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A Study for the Viscous Flow of Sodium Chloride Through a Cuprophane Membrane

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For the study of transport phenomena of an aqueous NaCl solution through a cuprophane membrane, a new apparatus was constructed. The volume flow rate Q , the permeability coefficient U , and the permeability constant K were measured or determined by using this apparatus. The experimental temperature range was 5 to 35°C, and the applied pressure increments were 10 to 40 psi. By assuming that the cuprophane membrane is composed of n parallel cylindrical capillaries of circular cross-section and that the flow of the solution through the capillaries follows the Poiseuille law, the mean radius r of the capillaries and the number n of the latter in the membrane were evaluated. By using a reasonable assumption concerning the radius η' of the species diffusing through the membrane, it was concluded that the contribution of the diffusive flow to the total flow rate Q is less than 10%. Thus, the Q was treated as the rate due to the viscous flow, and the viscosity η_m of the solution in the membrane phase was evaluated, and it was found that η_m is nearly equal to η_b , the bulk viscosity of the solution. From this fact, it was concluded that in the capillaries, no change occurs in the physical state of the NaCl solution. The value of ΔH_m^\ddagger (=4.27 kcal/mole) and ΔS_m^\ddagger (4.28 eu) were obtained for the viscous flow. A possible explanation was given.

Introduction

Application of the Eyring Viscosity Theory to the Viscous flow of Hydrated Ions Through a Porous Membrane. In the theory of liquid viscosity, Eyring considered that the molecules displaced relative to one another in the course of viscous flow¹⁻⁴ have to overcome the energy barrier between the adjacent equilibrium positions. The theory can be applied to the case that the hydrated ions of dilute electrolytic solutions diffuse through a porous membrane disregarding the electric potential gradient against the external pressure gradient. The rate of this process is determined by factors similar to those acting in chemical reactions, therefore the theory of viscous flow can be treated on the basis of the

absolute reaction rate theory.

According to the absolute reaction rate theory^{5,6} the net velocity (U) of a flow unit under shear stress f is given as follows:

$$U = (k_{mf} - k_{mb})\lambda = \lambda k_m \left\{ \exp \left[\frac{f\lambda_2\lambda_3\lambda}{2kT} \right] - \exp \left[-\frac{f\lambda_2\lambda_3\lambda}{2kT} \right] \right\} \quad (1)$$

$$= 2U_0 \sinh \left(\frac{f\lambda_2\lambda_3\lambda}{2kT} \right) \quad (2)$$

where U_0 is the velocity of the flow unit by other driving force such as concentration gradient, and is defined by

$$U_0 = \lambda k_m = \lambda \frac{kT}{h} \exp \left(-\frac{\Delta G_m^\ddagger}{RT} \right) \quad (3)$$

In the above equations, λ and $\lambda_2\lambda_3$ are the jumping distance

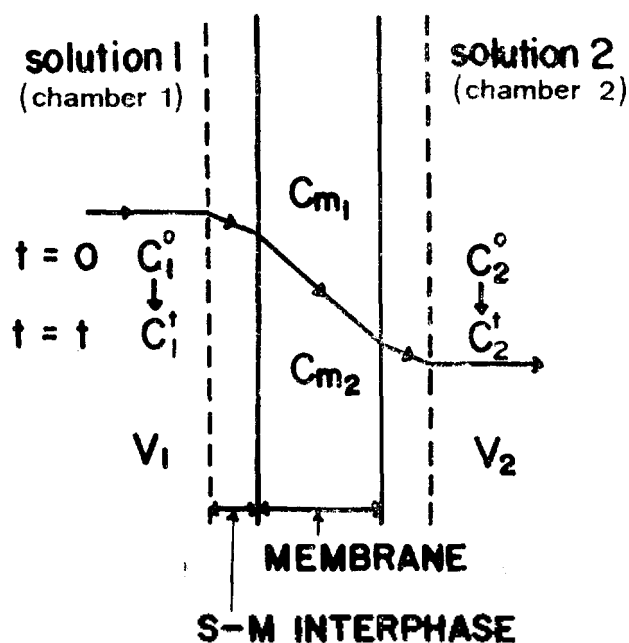


Figure 1. Concentration gradient across a membrane.

and the area occupied by a hydrated ion, respectively, k_{mf} and k_{mb} are the rate constants for forward and backward jumping rate constants of the ion passing through the membrane, k_m is the rate constant when the shear stress f is zero, and ΔG_0^\ddagger is the activation free energy for the jumping at $f=0$.

Fundamental Relationships of Permeability. For a description of mass flow due to diffusion, we can obtain the following mass flux equation from the basic law of transport processes:

$$J = U(C_1 - C_2) \quad (4)$$

where U is the flow velocity mentioned in Section (1), which is equal to the permeability coefficient, C_1 and C_2 are the concentrations of solutions 1 and 2, respectively, and the latter has lower concentration than that of the former. For solution 1 in compartment 1 of the diffusion cell shown in Figure 1, Eq. (4) can be transformed into the following equation:

$$-J = \frac{V_1}{A} \frac{\Delta C_1}{\Delta t} \quad (5)$$

where V_1 , A and Δt are the volume of compartment 1, the actual surface area of the membrane exposed to the experimental solution and the time interval of measurement, respectively.

Similarly, for compartment 2, the following equation is obtained:

$$J = \frac{V_2}{A} \frac{\Delta C_2}{\Delta t} \quad (6)$$

where V_2 is the volume of compartment 2.

