

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Treatment of Osmotic and Light Scattering Data for Dilute Solutions^{1,2}

BY T. G. FOX, JR., P. J. FLORY AND A. M. BUECHE

Accurate determinations of the molecular weights of high polymers by thermodynamic methods require appropriate extrapolation to infinite dilution from measurements made at finite concentrations. In the case of the osmotic method it is customary for this purpose to plot the ratio of the osmotic pressure to the concentration, π/c , vs. the concentration c . Light scattering measurements are handled in an equivalent manner by plotting c/τ vs. c where τ is the excess turbidity of the solution over that of the solvent. Although it is common practice to make linear extrapolations in such plots, neither theory nor experiment justifies this procedure.

Gee and Treloar³ were perhaps the first to show that experimental plots of π/c vs. c (in this case for rubber in benzene and other solvents) actually are appreciably concave upwards. This behavior appears to be general^{4,5,6} for various polymers except in poorer solvents (*cf. seq.*). Gee emphasized the need for a reliable extrapolation procedure by means of which the π/c vs. c curves could be extrapolated to $c = 0$. Earlier theories^{7,8} did indeed provide relationships for this purpose, but these have been shown to be invalid at dilutions such that the polymer molecules do not overlap each other extensively.⁹

A recent statistical mechanical treatment of dilute polymer solutions¹⁰ yields the relationship

$$\pi/c \cong (\pi/c)_0 [1 + \Gamma_2 c + (5/8) \Gamma_2^2 c^2] \quad (1)$$

where the coefficient of the square term is given in approximation, and higher terms, important at higher concentrations, are omitted. Here $(\pi/c)_0 = RT/\bar{M}_n$ is the limiting value of (π/c) at $c = 0$, R being the gas constant, T the absolute temperature, and \bar{M}_n the number average molecular weight of the polymer; and Γ_2 is a parameter de-

pendent on the polymer-solvent pair, the temperature and the molecular weight of the polymer. This relationship should hold for concentrations such that $(\pi/c)/(\pi/c)_0$ is small, *i. e.*, less than about three. Equation (1) predicts curvature which, qualitatively at least, is in accord with that observed. The corresponding expression for the

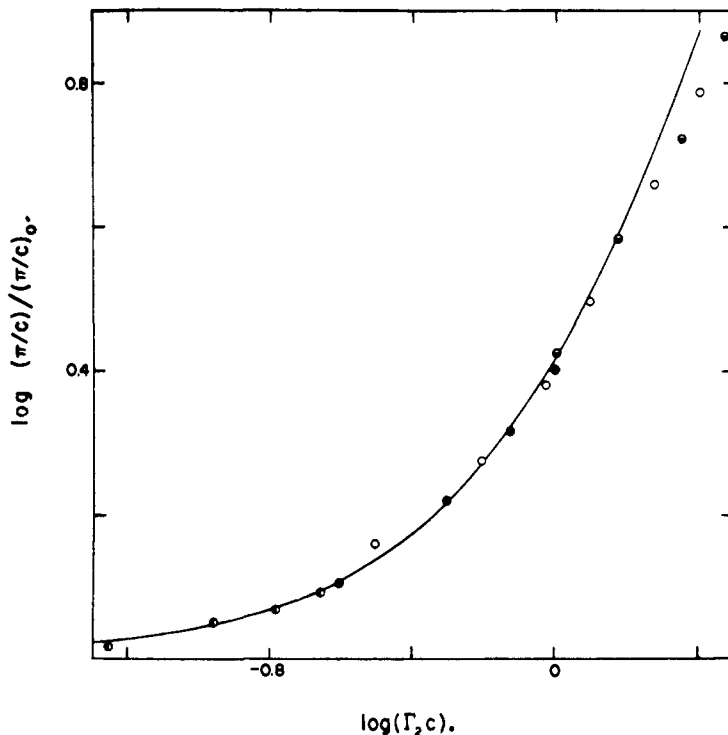


Fig. 1.—Log-log plot of $(\pi/c)/(\pi/c)_0$ vs. $\Gamma_2 c$ for cyclohexane solutions of several polyisobutylene fractions at 25°: ● B (0-3), $M = 770,000$; ○ C (4-9), $M = 256,000$; ● B (9-13), $M = 78,000$; ● A (14-23), $M = 29,000$.⁴ The curve represents the theoretical relationship expressed in equation (1).

