moles/hr.} \quad (3)$$

$$K_2 = Q_2 A c_i / d', \text{ moles/hr.} \quad (4)$$

The terms  $K_1$  and  $K_2$  are thus functions of the specific membrane used. Changes in the membrane structure which affect the flux should be reflected in  $K$ . The object of the investigation was to study the relationship between  $K$  and pressure.

## Experimental Procedure

### *Membrane Preparation*

The cellulose triacetate (Eastman) membranes used in this work were solution-cast. The membranes were cast on a glass plate at room temperature with a casting bar. They were allowed to air dry for about 2 min. and were then immersed in room-temperature water until used.

### *Apparatus*

The permeation test unit consisted of a Monel cell containing high- and low-pressure chambers separated by means of a porous Monel frit. The membrane was placed on a cushioning sheet of highly porous plastic on the high-pressure side of the frit. O-rings in the cell body pressed on the membrane to seal the high-pressure chamber.

The salt solution was pressurized by means of a cylinder containing either a "floating" piston or a rubber bag separating the solution and high-pressure nitrogen gas. The pressure was adjusted to  $\pm 2$  psi by means of a calibrated small-volume pressure regulator. Salt solution under pressure was pumped

through the high-pressure chamber by means of a positive displacement pump. The concentration of the circulated solution was monitored continuously by means of a "pressure let-down" capillary. The permeate from the low-pressure chamber was collected for rate and concentration measurements. The cell and sections of the lines were immersed in a water bath in which the temperature was controlled at  $25 \pm 0.02^\circ\text{C}$ .

### Results and Discussion

The experimental water and salt flux data and the permeation rate constants calculated from the data, in accordance with eqs. (1) and (2) are given in Table I. Results are presented for the composite polyvinyl

TABLE I  
Fluxes and Permeation Rate Constants for Water and Salt

Applied pressure, atm.	Water		Salt	
	Flux, moles/hr.	Permeation rate constant, moles/hr.	Flux, moles/hr.	Permeation rate constant, moles/hr.
PVM/MA-PVA Membrane				
7	$-0.4 \times 10^{-4}$	$2.2 \times 10^{-2}$	$-1.0 \times 10^{-3}$	$0.8 \times 10^{-3}$
13	-1.4 "	2.2 "	-1.5 "	1.1 "
27	-3.5 "	2.2 "	-1.8 "	1.3 "
41	-5.6 "	2.1 "	-1.8 "	1.3 "
55	-7.6 "	2.0 "	-1.4 "	0.9 "
Cellulose Triacetate Membrane				
14.6	$-1.3 \times 10^{-1}$	21.6	$-1.3 \times 10^{-4}$	$1.2 \times 10^{-3}$
21.4	-2.0 "	21.1	-1.1 "	1.1 "
28.2	-3.2 "	22.6	-1.6 "	1.6 "
35.0	-4.3 "	21.9	-1.7 "	1.4 "
41.9	-5.2 "	21.5	-1.4 "	1.1 "
48.7	-6.0 "	20.4	-1.4 "	1.7 "
Cellophane Membrane				
0.9	-2.05	$3.18 \times 10^3$	$-0.6 \times 10^{-4}$	17.6
2.1	-5.00	3.18 "	-1.2 "	17.7
3.4	-7.55	3.02 "	-1.6 "	17.7
4.3	-9.33	2.96 "	-1.9 "	19.3

alcohol membrane of Spencer, for the cellulose triacetate membrane, and for cellophane membranes studied by Ambard and Trautmann.<sup>3</sup> Breton's paper contained no flow rate information on the cellulose acetate membrane; hence no rate constant calculations were possible.

In all instances, the water flux was linearly related to the pressure (Fig. 2) and the water permeation rate constant did not vary significantly over the pressure range studied. No direct quantitative comparison of the rate constants from membrane to membrane was possible, because of unknown values of membrane area and thickness.

