

611. *High-polymer Solutions. Part I. Osmotic-pressure Measurements with Poly(vinyl alcohol) Membranes.*

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The behaviour of poly(vinyl alcohol) films as semipermeable membranes in non-aqueous systems has been examined. Membranes with different degrees of semipermeability have been prepared by varying the original water content (O.W.C.) of the films before conditioning them to the solvent. The permeability of the films decreases with increasing O.W.C. By using a membrane of O.W.C. 0.071 g. per g. of poly(vinyl alcohol) it has been possible to measure polymer molecular weights from $\bar{M}_n \sim 1 \times 10^6$ down to 2000; in no case was there evidence of solute diffusion through the film.

With the polymer-solvent systems studied it has been found that the relationship between π and C is best expressed by the equation $\pi/C = a + bC$ (π = osmotic pressure, C = concentration, a and b = constants).

THE reproducible and accurate determination of number average molecular weights by osmotic methods depends to a very large extent on the use of carefully prepared and truly semipermeable membranes. With solutions of many polymers which have low molecular weights or are heterodisperse, it has hitherto proved impossible to achieve complete retention of the solute without reducing the rate of passage of solvent through the membrane to negligible values.

The most widely used semipermeable membranes are based on gel cellophane or denitrated collodion. Melville and his co-workers (*Nature*, 1946, **157**, 74) have also used bacterial cellulose films. The lower limit of semipermeability for denitrated collodion membranes in non-aqueous systems is $\bar{M}_n \sim 30,000$ —40,000 (Flory, *J. Amer. Chem. Soc.*, 1943, **65**, 372) and for gel cellophane $\sim 10,000$ (Wagner, *Ind. Eng. Chem.*, 1944, **16**, 520). Philipp and Bjork (*J. Polymer Sci.*, 1951, **6**, 383) employed an old, slow, and much used gel cellophane membrane to evaluate a cellulose acetate fraction of \bar{M}_n 1450 (cryoscopically measured), but it was necessary to correct for solute diffusion. For this fraction, normal gel cellophane membranes were far too permeable for use.

By using the poly(vinyl alcohol) membranes described below it has been possible to make accurate measurements of the molecular weights in non-aqueous solutions of polymers from $\bar{M}_n \sim 2000$ upwards. The rate of solvent transfer across these membranes is sufficiently rapid to enable simple unsymmetrical osmometers to be used, equilibrium being reached in 2—3 hours.

EXPERIMENTAL.

Measurements of osmotic pressure were made in modified Zimm-Meyerson osmometers (*J. Amer. Chem. Soc.*, 1946, **68**, 911). A central tension-adjusting screw was used to clamp the plates in place of the original spring-loaded wing nuts. Precision-bore tubing was used for the measuring capillary (int. diam. 0.05 cm.), reference capillary (int. diam. 0.05 cm.), and filling capillary (int. diam. 0.2 cm.). In order to reduce distortion, the measuring capillary was not supported by the filling tube; the reference capillary was attached to the filling tube. The glass cell was 1.0 cm. deep and of 2.0-cm. internal diameter. The filling capillary was closed by a metal rod with a mercury seal, the rod being used to adjust the meniscus levels of the solutions. The glass cylinder containing osmometer and pure solvent was closed with a well-fitting cap.

The constant-temperature water-bath was kept in a draught-free room at $25^\circ \pm 1^\circ$. During 2—3 hours, temperature control in the bath was $\sim \pm 0.001^\circ$; $31.5^\circ \pm 0.002^\circ$ could be maintained for long periods. Despite the unsymmetrical nature of the osmometers, the combination of good temperature control and fast membranes resulted in stable osmotic heads with no sign of oscillation about an equilibrium position.

Poly(vinyl alcohol) Membranes.—The poly(vinyl alcohol) used was prepared from medium viscosity poly(vinyl acetate) and contained about 1% of residual acetate. Membranes were

prepared by evaporation of an aqueous (1.5% w/v) solution of poly(vinyl alcohol) at $26^\circ \pm 0.1^\circ$ and 40% relative humidity. Their normal thickness was 0.002–0.003 in. Before use, the membranes were conditioned to atmospheres of known relative humidity for 5 days and their water contents then estimated by displacement of the water with dry alcohol and titration of the wet alcohol with the Karl Fischer reagent.