Combining Eqs. (5) and (6) with (4), one obtains the following equation:

$$\frac{d(C_1 - C_2)}{C_1 - C_2} = -UA \left(\frac{1}{V_1} + \frac{1}{V_2} \right) dt. \quad (7)$$

If we integrate this equation in the limits of integration from C_1^0 and C_2^0 at $t=0$ to C_1^t and C_2^t at $t=t$ as shown in Figure 1, the following equation results:

$$\ln \frac{(C_1 - C_2)^t}{(C_1 - C_2)^0} = -UA \left(\frac{1}{V_1} + \frac{1}{V_2} \right) t \quad (8)$$

Considering the mass balance at $t=0$ and $t=t$, one obtains the following equation:

$$V_1 C_1^0 + V_2 C_2^0 = V_1 C_1^t + V_2 C_2^t \quad (9)$$

In the case where the initial concentration of compartment 2 is zero, i.e., a pure solvent ($C_2^0=0$), this equation can be rearranged to the following:

$$C_1^t = (V_1 C_1^0 - V_2 C_2^t) / V_1 \quad (10)$$

Substituting Eq. (10) into Eq. (8) for C_1^t , one obtains the following equation:

$$\ln \left[1 - \left(1 + \frac{V_2}{V_1} \right) \frac{C_2^t}{C_1^0} \right] = -UA \left(\frac{1}{V_1} + \frac{1}{V_2} \right) t \quad (11)$$

For the sake of convenience, C_1^0 and C_2^t are represented by $C_1(0)$ and $\bar{C}_2(t)$, respectively. Thus, we obtain the following equation:

$$\ln \left[1 - \left(1 + \frac{V_2}{V_1} \right) \frac{\bar{C}_2(t)}{C_1(0)} \right] = -UA \left(\frac{1}{V_1} + \frac{1}{V_2} \right) t \quad (12)$$

where $\bar{C}_2(t)$ is the average mole concentration of the electrolytic solution in cell compartment 2 at t , and $C_1(0)$ is the initial mole concentration of the solution in cell compartment 1. Equation (12) is very similar to that derived by Mah⁷, and was derived by a similar reasoning.

The $\bar{C}_2(t)$ in Eq. (12) is represented by the following equation:

$$\bar{C}_2(t) = \frac{1}{V_2} \{ [C_1(t_i) - C_1(t_j)] V_1 + \bar{C}(t) V(t) \} \quad (13)$$

where $C_1(t_i)$ and $C_1(t_j)$ are the concentrations in compartment 1 at two successive times t_i and t_j , respectively, $V(t)$ is the solution volume flowing out from compartment 2 at time $t = [(t_i + t_j)/2]$; the average concentration $\bar{C}(t)$ of the flowing out solution is given by

$$\bar{C}(t) = \frac{1}{2} [C_1(t_j) + C_1(t_i)] \quad (14)$$

The first term in the curled brackets in Eq. (13) represents the moles of solute flowing into cell compartment 2 from compartment 1, and the second term indicates the average mole quantity of the solute going out from cell compartment 2 at time t .

Viscosity Equation. According to Eyring's rate theory of flow¹, the viscosity coefficient η_m is given by

$$\eta_m = \frac{f}{\dot{\gamma}} \quad (15)$$

where η_m is the viscosity of the liquid in the membrane phase, and shear stress (f) is obtained from the following equation:⁸

$$f = \frac{rP}{2L} \quad (16)$$

where P , L and r are the pressure increment, the thickness of the membrane, and the radius of a pore (capillary) in

the membrane, respectively. The pore radius r can be evaluated from the following equation:⁹

$$r = (8K/S)^{1/2} \quad (17)$$

where the permeability constant K , which differs from U mentioned in Section (2), can be obtained from the following equation in accordance with its definition:

$$Q = \frac{dV(t)}{dt} = \frac{AKP}{L\eta_b} \quad (18)$$

Here $V(t)$ and A are referred to Section (2), and Q is the volume flow rate, η_b the bulk viscosity of the solution, and other parameters have been defined with regard to Eq. (16). The specific water contents S in Eq. (17) is calculated from the following equation:⁹

$$S = (W_{wm} - W_{dm}) / W_{wm} \quad (19)$$

where, W_{wm} is the wet weight of a dry membrane whose weight is W_{dm} .

Next, the shear rate \dot{s} in Eq. (15) can be calculated from the following equation:^{10,11}

$$\dot{s} = \frac{1}{n\pi r^3} \left(3Q + p \frac{dQ}{dP} \right) \sim \frac{4Q/n}{\pi r^3} \quad (20)$$

where n is the number of pores on area A of the membrane. The approximate equality holds only for a Newtonian liquid.

Here, it will be appropriate to make a comment on Eq. (17). The well known Poiseuille equation, $n = \pi r^4 P / 8LQ_1$, (where $Q_1 = Q/n$) is obtained by combining Eqs. (15), (16) and (20). From the Poiseuille equation, the following equation results:

$$Q_1 = \frac{\pi r^4 p}{8L\eta_m} = \frac{A_h r^2 p}{8L\eta_m} \quad (20a)$$

where A_h is the cross-sectional area of the capillary. Since $Q = nQ_1$, we obtain the following equation from Eqs. (18) and (20a):

$$\frac{AK}{\eta_b} = \frac{nA_h r^2}{8\eta_m} \quad (20b)$$

which yields

$$r = \left(8K \frac{A}{nA_h} \frac{\eta_m}{\eta_b} \right)^{1/2} \sim \left(\frac{8K}{S} \right)^{1/2}$$

where $(nA_h/A) \equiv S$, and $\eta_m \sim \eta_b$. The quantity nA_h/A can be given by Eq. (19) since $W_{wm} \propto A$ and $W_{wm} - W_{dm} \propto nA_h$, the latter being the total pore area on the membrane.