The PVM/MA-PVA membrane and the cellulose triacetate membrane had very low salt permeation rates. As a result the salt concentration in

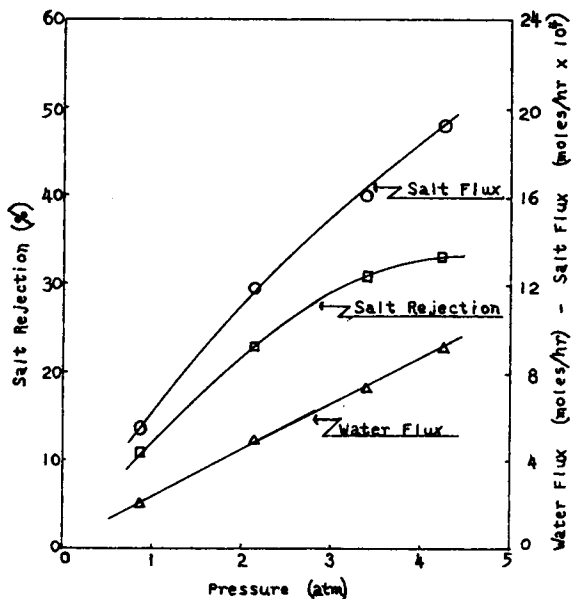


Fig. 3. Effect of pressure on salt rejection, salt flux, and water flux for cellophane membrane.

the permeate was low and part of the scatter in the salt flux data might be attributed to analytical error. The techniques used for sodium chloride analysis are not highly accurate at this low concentration level. Nevertheless, the salt fluxes and salt permeation rate constants show no significant trend with pressure, whereas Breton's theory proposes a decrease in the salt permeation rate constant with pressure.

The relationship of water and salt flux to pressure can best be illustrated from the data of Ambard and Trautmann given in Figure 3. They obtained low salt rejections (11–33%), using a cellophane membrane and dilute sodium chloride solutions. With membranes of low salt rejection, changes in the salt concentration difference across the membrane have a much more significant effect on the salt flux than with membranes of high rejection. An increase in pressure in the high-pressure chamber causes an increase in water flux and, as a result, the permeate concentration decreases. The drop in permeate concentration creates a greater salt concentration difference (activity driving force) across the membrane; hence the salt flux increases. With membranes of high salt rejection, similar flux changes occur with pressure; however, the change in permeate concentration is very small relative to the concentration in the high-pressure chamber. The increase in activity difference is small and the resulting increase in salt flux cannot be readily detected, as shown in Table I.

In Figure 4 plots are given of Ambard and Trautmann's data for flux as a function of activity difference calculated from eqs. (1) and (2). It is observed that the data for both fluxes plot well on straight lines. The

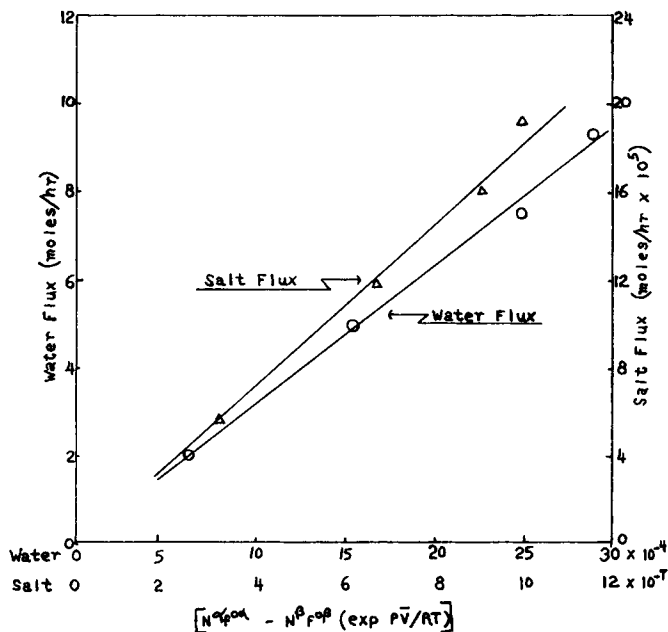


Fig. 4. Water and salt flux as a function of activity difference for cellophane membrane.

slopes of these lines are the permeation rate constants for the cellophane membranes.