Typical membranes were dried over phosphoric oxide to constant weight, it then being found that no water could be displaced with dry alcohol. Membranes which had been dried in this way, weighed, and then stored at different relative humidities were found to have a weight increase equal, within experimental error, to the weight of water removed by dry alcohol (Table 1).

TABLE 1. *Water content of poly(vinyl alcohol) membranes.*

Relative humidity (%)	Wt. of dry membrane (g.)	Wt. of H ₂ O absorbed (g.)	Wt. of H ₂ O displaced by dry alcohol (g.)	O.W.C. (g./g.)
0	0.3130	—	0.000	0.000
32	0.3106	0.0049	0.005	0.015
40	0.3462	0.0075	0.007	0.022
44	0.3501	0.0088	0.009	0.025
70	0.3034	0.0217	0.022	0.071
75	0.3130	0.0270	0.027	0.086
93	0.3687	0.1169	0.117	0.317

After dehydration by alcohol, the membranes were conditioned to benzene by immersion in 1:1 alcohol-benzene for 2 hours and then in benzene for 3 hours. The membranes were installed in the osmometers, and their "speeds" to benzene measured at $31.5^\circ \pm 0.002^\circ$ by observing the fall of the liquid meniscus in the measuring capillary. Fig. 1 shows the relation between original water content of membranes [O.W.C.; stated throughout in g. of water per g. of poly(vinyl alcohol)] and speed to benzene. In these experiments the fall of the benzene meniscus did not follow the simple exponential relation used by French and Ewart (*Ind. Eng. Chem., Anal.*, 1947, **19**, 165) to evaluate the permeability constant of their membranes. Nonetheless a family of curves was obtained such that for any two membranes at times t_1, t_2, t_3 , etc., $(h^I/h^{II})_{t_1} = (h^I/h^{II})_{t_2}$, etc. The "speeds" recorded in Table 2 have been calculated by arbitrarily assigning a speed of 1 to the membrane of O.W.C. 0.317 g./g. and relating the other membrane speeds to this value.

TABLE 2. *Relation between O.W.C. and speed to benzene at 31.5°.*

O.W.C. (g./g.)	0.015	0.025	0.050	0.071	0.086	0.317
Speed	97	88	11.8	7.1	5.9	1.0

The most striking feature in Table 2 is that membrane speed decreases with increasing O.W.C., in complete contrast to the behaviour of bacterial cellulose under the same conditions (authors, unpublished work) or of gel cellophane (Carter and Record, *J.*, 1939, 660) and bacterial cellulose (Melville and Masson, *J. Polymer Sci.*, 1949, **4**, 323) on swelling in alcohol-water. Semipermeability towards benzene solutions of polystyrene of $\bar{M}_n \sim 200,000$ was shown with membranes possessing an O.W.C. of 0.05 g./g., and equilibrium osmotic heads were obtained with membranes of O.W.C. 0.06 g./g. The work described subsequently in this paper was carried out with a membrane of O.W.C. 0.071 g./g. With this membrane, and the osmometers described above, an osmotic head of 1 cm. is developed in about 2 hours.

Materials.—Benzene, butanone, and toluene were purified by drying and careful fractionation. One particularly pure sample of benzene was obtained by distillation, treatment with mercuric acetate, re-distillation, and repeated crystallisation. The densities and refractive indices of these materials were in excellent agreement with accepted values.

Ethyl alcohol was dried and purified by Smith's method (*J.*, 1927, 1288).

Preparation of Polymer Solutions.—All solutions were made up by weight. A stock solution of the most concentrated solution to be used was made up and portions diluted by weight to give the lower concentrations.

Measurement of Osmotic Head.—The head developed by the most dilute solution was measured first, then those by the other solutions in order of increasing concentration. The cells were washed 3–6 times with solution, filled with solution, and placed in the solvent container which was already in the thermostat bath. Equilibrium was then allowed to be established, a static method of measurement being used. The change of concentration due to the small amount of

solvent which moved through the membrane in establishing a head of 1 cm. was about 0.06%. When osmotic heads in excess of 2 cm. were measured, the expected equilibrium position was roughly determined and the solution meniscus then set about 1 cm. below this position. An osmometer was not considered satisfactory if, with solvent on both sides of the membrane, the difference in level between measuring and reference capillary menisci exceeded ± 0.001 cm. The speed of the membranes to pure solvent and the heights of solvent in the measuring and the reference capillary were checked at the beginning and end of each set of measurements. The stability of the equilibrium osmotic heads was usually observed during 24 hours for at least 3 of the concentrations measured.