The Relation Between Viscosity and Diffusion. According to Stokes' hydrodynamic theory¹², the relation between diffusion and viscosity coefficients is given by

$$D_m \eta_m = \frac{kT}{6\pi r'} \frac{\partial \ln a}{\partial \ln C} \sim \frac{kT}{6\pi r'} \quad (21)$$

where D_m is the diffusion constant through the membrane, η_m is the viscosity in the membrane phase, a and C are the thermodynamic activity (effective concentration) and concentration of the diffusing species, respectively, the radius of the latter being r' . For a dilute solution, $\ln a / \ln C = 1$, thus, the second approximate equality in Eq. (21) holds, which is the so-called the Stokes-Einstein formula.^{13,14}

Self-diffusion is a special case of free diffusion. From

absolute reaction rate theory, Ree *et al.*¹⁵ derived the following equation for self-diffusion:

$$D_m \eta_m = \frac{kT}{\xi \lambda_m} \frac{d \ln a}{d \ln C} \sim \frac{kT}{\xi \lambda_m} \quad (22)$$

which is very similar to the Stokes-Einstein equation. In Eq. (22), λ_m is the jumping distance of the diffusing species in the membrane phase, and ξ is about 6, in general. Equation (22) applies not only to self-diffusion but also to diffusion in non-ionic solutions.¹⁵

Theory for Membrane Permeation. In the permeation of solution through a membrane, two phenomena, viscous and diffusive flows, occur simultaneously. In Sections (1) to (3), we have implicitly assumed that only the viscous flow occurs. Next, we treat the diffusive flow.

Hartley¹⁶, Mauro¹⁷ and Tricknor¹⁸ derived the following equation for the diffusive flow through a membrane from a sound theoretical consideration:

$$Q_d = \frac{D_m A S V P}{RT L} \quad (23)$$

where Q_d is the diffusive flow rate, V is the molar volume of the flowing species, and other quantities have the same meaning as previously defined. If we define the diffusive permeability constant K_d as in the case of viscous flow [Eq. (18)], Q_d is given by the following equation:

$$Q_d = K_d \frac{AP}{L\eta_b} \quad (24)$$

By combining Eqs. (23) and (24), one obtains

$$D_m = \frac{RT}{SV\eta_b} K_d \quad (25)$$

From Eqs. (21) and (25), the following equation results:

$$r' = \frac{SV}{6\pi N K_d} \quad (26)$$

where N is the Avogadro number. Equation (26) allows us to evaluate r' , the radius of the diffusing species in Eq. (21).

Zwolinsky *et al.*¹⁹ treated the permeability of various biological membranes from the view point of absolute reaction rate theory. An analogous type of kinetic approach to membrane transport under steady state conditions has been presented by Laidler and Shuler.²⁰ Nagasawa and Kobatake²¹ have utilized the ideas of the theory of rate processes²² to calculate the net flux of ions through a membrane subject to an electric field.

In the past, however, the studies on the membrane transfer of ionic solution are not satisfactory, for example, the viscosities η_m of ionic solutions permeating through membranes were not determined. Thus, a new experimental apparatus was designed in this laboratory for the study of viscous flow of aqueous NaCl solution through a cuprophane membrane. The experimental volume flow rates Q were analyzed by using the following model:

(1) The membrane is composed of n parallel cylindrical capillaries of circular cross section, and all the capillaries are open to the surface of cuprophane

(2) The $(\text{Na}^+)_{aq}$ and $(\text{Cl}^-)_{aq}$ ions in the NaCl solution behave independently, each of the ions being assumed to

have radius r' which is the average of the radii of $(\text{Na}^+)_{\text{aq}}$ and $(\text{Cl}^-)_{\text{aq}}$. The rates of flow through the membrane of the cation and anion are equal to keep the electro-neutrality.

(3) The flow of the ions is governed by the Poiseuille law. The contribution of diffusive flow to the total flow rate Q was assumed to be within 10%.

By using this model, the average radius r of the capillaries was evaluated, and viscosity η_m of the solution in the membrane phase was obtained. The flow activation parameters, ΔH_m^\ddagger and ΔS_m^\ddagger , were also determined. The details of the results and discussions will be reported in this paper.

Experimental

Cuprophane Membrane and Reagents. Cuprophane membrane, which was obtained from Seattle Artificial Kidney Supply Company, Seattle, Washington, U.S.A., was made from natural cellulose and cuproammonium (copper hydroxide plus ammonia), with some additives such as diethylglycol, urea and glycerol which improve the membrane characters. A piece of the membrane, which was cut in a certain size, was placed in a large volume of di-distilled water for at least two weeks during which the water was frequently replaced to remove impurities in the membrane.

The thickness ($L=1.6934 \times 10^{-3}$ cm) of the swollen membrane was obtained by the following procedure: the wet membrane was lightly dried with filter paper, then this was immediately inserted between two transparent plastic plates. The thickness of the swollen membrane was obtained by measuring the thickness of the sample assembly by using a micrometer, the thickness of the two plastic plates having been measured previously. The area (A) of the cuprophane membrane used are equal to the inner area of the measuring cell, $A=32.02$ cm².

Sodium chloride was extra pure reagent grade (MERK) and used as received, and the water used for aqueous solution was conductivity water which was di-distilled.

Cell for Permeability Measurement and Experimental Procedure. A modified high pressure cell (model 420) for reverse osmosis made by AMICON CORPORATION in U.S.A.