Thus, these data show good agreement with the proposed equations. Over the salt rejection range of 11–33%, the permeation rate constants were unchanged. With the other membranes studied, the permeation rate constants did not change significantly in the rejection range 70–99%, and the pressure range 0–60 atm. The constant values of  $K$  over the entire pressure range indicate that the resistance of these membranes to salt flux was independent of pressure.

This interpretation of ultrafiltration data is limited to a pressure range in which no structural changes affecting the flux occur in the membrane. Some additional work of Reid and Spencer<sup>8</sup> at considerably higher pressures (70–350 atm.) and the data of Loeb and Sourirajan<sup>9</sup> do not follow this interpretation. These workers have studied permeation through synthetic membranes in which the water flux did not increase linearly with pressure (in some instances the water flux decreased at high pressures). The results indicate that actual compression of the membrane occurred. Interpretation of this high-pressure data by the method given in this paper is not applicable since the resistance of the membranes to water and salt flux was not constant.

### References

1. Reid, C. E., and H. G. Spencer, *J. Appl. Polymer Sci.*, **4**, 354 (1960).
2. Breton, E. J., Jr., "Water and Ion Flow Through Imperfect Osmotic Membranes," Research and Development Progress Rept. No. 16, Office of Saline Water, U. S. Dept. Interior, April 1957.
3. Ambard, L., and S. Trautmann, *Ultrafiltration*, Thomas, Springfield, Ill., 1960.
4. Reid, C. E., and J. R. Koppers, *J. Appl. Polymer Sci.*, **2**, 264 (1959).
5. McKelvey, S. G., Jr., K. S. Spiegler, and M. J. R. Wyllie, *Chem. Eng. Progr. Symp. Ser.*, **55**, 199 (1959).
6. Loeb, S., and S. Sourirajan, "Sea Water Demineralization by Means of a Semi-permeable Membrane," Rept. No. 60-60, Dept. Eng., Univ. Calif., Los Angeles, July 1960.
7. Laidler, K. J., and K. E. Schuler, *J. Chem. Phys.*, **17**, 851 (1949).
8. Reid, C. E., and H. G. Spencer, *J. Phys. Chem.*, **64**, 1587 (1960).

### Synopsis

Water and salt fluxes through synthetic membranes were measured as functions of pressure. In the pressure range 0-60 atm. both the water permeation rate constant and the salt permeation rate constant were independent of pressure. The water flux increased linearly with pressure driving force (hydraulic-osmotic). The changes in salt flux were small. These changes were proportional to changes in the activity of the salt solutions due to concentration and pressure effects. Good agreement was obtained between the experimental flux data and the kinetic equations describing the process.

### Résumé

On a mesuré les flux d'eau et de sel à travers des membranes synthétiques en fonction de la pression. Dans le domaine de 0 à 60 atm les constantes de vitesse des perméations de l'eau et du sel restaient indépendantes de la pression. Le flux d'eau augmentait linéairement avec la force motrice de la pression (hydraulique-osmotique). Par contre le flux de sel n'était que légèrement influencé. Ces changements étaient proportionnels aux changements dans l'activité des solutions de sel (dûs à des effets de concentration et de pression). On constatait un bon accord entre les données expérimentales de flux et les équations cinétiques décrivant le processus.

### Zusammenfassung

Der Fluss von Wasser und Salz durch synthetische Membranen wurde in Abhängigkeit vom Druck gemessen. Im Druckbereich von 0 bis 60 atm. waren sowohl die Geschwindigkeitskonstante der Wasserpermeation als auch die der Salzpermeation von Druck unabhängig. Der Fluss des Wassers nahm mit der treibenden Druckkraft (hydraulisch-osmotisch) linear zu. Die Änderung des Salzflusses war klein. Sie war der durch Konzentrations- und Druckeinfluss verursachten Aktivitätsänderung der Salzlösungen proportional. Zwischen den experimentellen Ergebnissen bezüglich des Flusses und den kinetischen Gleichungen für den Prozess wurde gute Übereinstimmung erhalten.

Received May 31, 1962