RESULTS.

In order to establish the precision of the experimental technique, osmotic pressure measurements were made on an unfractionated emulsion of polystyrene in benzene, toluene, and butanone solutions. The graphs of π/C against C (concentration) are shown in Fig. 2. The concentration units have been converted into g./100 c.c. of solution at 31.5°, by using values of 0.8665, 0.8552,

FIG. 1. Relation between O.W.C. and speed to benzene.

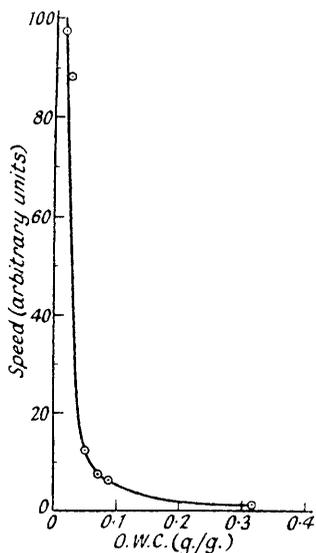
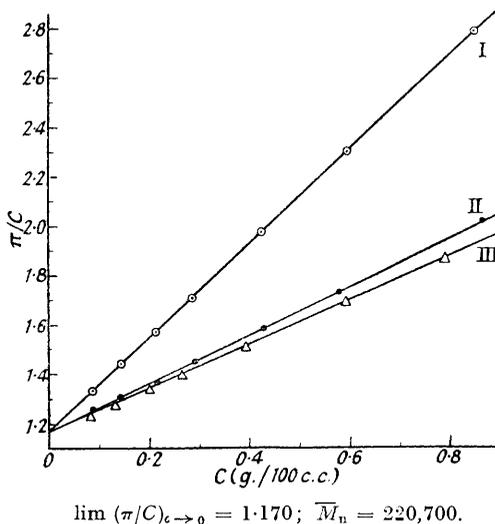


FIG. 2. Variation of π/C with C for polystyrene in (I) toluene, (II) benzene, (III) butanone.



0.7896 g./c.c. for the densities of benzene, toluene, and butanone respectively and 1.08 g./c.c. for polystyrene (cf. Boyer and Spencer, *J. Polymer Sci.*, 1948, 3, 125).

The osmotic pressures (π) were calculated from the relation :

$$\pi = (h_s - h_0)\rho_s \dots \dots \dots (1)$$

where h_0 is the capillary rise in the reference capillary, h_s is the combined osmotic and capillary rise in the measuring capillary, and ρ_s is the density of the polymer solution. The difference between the surface tension of the pure solvents and that of the most concentrated solutions of the polymer was shown to be negligible. Strictly, equation (1) does not yield the true osmotic pressure since the reference level should not be that of pure solvent in the outer container, but rather the point at which true osmotic equilibrium obtains (Lang, *Kolloid Z.*, 1951, 122, 165; Gilbert, Graff-Baker, and Greenwood, *J. Polymer Sci.*, 1951, 6, 585). With the Zimm-Meyerson osmometer, equilibrium will obtain at the centre of the vertical membranes. Thus, if h is the depth of immersion of the membrane centre,

$$\pi^* = (h_s + h)\rho_s - (h_0 + h)\rho_0 \dots \dots \dots (2)$$

where ρ_0 is the density of the solvent and π^* the true osmotic pressure.

Hence
$$\pi^* - \pi = (h_0 + h) (\rho_s - \rho_0) \dots \dots \dots (3)$$

TABLE 5.