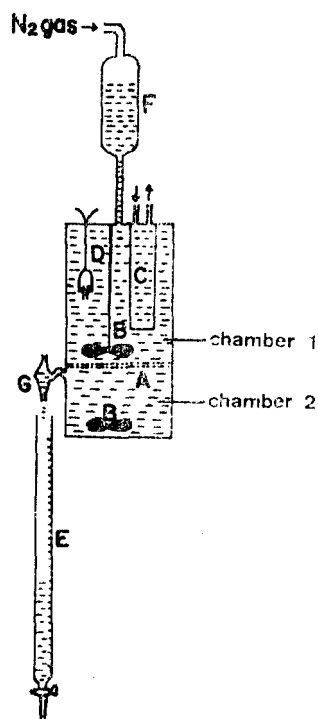


Figure 2. Schematic drawing of a high pressure cell for viscous flow measurement. A: Stainless steel support disk, B: magnetic stirrer bar, C: water circulating thermostat, D: electrode, E: burette, F: feeding chamber, G: leveling valve.

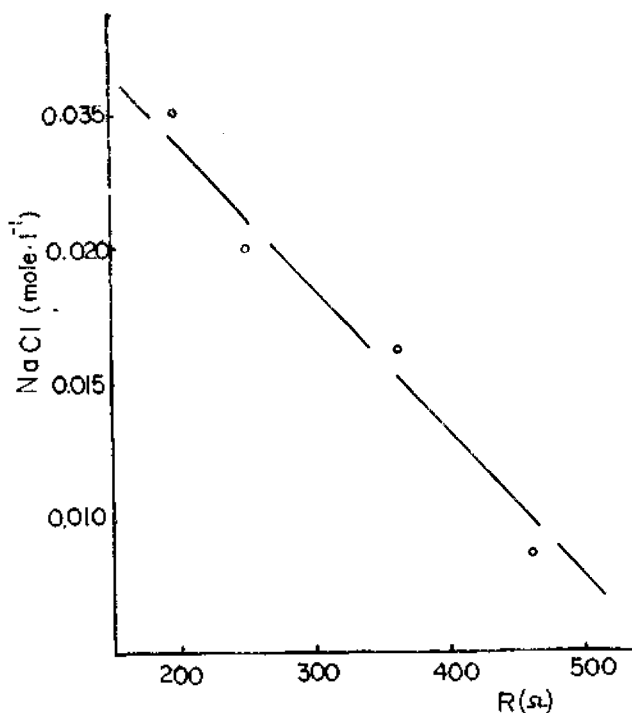


Figure 3. A typical standard curve for concentration C vs. resistance R on the bridge for the aq. NaCl solution at 25°C.

was employed to obtain the data of permeability coefficient (U) and permeability constant (K) mentioned with regard to Eqs. (12), and (18).

The schematic diagram of the modified high pressure cell is shown in Figure 2. The cell is divided into two chambers, chamber 1 and 2, by a porous stainless steel support disc A . The solutions in each chamber were sufficiently stirred by a magnetic stirring table B to reduce a boundary layer effect.^{23,24}

An aqueous sodium chloride solution (0.025 M) of interest was filled in chamber 1 (355 ml), and chamber 2 (55 ml) was filled with di-distilled water. The hydrated ions in the solution diffuse through the cuprophane membrane supported by a porous stainless steel disc A .

The conductivity of the ionic solution in chamber 1 was measured at an interval of 30 minutes with a conductivity bridge model RC-18A made by BECKMAN INSTRUMENTS, INC. U.S.A. And the concentration of the solution was determined by using a standard curve for the linear relation between the concentration of sample solutions and the resistance reading on the conductivity bridge (Figure 3).

The quantity of the ionic solution which diffused through the cuprophane membrane was measured by using a burette E for each constant time interval mentioned above. During the experiment, the experimental temperature was kept at 5, 15, 25 or 35°C ($\pm 0.05^\circ\text{C}$), and experimental pressure increments were regulated by using a nitrogen gas bomb with a regulator keeping at 10, 20, 30 or 40 psi (± 0.1 psi).

Typical experimental data for the 0.025 M NaCl solution at 25°C and 30 psi were listed in Table 1. From the data of Table 1, we obtain the U value in Eq. (12) and the K value in Eq. (18) for the 0.025 M aqueous NaCl solution flowing through the cuprophane membrane at 25°C under 30 psi

pressure increment. The results obtained at other experimental conditions will be shown later.

The bulk viscosities (η_b) of the 0.025 M aqueous sodium chloride solution were measured by using an Ostwald viscometer at 5, 15, 25 and 35 °C, η_b values at these temperatures were 1.54, 1.17, 0.90 and 0.74 CP, respectively. The η_b values were used to calculate the permeability constant K from Eq. (18).

Measurement of Water Content. The water swollen cuprophane membrane of a certain size mentioned in Section (1) was dried by pressing it lightly between two pieces of filter paper to get rid of the surface water in the membrane. After weighing the weight (W_{wm}) of the membrane, we dried it in a vacuum thermostat (50 °C) by putting it in a bottle whose weight (W_b) was known. When sufficiently dried, the bottle was covered with its stopper, and pulled it out of the thermostat to weigh the weight of the bottle plus dried membrane ($W_b + W_{dm}$). This procedure kept the sample from absorbing atmospheric moisture and secured for obtaining W_{dm} , the weight of the dried membrane. The S value (0.59) was calculated from Eq. (19).

