841. *High-polymer Solutions. Part II.* The Determination of Number-average Molecular Weights from Measurements of Osmotic Pressure.*

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Careful measurements of the osmotic pressures of benzene solutions of polymethyl methacrylate and of polyvinyl thiolacetate have been statistically analysed to find the best equation for extrapolation of the reduced osmotic pressure–concentration relation to infinite dilution. A similar analysis of results obtained with solutions of polystyrene in benzene, toluene, and butanone is also reported. In the concentration range studied there is no advantage in expressing the results by other than the rectilinear relation $\pi/C = a + bC$ (π = osmotic pressure, C = concentration, a and b = constants).

The limiting value of π/C at infinite dilution may be shown to be a true measure of the molecular weight of a polymer, independent of its size or shape or the nature of the solvent used. Thus the accuracy of determination of the molecular weight of a polymer depends to a considerable extent on the nature and reliability of the extrapolation of experimental measurements to infinite dilution. A number of authors (see, *e.g.*, McMillan and Mayer, *J. Chem. Phys.*, 1945, **13**, 276; Zimm, *ibid.*, 1946, **14**, 164) have suggested that the concentration dependence of osmotic pressure may be expressed as a convergent series

$$\pi = \boldsymbol{R}T(aC + bC^2 + dC^3 + \cdots) \quad \ldots \quad \text{(i)}$$

Recently Fox, Flory, and Bueche (*J. Amer. Chem. Soc.*, 1951, **73**, 285) have used published osmotic data in support of a theoretically derived equation which has been expressed in equation (iv) (below) as a restricted form of equation (i).

In Part I * of this series, Hookway and Townsend reported a series of measurements of osmotic pressure with a number of different polymers. In order so far as possible to render the interpretation of these and other results truly objective, the results have been statistically analysed to determine whether they best fit equations of the form (ii), (iii), or (iv).

$$\pi/C = a + bC \quad \ldots \quad \text{(ii)}$$

$$\pi/C = a + bC + dC^2 \quad \ldots \quad \text{(iii)}$$

$$\pi/C = a_1[1 + b_1C + \tfrac{5}{8}b_1^2C^2] \quad \ldots \quad \text{(iv)}$$

* Part I, *J.*, 1952, 3190.

Results.—Measurements of osmotic pressure were made by means of the membranes and apparatus described in Part I (*loc. cit.*). The results presented in Table 1 for polymethyl methacrylate (D), polyvinyl thiolacetate (E), and polystyrenes (A) and (B) are based on data given in Tables 3 and 4 of Part I. In Table 2 the osmotic pressures of solutions of polystyrene in various solvents at 31·5° are recorded; C_1 = polymer concentration in g./100 c.c. of solvent; C_2 = polymer concentration in g./100 c.c. of solution; π_2 = osmotic pressure based on concentration C_2; π_3 = osmotic pressure corrected for depth of immersion of osmometer (see Part I for details).

In the calculations underlying Tables 1 and 3, equations (ii) and (iii) were rewritten in the forms

$$\pi = aC + bC^2 \qquad \text{(v)}$$

$$\pi = aC + bC^2 + dC^3 \qquad \text{(vi)}$$

and fitted to the observed data by the ordinary least-squares technique. Equation (iv) was rewritten as

$$\pi = a_1C + a_1b_1C^2 + \tfrac{5}{8}a_1b_1^2C^3 \qquad \text{(vii)}$$

leading to least-squares estimates of a_1 and b_1 satisfying the pair of equations

$$\Sigma\{(C + b_1C^2 + \tfrac{5}{8}b_1^2C^3)(\pi - a_1C - a_1b_1C^2 - \tfrac{5}{8}a_1b_1^2C^3)\} = 0 \qquad \text{(viii)}$$

$$\Sigma\{(C^2 + \tfrac{5}{4}b_1C^3)(\pi - a_1C - a_1b_1C^2 - \tfrac{5}{8}a_1b_1^2C^3)\} = 0 \qquad \text{(ix)}$$

where Σ denotes a summation over all pairs of observations (π, C). Equations (viii) and (ix) are equivalent to the pair (x) and (xi):

$$a_1\Sigma\{(C^2 + \tfrac{5}{4}b_1C^3)(C + b_1C^2 + \tfrac{5}{8}b_1^2C^3)\} = \Sigma\{\pi(C^2 + \tfrac{5}{4}b_1C^3)\} \qquad \text{(x)}$$

$$a_1\Sigma\{(2C + b_1C^2)(C + b_1C^2 + \tfrac{5}{8}b_1^2C^3)\} = \Sigma\{\pi(2C + b_1C^2)\} \qquad \text{(xi)}$$

and a_1 may be eliminated from these to yield a quartic equation which b_1 must satisfy. Tables 1 and 3 give for each system the appropriate root of this quartic and the corresponding value of

TABLE 1.