turbidity is

$$(c/\tau) \cong (c/\tau)_0 [1 + 2\Gamma_2 c + (15/8)\Gamma_2^2 c^2] \quad (2)$$

from which higher terms have been omitted, as in equation (1).

It is the purpose of the present paper to examine the adequacy of equation (1) for the representation of osmotic pressure-concentration data from the literature, and to illustrate the application of equation (2) to turbidity measurements using new data obtained on polystyrene in benzene. It should be pointed out that theory¹⁰ permits derivation of the coefficients of c^2 in equations (1) and (2) only for the case of homogeneous polymers, and then only in an approximate manner; a corresponding evaluation of these third coefficients for heterogeneous polymers appears to be out of the question at present. While it is plausible to assume that the relationship of the second to the third coefficient as specified by equations (1) and (2) is not much affected by molecular weight hetero-

(1) This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

(2) Presented in part before the High Polymer Forum at the Detroit Meeting of the American Chemical Society, April 18, 1950.

(3) G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942). See also H. M. Spurlin, "Cellulose and Cellulose Derivatives," edited by E. Ott, Interscience Publishers, Inc., Co., New York, N. Y., 1943, p. 919.

(4) P. J. Flory, *THIS JOURNAL*, **65**, 372 (1943).

(5) C. R. Masson and H. W. Melville, *J. Polymer Sci.*, **4**, 337 (1949).

(6) M. J. Schick, P. Doty and B. H. Zimm, *THIS JOURNAL*, **72**, 530 (1950).

(7) M. I. Huggins, *J. Chem. Phys.*, **46**, 151 (1942); *Ind. Eng. Chem.*, **35**, 980 (1943).

(8) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(9) P. J. Flory, *ibid.*, **13**, 453 (1945).

(10) P. J. Flory, *ibid.*, **17**, 1347 (1949); P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

generality (and, hence, that the shape of the π/c vs. c and the c/τ vs. c curves are the same for heterogeneous as for homogeneous polymers), this matter remains to be settled by experiment.

Method of Treating Data.—For the purpose of comparing equation (1) with experimental data, the logarithm of the quantity in brackets in equation (1) was plotted against $\log c$ on transparent graph paper. This was superimposed on a plot of the experimental data expressed as $\log (\pi/c)$ vs. $\log c$ using the same scale as above, the calculated curve being shifted to obtain the best possible fit while keeping the axes of the two graphs parallel. The values of $(\pi/c)_0$ and Γ_2 were obtained directly from the displacements between the respective axes of the two graphs. Only those sets of data were selected from the literature which offer an adequate number of points in the required region $(\pi/c) < 3(\pi/c)_0$, and which were sufficiently accurate for a significant test of equation (1).

Light scattering data for polystyrene in benzene were treated similarly using for this purpose equation (2) in place of (1).

Application to Osmotic Measurements.—Osmotic data for cyclohexane solutions of four

polyisobutylene fractions⁴ were treated as described above. In each case it was possible to fit the values of π/c to the theoretical curve based on equation (1); the values of $(\pi/c)_0$, the molecular weights calculated therefrom, and the Γ_2 values thus obtained are given in Table I.

TABLE I

OSMOTIC DATA FOR SOLUTIONS OF POLYISOBUTYLENE FRACTIONS IN CYCLOHEXANE AT 25°⁴

Polymer designation	$(\pi/c)_0^a$	M	Γ_2	Initial slope, $(\pi/c)_0\Gamma_2$
B(0.3)	0.33	770,000	2.95	0.98
C(4.9)	0.99	256,000	1.26	1.25
B(9.13)	3.24	78,000	0.50	1.62
A(14.25)	8.67	29,000	0.22	1.91

^a π in g./sq. cm., c in g./100 cc.