Result and Discussion

Permeability Coefficient (U). We plotted the data of $\ln[1 - (1 + V_2/V_1)\bar{C}_2(t)/C_1(0)]$ vs. t (min) by using the data shown in Table 1 to obtain the permeability coefficient U of 0.025 M aqueous sodium chloride solution. The plot represents a good linearity as shown in Figure 4. According to Eq. (12), the U values are calculated from the slopes of the straight lines in Figure 4. The U values obtained at various temperatures and pressure increments are listed in Table 2. The U values increase with increasing pressure increments and temperatures, in agreement with Eqs. (1) to (3).

Permeability Constant (K) and the Pore Radius of the Membrane. If we measure $V(t)$, the volume of the sample solution flowed out of chamber 1 at time (t), temperature (T) and pressure increment (P), the permeability constant (K) is calculated from Eq. (18) by using the known L , A and η_b values. A typical plot of $V(t)$ vs. t (min) shows a good linearity as shown in Figure 5. The K values calculated from Eq. (18) by using Figure 5 are shown in Table 3.

Inserting the K values in Table 3 and S value ($=0.59$) in Section (3) of the Experimental into Eq. (17), we can calculate the pore radius r of the cuprophane membrane. The results are represented in Table 4. From Tables 3 and 4 one notes that the K and r values do not change

TABLE 1: Typical Experimental Data for the 0.025 M Aqueous Sodium Chloride Solution Flowing Through the Cuprophane Membrane at 25 °C and 30 psi Pressure Increment

t (min)	$R(Q)$	$V(t)$ (l)	$\bar{C}_1(t)$ (mole/l)	$\bar{C}_2(t)$ (mole/l)	$-\ln\left[1 - \left(1 + \frac{V_2}{V_1}\right) \frac{\bar{C}_2(t)}{C_1(0)}\right]$
		$\times 10^3$	$\times 10^2$	$\times 10^3$	$\times 10^2$
30	165.5	2.4	2.57	1.12	5.8
60	165.4	5.30	2.57	2.48	11.8
90	164.3	8.10	2.58	3.79	18.7
120	163.2	10.9	2.59	5.12	26.2
150	163.0	13.6	2.59	6.40	33.9

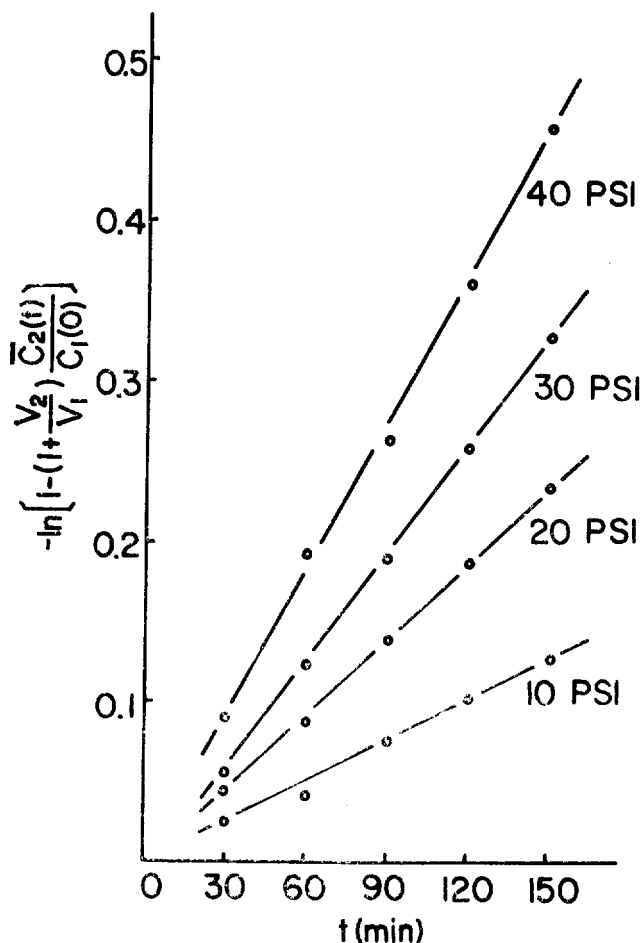


Figure 4. The plot of $\ln[1 - (1 + V_2/V_1)\bar{C}_2(t)/C_1(0)]$ vs. t (min) at 25 °C for the 0.025 M aq. NaCl solution. From the slopes of the straight lines, the permeability coefficients U are obtained.

TABLE 2: Permeability Coefficient ($U \times 10^5$ cm/sec) of the 0.025 M Aqueous Sodium Chloride Solution Flowing Through the Cuprophane Membrane

Press. increm. (psi)	10	20	30	40
5 °C	1.97	3.94	5.01	7.04
15 °C	2.27	4.44	6.32	8.59
25 °C	2.53	5.37	6.97	9.55
35 °C	3.15	6.63	9.65	12.12

TABLE 3: Permeability Constants $K \cdot 10^{16}$ cm² of the 0.025 M Aqueous Sodium Chloride Solution Flowing Through the Cuprophane Membrane

Press. increm. (psi)	10	20	30	40
5 °C	5.92	5.80	5.74	5.88
15 °C	5.48	4.85	4.58	4.67
25 °C	4.36	3.84	3.64	3.68
35 °C	4.37	4.29	3.95	3.97

distinctly with increasing pressure increment P and temperature. This is due to the fact that the effects of T and P to the parameters included in $K (=QL\eta_b/AP)$ cancel each other keeping K about constant; as a result, r becomes constant.

