Diffusion of Poly(vinylpyrrolidone) Through Cellulose Ester Membranes

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Synopsis

Diffusion coefficients of poly(vinylpyrrolidone) in aqueous solutions were ascertained by the diaphragm method as a function of molecular weight and temperature using mixed cellulose ester (Millipore) membranes. The results agree satisfactorily with diffusion coefficients obtained by other methods. Separation of polymer according to molecular size takes place on diffusion as a function of membrane pore diameter. Also, interaction between the polymer and membrane has been observed resulting in a distribution coefficient between solution and membrane larger than 1. The energy and entropy of activation, repectively, increase with polymer chain length, and their magnitudes are in agreement with the view that segment mobility is operative for the diffusion process.

INTRODUCTION

Diffusion of poly(vinylpyrrolidone) (PVP) in aqueous solutions has been studied previously by Scholtan,[1] Miller and Hamm,[2] and Dialer and Vogler.[3] Diffusion coefficients obtained by the diaphragm method as function of molecular weight and temperature are presented in this paper. The results agree quite satisfactorily with those obtained by other methods at 20°.

EXPERIMENTAL

Apparatus

A typical diffusion cell is shown in Figure 1. It consists of two "half" cells, separated by a membrane fixed in a Millipore filter holder (Type XX3002500, Millipore Corp., Bedford, Mass.). The whole assembly is made liquid tight with epoxy resin. The two glass "half" cells are usually not quite equal in length but are equal as far as the diameters are concerned (i.d. ca. 1.6 cm). Their lengths range from ca. 4.5 cm to 6 cm. Each "half" cell comprises a volume of about 12 to 16 ml. Each side is equipped with a short side arm closed by a Teflon stopcock. Thirty glass beads of 3-mm diameter each were placed into each "half" cell for stirring. The cells were mounted on a tumbler and placed in a thermostat constant to ±0.05°C rotating at 34 rpm. It was ascertained that a rate beyond 17 rpm did not influence the results. The volumes of PVP solutions in each "half" cell, corrected for glass spheres, were ascertained.
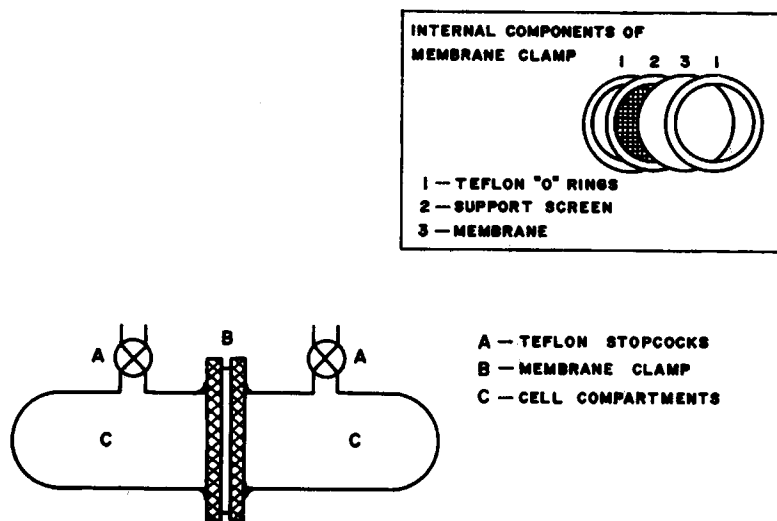
Fig. 1. Diffusion cell.

The cell constant was determined with $0.1N$ KCl solution at 25°C ($D =$ 1.83×10^{-5} cm²/sec).[4] The analysis was done with a conductivity bridge (Model RC16B2, Industrial Instruments Inc.). PVP concentrations were ascertained in 1-cm cells with a Beckman DB-G spectrophotometer at 1940 Å and room temperature. Intrinsic viscosities were measured in Canon-Fenske viscometers at 25° ± 0.02°C expressed in dl/g.