Polymer	Equation	a	b	d	Mean-squared deviation, $\times 10^6$
D	ii	1·8394 ± 0·0032	0·9334 ± 0·0045		1·486
	iii	1·8407 ± 0·0086	0·9282 ± 0·0315	0·0043 ± 0·0260	1·844
	iv	1·8929 ± 0·0093	0·3826 ± 0·0066		17·053
E	ii	2·5790 ± 0·0027	1·1338 ± 0·0050		0·535
	iii	2·5871 ± 0·0040	1·0908 ± 0·0195	0·0481 ± 0·0216	0·182
	iv	2·6153 ± 0·0055	0·3605 ± 0·0037		2·786
A	ii	16·3068 ± 0·0070	2·2557 ± 0·0280		0·546
	iii	16·2908 ± 0·0182	2·4346 ± 0·1873	−0·4341 ± 0·4487	0·634
B	ii	6·1066 ± 0·0133	0·9894 ± 0·0341		6·188
	iii	6·1610 ± 0·0198	0·6160 ± 0·1281	0·5574 ± 0·1894	1·732

TABLE 2.

Solvent: benzene.

C_1, g./100 c.c.	C_2, g./100 c.c.	π_1, g./cm.^{2}	π_2, g./cm.^{2}	π_3, g./cm.^{2}	C_1, g./100 c.c.	C_2, g./100 c.c.	π_1, g./cm.^{2}	π_2, g./cm.^{2}	π_3, g./cm.^{2}
0·0861	0·0861	0·108	0·108	0·109	0·4303	0·4307	0·681	0·682	0·687
0·1437	0·1437	0·188	0·188	0·190	0·5767	0·5776	0·996	0·997	1·003
0·2511	0·2152	0·294	0·295	0·297	0·8665	0·8682	1·741	1·744	1·753
0·2881	0·2883	0·417	0·417	0·420					

Solvent: toluene.

C_2, g./100 c.c.	π_2, g./cm.^{2}	π_3, g./cm.^{2}	C_2, g./100 c.c.	π_2, g./cm.^{2}	π_3, g./cm.^{2}	C_2, g./100 c.c.	π_2, g./cm.^{2}	π_3, g./cm.^{2}
0·0858	0·114	0·115	0·2851	0·487	0·490	0·5985	1·372	1·379
0·1424	0·205	0·207	0·4247	0·836	0·841	0·8546	2·371	2·381
0·2134	0·335	0·337						

Solvent: butanone.

C_2, g./100 c.c.	π_2, g./cm.^{2}	π_3, g./cm.^{2}	C_2, g./100 c.c.	π_2, g./cm.^{2}	π_3, g./cm.^{2}	C_2, g./100 c.c.	π_2, g./cm.^{2}	π_3, g./cm.^{2}
0·0789	0·098	0·099	0·2640	0·369	0·373	0·5918	1·000	1·008
0·1314	0·168	0·170	0·3943	0·595	0·601	0·7897	1·473	1·484
0·1971	0·265	0·268						

a_1 as determined by (x) or (xi). Convenient expressions for the sampling variances of a_1 and b_1 were obtained, as may always be done for maximum likelihood estimates (Kendall, " Advanced Theory of Statistics," 1946, Vol. II, Charles Griffin & Co. Ltd.), from the Hessian of the sum of squared residuals

$$\Sigma(\pi - a_1C - a_1b_1C^2 - \tfrac{4}{9}a_1b_1{}^2C^3)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xii)}$$

The values of a, b, and d entered in Tables 1 and 3 are given in each case in the form estimate $\pm$ standard error. The final column in these tables gives the mean-squared deviation of the observed values of π from those calculated from the fitted curve. These entries were computed by dividing the sum of squared deviations by the appropriate degrees of freedom [2 less than the number of observations in the case of equations (v) and (vii); 3 less in the case of equation (vi)].

TABLE 3.