In Table 4, the parenthesized data are the number of

TABLE 4: Pore Radius ($r \times 10^8 \text{cm}$) and the Number of Pores ($n \times 10^{-19}$) in the Cuprophane Membrane Through which the 0.025 M Aqueous Sodium Chloride Solution flows*

Press. increm. (psi)	10	20	30	40
5°C	8.95 (0.751)	8.85 (0.768)	8.82 (0.773)	8.92 (0.755)
15°C	8.63 (0.807)	8.10 (0.916)	7.87 (0.971)	7.97 (0.947)
25°C	7.68 (1.02)	7.21 (1.16)	7.02 (1.22)	7.05 (1.21)
35°C	7.68 (1.02)	7.62 (1.04)	7.30 (1.13)	7.34 (1.12)

*The data in parentheses are the numbers of pores in the cuprophane membrane.

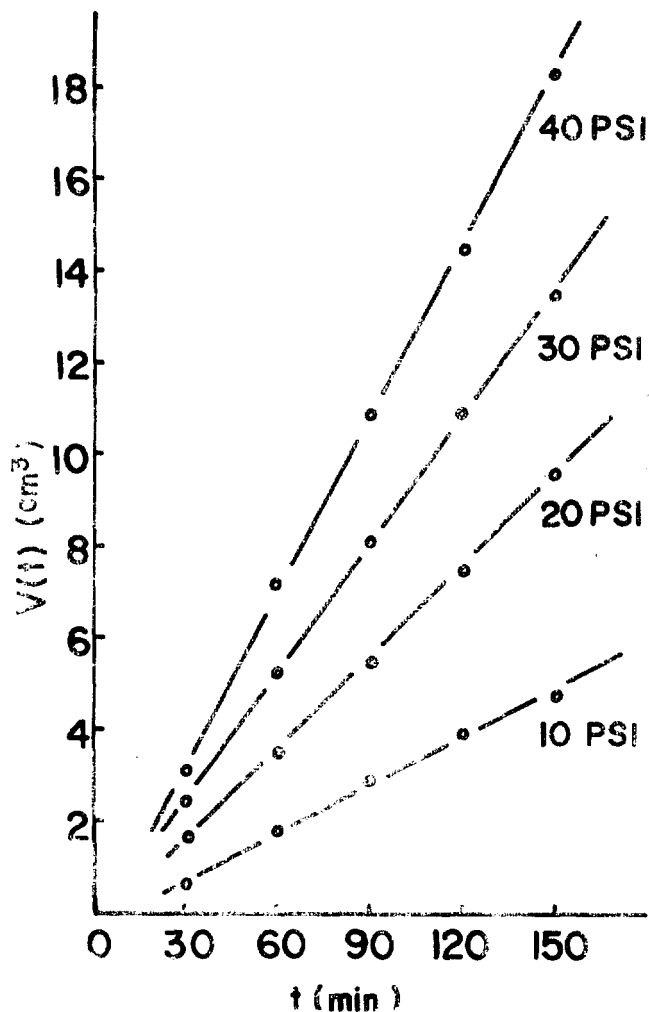


Figure 5. The plot of $V(t)$ (cm^3) vs. t (min) at 25°C. The $V(t)$ is the volume of the solution flowed at time t . From the slopes of the straight lines the volume flow rates Q are obtained.

pores (n) on the cuprophane membrane, and they were calculated from the following equation:

$$n = \frac{AS}{\pi r^2}$$

by using the known values of A ($=32.02 \text{cm}^2$) and S ($=0.59$) with the r values (unparenthesized data) in Table 4.

The Calculation of Viscosity. The values of the shear stresses (f) were calculated from Eq. (16) by using the known value of L [Section (1) of the Experimental] and the r values in Table 4. The results are listed in Table 5.

The v_a values of the volume flow rate (Q) calculated from the

TABLE 5: Shear Stresses (f dyne/cm²) when the 0.025 M Aqueous NaCl Solution Flows Through the Cuprophane Membrane

Press. increm. (psi)	10	20	30	40
5°C	18.19	35.98	53.79	72.53
15°C	17.54	32.93	47.99	64.81
25°C	15.61	29.31	42.81	57.33
35°C	15.61	30.98	44.52	59.68

TABLE 6: Volume flow Rates ($Q \times 10^3 \text{cm}^3/\text{sec}$) when the 0.025 M Aqueous NaCl Solution Flows through the Cuprophane Membrane, the Area of which is 32.02 cm²

Press. increm. (psi)	10	20	30	40
5°C	0.50	0.98	1.46	1.99
15°C	0.61	1.08	1.53	2.08
25°C	0.63	1.11	1.58	2.13
35°C	0.78	1.53	2.11	2.83

TABLE 7: Shear Rates ($\dot{\gamma} \times 10^{-3} \text{sec}^{-1}$) when the 0.025 M Aqueous Sodium Chloride Solution Flows Through The Cuprophane Membrane, the Thickness of which is $1.69 \times 10^{-3} \text{cm}$

Press. increm. (psi)	10	20	30	40
5°C	1.18	2.35	3.50	4.72
15°C	1.43	2.82	4.12	5.52
25°C	1.73	3.24	4.77	6.39
35°C	2.14	4.22	6.11	8.13

TABLE 8: The Viscosity (η_m) for the 0.025 M Aqueous Sodium Chloride Solution Flowing Through the Cuprophane Membrane*

Temp. (°C)	5	15	25	35
η_m (CP)	1.54	1.18	0.900	0.732
η_s (CP)	1.54	1.17	0.900	0.750

*In this table, the η_s values are listed for comparison.