Materials

PVP (Plasdone K29-32 and K90, General Aniline and Film Corp.) was purified by precipitation from a 3% w/v aqueous (double-distilled water) PVP solution with a fivefold excess of reagent-grade acetone. The precipitate was dried to constant weight in a vacuum oven at 60°C. Plasdone K29-32 had an intrinsic viscosity $[\eta]$ of 0.281 dl/g and a viscosity-average molecular weight $\overline{M}_v$ of 5.70×10^4; K90 had $[\eta] = 1.10$ dl/g and $\overline{M}_v = 7.0\times10^5$. The relationship used was $[\eta] = 6.75\times10^4\,\overline{M}_v^{0.55}$ dl/g.[5] K29-32 was also fractionated by controlled addition of acetone to a 2.0% (w/v) aqueous polymer solution (FXI, $\overline{M}_v = 5.4\times10^4$; FXII, $\overline{M}_v = 1.4\times10^5$). The following Millipore mixed cellulose ester membranes were used for the diffusion experiments: SM (5 μm pore diameter), SS (3 μm), HA (0.45 μm), and VM (0.05 μm).

Procedure

"Half" cell, or side B, was filled with water, and A, with PVP solution. Air was carefully removed. The results were not influenced whether the membranes were pretreated by diffusion experiments or not.

Two methods of sample withdrawal for analysis were tried. The first method consisted of withdrawing samples at definite time intervals from

side B. The second method consisted of a series of experiments with one withdrawal each at the end of each respective experiment.

The first method gave results which showed diffusion rates at least three times larger than those found by the second method. Apparently, the air bubble, which is left in side B and increases with each new withdrawal, is compressed and causes ballooning of the membrane, thus increasing the pore diameter. This contention is supported by the following experiment: 0.3 cm³ were withdrawn from side B at the beginning of the experiment, and the concentration of PVP in B was determined after 2 hr. Similarly, 1.0 cm³ was withdrawn from B at the start of another similar experiment, and again the concentration of PVP in B was ascertained after 2 hr. The ratio of the diffusion constants for these two experiments, D (1.0 cm³ removed)$:D$ (0.3 cm³ removed), was found to be $\cong 3.0$. All results reported in this paper were obtained using the second method.

Evaluation and Diffusion Coefficients and Experimental Results

Diffusion coefficients were evaluated according to the diaphragm cell equation of Northrup and Anson[6]:

$$\ln \frac{(\Delta C)_t}{(\Delta C)_0} = -\frac{DAFT}{lV} = -\beta DFT \tag{1}$$

where $\beta = A/V$ is the cell constant, and $(\Delta C)_t$ and $(\Delta C)_0$ are the concentration differences across the membrane at times t and 0, respectively; A is the effective area of the membrane, l is membrane thickness, and $1/V = 1/V_A + 1/V_B$, where V_A and V_B are the volumes of cell compartments A and B, respectively. F is a distribution coefficient for the solute between solution and membrane, which was determined gravimetrically as follows: Five similar membranes were placed each in 20 cm³ PVP solution ($C = 1.9$ mg/ml) and soaked for 48 hr at room temperature. Blanks were run with water. From the differences in the initial and final solution concentrations, respectively, and the geometric volume of the membrane, the coefficient F was ascertained. The results are shown below:

Pore diameter, μm	0.05	0.45	3.0; 5.0
$F = \dfrac{C(\text{membrane})}{C(\text{solution})}$	4.3 ± 0.3	2.3 ± 0.5	1.7 ± 0.2

Here, C is a concentration term.

For the 0.05-μm membrane, analysis of the solutions was also performed with ultraviolet light. The F-value determined in this way agrees within a few per cent with the one determined gravimetrically. The membranes have approximately 80% free space (i.e., pores). It is clear from these results that there is some interaction between PVP and the membranes.