Polymer	C (g./100 c.c.)	π (g./sq. cm.)	π/C	a	b	$(\pi/C - a)/C$	\bar{M}_n
F	0.0867	0.598	6.893			1.188	
	0.1460	1.016	6.962			1.178	
	0.2173	1.532	7.050	6.79	1.200	1.196	3.8×10^4
	0.2900	2.070	7.140			1.202	
	0.4309	3.150	7.309			1.205	
G	0.0872	0.827	9.485			1.204	
	0.1464	1.399	9.555			1.195	
	0.2166	2.088	9.640	9.38	1.200	1.200	2.75×10^4
	0.2912	2.834	9.730			1.203	
	0.4350	4.306	9.899			1.193	
H	0.0436	0.958	21.95			1.147	
	0.0872	1.918	22.00			1.147	
	0.1462	3.225	22.06	21.90	1.125	1.094	1.18×10^4
	0.2175	4.813	22.14			1.103	
	0.2892	6.424	22.21			1.072	

Table 6 shows the relation between π/C and C for a styrene-divinylbenzene soluble copolymer (J) containing a nominal 0.1% of divinylbenzene and polymerised at 60° with 2% of benzoyl peroxide as catalyst. The polymer was freed from polymer of very low molecular weight by dissolution in benzene and precipitation of the polymer with methyl alcohol. The measurements were carried out on benzene solutions.

TABLE 6.

Polymer	C (g./100 c.c.)	π (g./sq. cm.)	π/C	a	b	$(\pi/C - a)/C$	\bar{M}_n
J	0.2171	0.077	0.355			0.460	
	0.2887	0.113	0.390			0.371	
	0.4365	0.199	0.456	0.255	0.456	0.460	1×10^6
	0.5208	0.255	0.489			0.449	
	0.6435	0.354	0.549			0.457	
	0.8656	0.562	0.649			0.455	

Osmotic-pressure measurements on a phenol-formaldehyde "Novolac" fraction in butanone are summarised in Table 7.

TABLE 7.

C (g./100 c.c.)	π (g./sq. cm.)	π/C	\bar{M}_n	M_n (cryoscopic)
0.0791	9.482	119.8 _a		
0.0591	7.080	119.8		
0.0395	4.734	119.8	2156	2140
0.0198	2.369	119.7 _a		

The measurements recorded in Table 8 were made on benzene solutions of a polystyrene of low molecular weight, prepared by stannic chloride catalysis in ethylene dichloride (Pepper, *Sci. Proc. Roy. Dublin Soc.*, 1951, **25**, 239).

TABLE 8.

C (g./100 c.c.)	π (g./sq. cm.)	π/C	\bar{M}_n	\bar{M}_n (cryoscopic)
0.0435	5.959	137.1		
0.0216	2.954	136.5	1900	1900

DISCUSSION

The membranes described in this paper considerably extend the scope and accuracy of osmotic-pressure measurements on polymer solutions. Since the molecular weight obtained from osmotic measurements is a number average it is of particular importance to avoid diffusion of polymer. In our view a membrane should be characterised, where possible, by measurements with a polymer whose number average molecular weight has been checked by an independent method. Stability of osmotic head and non-precipitability of polymer from the solvent side of the osmometer do not always constitute a rigid test for the diffusion of polymer of low molecular weight. Thus three independent measurements of the molecular weight of a broad fraction of a commercial polystyrene from

which polymer of low molecular weight had been (partly) removed yielded the following results. Laboratories A and B used Fuoss-Mead osmometers and denitrated collodion membranes; in both cases apparently rigorous checks were made for solute diffusion.

Laboratory :	A	B	This work
\bar{M}_n	210,000	222,500	156,500

Fox, Flory, and Bueche suggested recently (*J. Amer. Chem. Soc.*, 1951, **73**, 285) that, at the polymer concentrations normally used in osmotic measurements of molecular weight, the curvature of the π/C against C plot is sufficiently marked to require its extrapolation to zero concentration as a curve rather than as a straight line. It will be apparent that with none of the heterodisperse polymers investigated in this work is there any justification for other than a rectilinear extrapolation. A statistical justification of this view will be the subject of a further communication. It appears that, whilst the ultimate form of the π/C against C relationship may well be curvilinear, the errors introduced in a general application of the Flory equation to heterodisperse polymers may be greater than those encountered experimentally (cf. Cleverdon and Laker, *Chem. and Ind.*, 1951, 272).

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