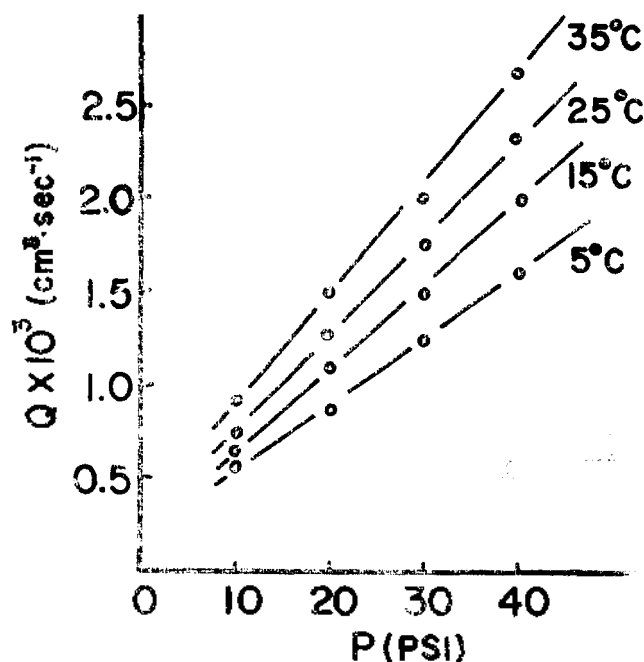


Figure 6. The plot of Q ($\text{cm}^3 \text{sec}^{-1}$) vs. pressure increment P (psi). The Q is the volume flow rate.

data of Section (2) of the Experimental are shown in Table 6. These Q values increase with increasing pressure increments and temperatures.

The plots of Q vs. P have a good linearity as shown in Figure 6. The linearity shows that the solution passing through the membrane is a Newtonian liquid, and that the second equality in Eq. (20) holds. In Eq. (20), $Q/n=Q_1$, the latter indicates the volume flow rate through a capillary in the membrane. By using the values of r and n in Table 4 in conjunction with the Q values in Table 6, we calculated the shear rate ($\dot{\gamma}$) from Eq. (20). The results are listed in Table 7.

Inserting the f and $\dot{\gamma}$ values shown in Table 5 and 7 into Eq. (15), we obtain the values of viscosity (η_m) for aqueous sodium chloride solution flowing through the membrane. The η_m values are listed in Table 8, where, because of the negligible P effect on η_m , only the average η_m at each temperature is shown. Comparing the η_m with the η_b (bulk viscosity of the 0.025 M NaCl solution) mentioned in Section (2) of the Experimental, one notes that η_m are exactly equal to η_b showing that no change occurs in the solution in the membrane phase.

On the Radius of the Diffusing Species. In Eq. (21), r' is the radius of the diffusing species. In NaCl solution, there are Na^+ and Cl^- which diffuse through the cuprophane membrane in addition to the solvent H_2O molecules. We take $r'=4.83 \text{ \AA}/2=2.42 \text{ \AA}$, where 4.83 \AA is the sum of radii of hydrated Na^+ and Cl^- ions.²⁵ Thus r' is assumed to be the average of radii of the two hydrated ions. In other words, we treat the diffusion of NaCl solution as that of the particles with radius r' . The r' value is larger than the radius of unhydrated Cl^- (1.81 \AA),²⁶ but a little smaller than the radius of $(\text{Cl}^-)_{\text{aq}}=2.55 \text{ \AA}$.²⁵ The radius of $(\text{Na}^+)_{\text{aq}}$ is 2.28 \AA .²⁵ whereas an unhydrated Na^+ has the radius of 0.95 \AA .²⁶ Since we cannot measure the diffusive rates of $(\text{Na}^+)_{\text{aq}}$ and (Cl^-) separately, the use of the average r' value seems to be reasonable, and is not far from the actual situation.

From Eq. (26), we can calculate r' for the diffusing species by using the known values of S ($=0.59$) and K , the V being taken as the molar volume of water (18 ml) because of the diluteness of the NaCl solution. As a typical example, the K value ($3.64 \times 10^{-16} \text{ cm}^2$) at 25°C and 30 psi was taken from Table 3, and r' was calculated from Eq. (26) as 0.257 \AA . The r' values calculated at other T and P do not change significantly from $r'=0.257 \text{ \AA}$ since K is about constant irrespective of T and P as mentioned previously. Comparing the value $r'=0.257 \text{ \AA}$ with the estimated value ($r'=2.42 \text{ \AA}$) mentioned above, one finds that the former is unreasonably too small. The smallness is caused by the fact that in the calculation of r' from Eq. (26), we used the K value from Table 3 for K_d (diffusive permeability constant), i.e., $K \approx K_d$, the former might include only K_v (the permeation due to the viscous flow) or both K_v and K_d .