Solvent	π, C	Equation	a	b	d	Mean-squared deviation, $\times 10^6$
Benzene	π_1, C_1	ii	1·1637 ± 0·0023	0·9759 ± 0·0032		0·741
		iii	1·1634 ± 0·0061	0·9771 ± 0·0225	−0·0010 ± 0·0187	0·927
		iv	1·2374 ± 0·0122	0·5557 ± 0·0132		31·523
	π_2, C_2	ii	1·1651 ± 0·0012	0·9716 ± 0·0017		0·221
		iii	1·1667 ± 0·0032	0·9655 ± 0·0119	0·0051 ± 0·0099	0·262
		iv	1·2385 ± 0·0117	0·5532 ± 0·0127		29·292
	π_3, C_2	ii	1·1764 ± 0·0019	0·9705 ± 0·0026		0·494
		iii	1·1781 ± 0·0049	0·9639 ± 0·0180	0·0055 ± 0·0149	0·596
		iv	1·2493 ± 0·0117	0·5491 ± 0·0125		29·064
Toluene	π_2, C_2	ii	1·1711 ± 0·0015	1·8758 ± 0·0021		0·289
		iii	1·1740 ± 0·0034	1·8639 ± 0·0128	0·0101 ± 0·0108	0·296
		iv	1·3552 ± 0·0284	0·8485 ± 0·0295		186·138
	π_3, C_2	ii	1·1821 ± 0·0017	1·8766 ± 0·0024		0·379
		iii	1·1844 ± 0·0042	1·8674 ± 0·0155	0·0079 ± 0·0131	0·435
		iv	1·3657 ± 0·0285	0·8441 ± 0·0294		186·608
Butanone	π_2, C_2	ii	1·1623 ± 0·0031	0·8901 ± 0·0047		1·072
		iii	1·1674 ± 0·0072	0·8671 ± 0·0291	0·0215 ± 0·0268	1·154
		iv	1·2167 ± 0·0093	0·5366 ± 0·0111		13·497
	π_3, C_2	ii	1·1777 ± 0·0028	0·8880 ± 0·0042		0·864
		iii	1·1840 ± 0·0060	0·8597 ± 0·0243	0·0265 ± 0·0224	0·801
		iv	1·2315 ± 0·0089	0·5306 ± 0·0105		12·303

Discussion.—The principal object of this work has been to find the best method of determining the coefficient a. In view of the hetero-disperse nature of the polymers studied, no attempt has been made to attach any physical significance to the coefficients b and d.

The close agreement between the observed and calculated values of π, in the case of equations (v) and (vi), is at once apparent from the small size of the mean-squared deviations, and is illustrated in detail for polymer E in Table 4.

TABLE 4. *Observed and calculated values of* π.

	π, g./cm.^{2}			
C, g./100 c.c.	Obs.	Eqn. (v)	Eqn. (vi)	Eqn. (vii)
0·0866	0·232	0·2318	0·2323	0·2337
0·1454	0·399	0·3990	0·3994	0·4008
0·2165	0·612	0·6115	0·6117	0·6126
0·2892	0·841	0·8407	0·8406	0·8403
0·4332	1·329	1·3300	1·3293	1·3271
0·6481	2·148	2·1477	2·1479	2·1487

It can be seen from the values of the mean-squared deviations in Tables 1 and 3 that in no case is the unrestricted parabola [equation (iii)] significantly superior to the straight line [equation (ii)]; indeed, to discriminate between them would appear to demand more precise measurements of π than can as yet be made. The virtual agreement between equations (ii) and (iii) is indicated also by the agreement between the pairs of values of a

that they supply, and also by the relatively high values found for the standard error of the coefficients d. In the light of the results found, Fox, Flory, and Bueche's equation (iv) appears to have little to recommend it. It is true that, if we ignore the results of fitting (ii) and (iii), (iv) appears to explain the experimental data reasonably well; but (ii) and (iii) explain them better, and involve less complicated calculations. Cleverdon and Laker (*Chem. and Ind.*, 1951, 272) and McLeod and McIntosh (*Canadian J. Chem.*, 1951, **29**, 1104) have also made measurements which suggest that equation (iv) may not be of general application.

The data for polystyrene in three solvents presented in Tables 2 and 3 show that the values of a cover a range of $\pm 0{\cdot}0044$ for equation (ii) and $\pm 0{\cdot}0036$ for equation (iii). The uncertainty in molecular weight is thus about 0·75%—a satisfactory indication of the soundness of the experimental technique. Conversion of concentration units from g./100 c.c. of solvent ($\pi_1 C_1$) to g./100 c.c. of solution ($\pi_2 C_2$) does not affect the results appreciably. Similarly, correction of the osmotic pressure to allow for the depth of immersion of the osmometer ($\pi_3 C_2$) causes a change of less than 1% in the value of a and causes no significant change in the mean-squared deviations.

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