Separation of chains of different lengths takes place when membranes of small pore size are used. This separation was determined after 120 hr of diffusion when equilibrium was practically attained. At the end of this time, concentrations and intrinsic viscosities were measured on both

sides of the membrane.   From the concentrations, the ratio R of the mass of PVP capable of diffusing through the membrane to the total mass of PVP (or mass at $t = 0$ in side A) was determined. R was used for correcting the initial concentration of PVP to that concentration capable of diffusing through the membrane;   the diffusion coefficient could thus be corrected in this way.   The following results were obtained for K90 at 25°C:

| Pore diameter, | $\overline{M}_v \times 10^5$ | | R |
μm	Side A	Side B	
0.45	7.7 ± 0.4	4.9 ± 0.2	0.65
0.05	6.0 ± 0.6	2.0 ± 1.0	0.13

For larger porosities, the observed values of R are near 1.0.
   All diffusion coefficients obtained in this work are comprised in Table I.

TABLE I
Diffusion Coefficients for Various PVP Samples

Initial PVP concn., % w/v	Pore diam., μm	Temp., °C	$D \times 10^7$ cm²/sec	Standard deviation, cm²/sec	No. of exper.	Polymer sample
0.38	3.0	15	5.7	±0.2	9	K29–32, $\overline{M}_v = 5.7 \times 10^4$
—	3.0	20	6.5[a]	—	—	
0.40	3.0	25	7.5	±0.3	8	
0.38	3.0	35	10.7	±0.4	5	
0.39	3.0	15	3.0	±0.2	6	
—	3.0	20	3.8[a]	—	—	
0.40	3.0	25	5.1	±0.3	12	
0.40	3.0	35	7.8	±0.6	10	K90, $\overline{M}_v = 7.0 \times 10^5$
0.41	3.0	45	14.1	±1.2	5	
0.38	0.45	25	1.8	±0.2	9	
0.38	0.05	25	0.35	±0.2	7	
0.40	3.0	25	8.3	±0.4	6	fraction XI, $\overline{M}_v = 5.4 \times 10^4$
0.30	3.0	25	7.6	±0.4	8	fraction XI, $\overline{M}_v = 1.4 \times 10^5$

[a] Calculated from Arrhenius plot (Fig. 2); $F = 1.7$.

DISCUSSION

The diffusion coefficients measured in this work can be compared with those obtained by other methods.   Scholtan,[1] Miller and Hamm,[2] and Dialer and Vogler[3] have determined diffusion coefficients of PVP in aqueous solution by measurements in cells without diaphragms and by sedimentation.[2]   It is difficult to compare Scholtan's values with those reported here because of uncertainties in assigning corresponding molecular weights. Some of the values obtained by these authors (120°C) are given in Table II.

Hamm and Miller[2] remark that the sedimentation method gives unreliable values compared with those obtained by conventional methods.

TABLE II
Diffusion Coefficients Obtained by Various Methods

$\overline{M}_v \times 10^4$	C, % w/v	$D \times 10^7$ cm²/sec	
		Conven- tional method	Sedimen- tation
Dailer and Vogler[3]			
8.6, fractionated	0.5	2.44	
4.2, fractionated	0.5	4.31	
1.06, fractionated	0.5	8.66	
Miller and Hamm[2]			
3.2, unfractionated	0.25–1.0	4.81	3.9
4.15, fractionated	0.25–1.0	4.14	4.8
2.3, fractionated	0.25–1.0	5.87	3.1
2.4, unfractionated	0.25–1.0	3.1	3.1
Scholtan[1]			
ca. 5, unfractionated	0.5	5.8	
ca. 5, fractionated	0.5	5.8	
Jellinek and Blom (this work)			
5.7, unfractionated	0.4	6.5[a]	

[a] Calculated from Figure 2 for 20°C; $F = 1.7$.