Let us assume that the estimated $r'=2.42 \text{ \AA}$ is a true value. Then the K_d value is calculated from Eq. (26) in a converse way. We obtained $K_d=3.85 \cdot 10^{-17} \text{ cm}^2$. By assuming $K=K_v+K_d$, the ratio K_d/K is calculated as 0.106 by taking $K=3.64 \cdot 10^{-16} \text{ cm}^2$ at 25°C and 30 psi (Table 3). Thus we may conclude from this ratio that about 10% of the total flux

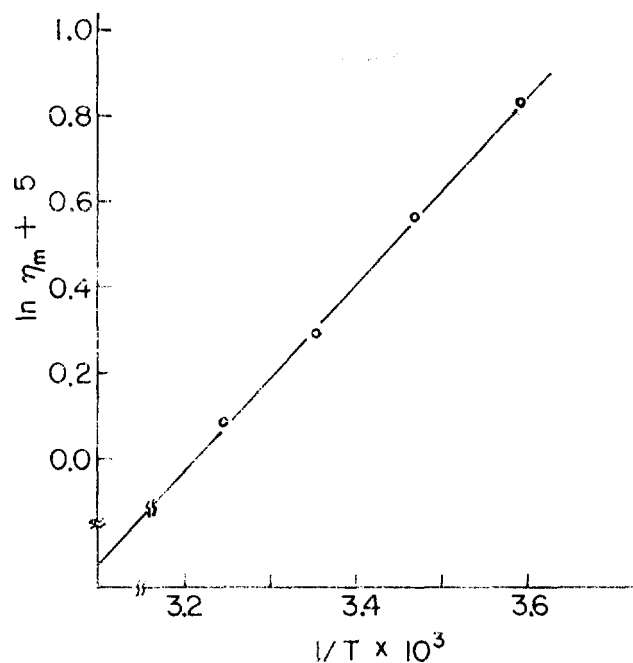


Figure 7. The plot of $\ln \eta_m$ vs. $1/T$. From the slope of the straight line, the ΔH_m^\ddagger value is obtained whereas ΔS_m^\ddagger is obtained from the intercept.

is due to the diffusive flow.

Tricknor¹⁸ derived theoretically an equation for $r/2r'$ in terms of Q_v and Q_d , where r is the radius of the capillary, and Q_v is the volume-flow rate by viscous flow mechanism. From the equation, Tricknor concluded

$$Q_v = Q_d \text{ if } r \approx 2r'$$

i.e., if the capillary radius much larger than twice of the radius of flowing species, the viscous flow is more predominant than the diffusive flow. Since in our case, $\langle r \rangle = 7.94 \text{ \AA}$ from Table 4 and $r' = 2.42 \text{ \AA}$ (the estimated value), we obtain $r/2r' \approx 2$. Thus, the condition $r \gg 2r'$ is not satisfied in our case. Consequently it cannot be concluded that the viscous flow exclusively predominant than the diffusive flow in our case. But, combing the above fact ($r/2r' \approx 2$) with the previously mentioned fact ($K_d/K = 0.106$), it may be concluded with confidence that in our experiment the diffusive flow is involved about 10% or less. Thus, in this paper, we treated our experimental data as due to the viscous flow neglecting the contribution of diffusive flow.

Thermodynamic Activation Parameters. According to Eyring's rate theory,¹ the following equation holds for viscosity η_m of the solution in the membrane:

$$\eta_m = \frac{h}{\lambda_m^3} \exp\left(\frac{-\Delta S_m^\ddagger}{R}\right) \exp\left(\frac{\Delta H_m^\ddagger}{RT}\right) \quad (27)$$

where $\lambda_m^3 \equiv \lambda_2 \lambda_3 \lambda^2 / \lambda_1$, ΔH_m^\ddagger and ΔS_m^\ddagger are the activation enthalpy and activation entropy for the viscous flow, respectively.

By using the η_m data in Table 8 a plot of $\ln \eta_m$ vs. $1/T$ was made in Figure 7. From the slope and intercept of the plot, we obtained the following values of the activation parameters:

$$\Delta H_m^\ddagger = 4.27 \text{ kcal/mole}, \quad \Delta S_m^\ddagger = 4.32 \text{ eu}$$

where the value of λ_m ($=2.42 \text{ \AA} \times 2$) was used in the cal-

ulation of $\Delta S_{\text{um}}^{\ddagger}$. The positive value of $\Delta S_{\text{um}}^{\ddagger}$ indicates that some amount of liberation of water molecules occurs in the activation process of the hydrated ion. Since the melting entropy of ice is 5.26 eu (=1.46 kcal/273), about 0.8 ($\approx 4.32/5.26$) parts of water molecules are liberated from the hydrated ion.

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Photochemical and Thermal Solvolysis of Picolyl Chlorides

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Photochemical and thermal solvolysis of 2,3,4-picolyl chlorides (2,3,4-PC) were studied in amine solvents and the results were correlated with the electronic structures calculated by PPP-SCF-MO CI method. Activation parameters show that the thermal solvolysis of PC is S_N2 type reaction. The rates of thermal reaction in pyridine or *t*-butylamine solvent decrease in the order of 2-PC > 3-PC > 4-PC. These results are consistent with the predictions based on the electron densities of picolyl chlorides. In photosolvolysis, the same products as those of thermal reactions were obtained. The results indicate that photochemical solvolysis undergoes through heterolytic cleavage. Relative quantum yields of photosolvolysis of 2,3,4-picolyl chlorides in *n*-butylamine solvent were determined to be 0.73, 1, and 0.50 respectively. These results are in good agreement with the electron densities of the excited triplet state of picolyl chlorides.

Introduction

Interest in the photosolvolysis has been stimulated since the discovery that nitrophenyl phosphates and sulphates show a substitution reaction to yield the corresponding nitrophenol upon ultraviolet irradiation of their aqueous solutions¹. There has been especially a considerable amount of work on the photosolvolysis of benzyl compounds in

nucleophilic solvents since the photosolvolysis study of certain benzyl derivatives by Zimmerman and Sandel². The compounds studied include benzyl (or substituted benzyl) sulfonium salts, ammonium salts, and halides. It has been reported that products resulting from both heterolysis and homolysis of the benzyl-heteroatom bond are formed either upon direct irradiation or upon photosensitization. When benzyl or substituted benzyl chlorides are photolyzed