These authors give a mean deviation of $\pm 5\%$ for the conventional method. They also note that the concentration dependence of the diffusion coefficients is quite small. This was also observed by Scholtan.[1]

The diffusion coefficients obtained in this work agree satisfactorily with those found by the other workers. This indicates that the diaphragm method is suitable for the determination of diffusion constants of PVP. Actually, the fact that $F > 1$ shows that interaction between the cellulose ester membranes and PVP occurs. Most likely some adsorption of the polymer on pore walls takes place.

Figure 2 shows Arrhenius plots for the D-values of samples K29-32 and K90, for 3 μm pore diameter. The respective equations are as follows:

K29-32

$$D = [(9.0 \pm 5.0) \times 10^{-3} \exp(-5,500 \pm 300)/RT] \text{ cm}^2/\text{sec}$$

K90

$$D = [(2.9 \pm 0.3) \exp(-9,200 - 1600)/RT] \text{ cm}^2/\text{sec}$$

The diffusion coefficients as function of temperature can also be expressed according to Glasstone, Laidler, and Eyring[7] as follows:

$$D = e\sigma^2(kT/h) \exp(\Delta S^*/R) \exp(-\Delta E/RT) \text{ cm}^2/\text{sec} \qquad (2)$$

where e is the base of the natural logarithms, σ is the distance between equilibrium positions of the diffusing unit, k and h are, respectively, Boltzmann's and Planck's constants; ΔS^* and ΔE are the entropy and Arrhenius energy of activation, respectively. The values for $(e^{\Delta S^*/R})^{1/2}$ in Å
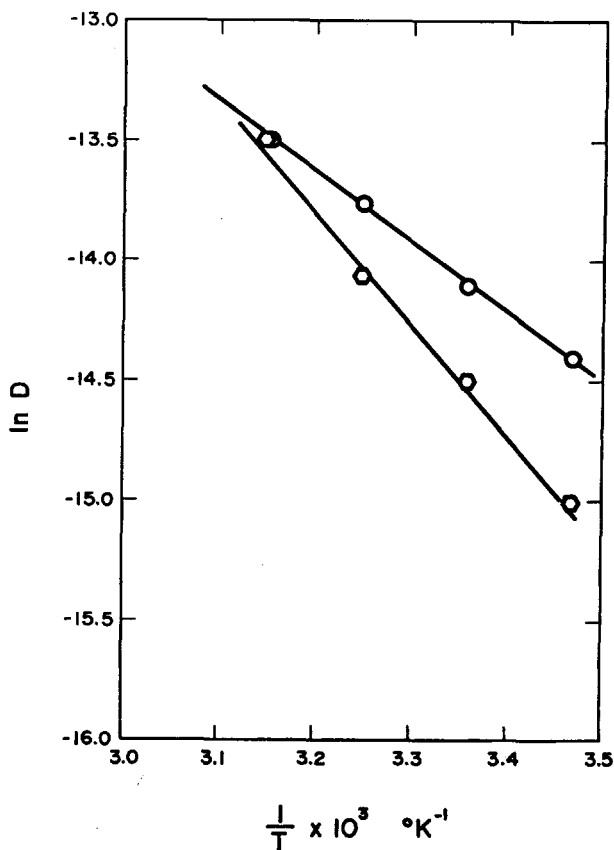
Fig. 2. Arrhenius plots: (O) K-29-32; (O) K-90.

units are as follows: K29-32, $\sim+2.3$; K90, $\sim+41.6$. If $\sigma = 1$ Å, ΔS^* becomes $+3.3$ e.u. and $+14.8$ e.u., respectively.

The energy of activation for K29-32 is of similar magnitude as the energy of activation of self-diffusion of water. This agrees with the concept of segmental diffusion for polymers. The segment size increases with polymer chain length and with it the energy of activation. This is in agreement with Eyring's views. Also the magnitude of the entropy term agrees with the concept of segment mobility.[8] Barrer[9] takes a somewhat different view which, however, in principle, amounts to the same fundamental picture. According to this author, a large entropy of activation implies a large zone of activation. This zone of activation, of course, increases with the size of the mobile segment and thus with polymer chain length.

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