Representation of these data by equation (1) is illustrated by the log-log plot of $(\pi/c)/(\pi/c)_0$ vs. $\Gamma_2 c$ for these four polymers shown in Fig. 1. The curve has been calculated by equation (1). The agreement between theory and the experimental data for concentrations such that $(\pi/c)/(\pi/c)_0 < 3$ appears to be within the experimental error as judged by irregularities. The present values of $(\pi/c)_0$ are in agreement with those previously reported.⁴ For the two polymers of highest molecular weight these were independently established previously⁴ from measurements of π in the poor solvent, benzene, wherein the ratio π/c is nearly independent of c and hence the extrapolation is greatly simplified. Examination of Table I shows that Γ_2 increases with molecular weight, but $(\pi/c)_0\Gamma_2$, representing the initial slope of the π/c vs. c plot, decreases with increase in M . The magnitude of this change is in approximate accord with the theoretically predicted¹⁰ constitution of Γ_2 .

The excellent osmotic data of Masson and Melville⁵ on unfractionated polymers are also represented satisfactorily by equation (1). All of these data are within the range wherein $(\pi/c)/(\pi/c)_0 < 3$. In Table II are given the polymer-solvent combinations they employed, the values of $(\pi/c)_0$ and Γ_2 obtained here, and the values of $(\pi/c)_0$ obtained by Masson and Melville's empirical extrapolation. The values of $(\pi/c)_0$ resulting from the use of equation (1) are generally higher than those of Masson and Melville by amounts varying from 1 to 30%, and the discrepancy usually increases with increasing M . The values of $\Gamma_2(\pi/c)_0$ depend on the nature of the solvent-polymer pair as should be expected and, even for the narrow range covered here, they decrease with increasing molecular weight. A comparison of the π/c vs. c relationship calculated by equation (1), using the parameters of Table II, with the corresponding experimental points for several of these polymers is given in Fig. 2. The agreement between equation (1) and the data for these unfractionated polymers is even better than that found for the fractionated polyisobutylenes above.

The osmotic data of Schick, Doty and Zimm⁶ on an unfractionated polystyrene in cyclohexane and ethyl acetate, although somewhat scattered, may be represented by equation (1) over the range

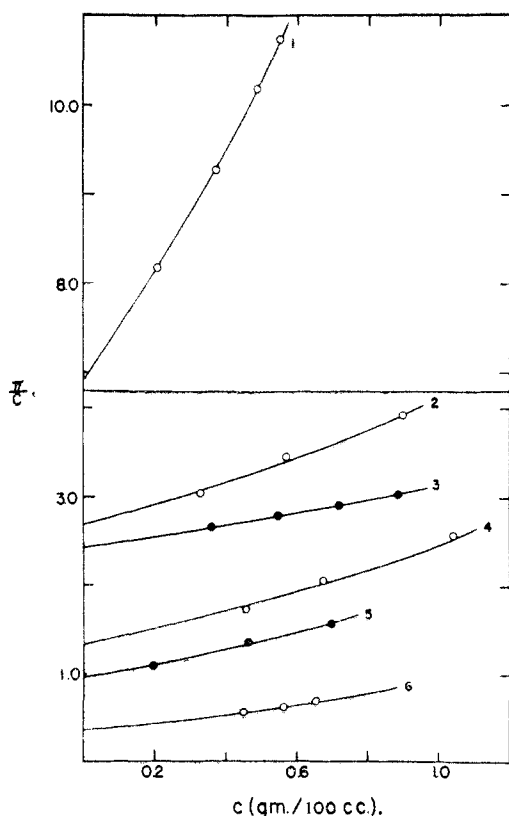


Fig. 2.—Osmotic pressure-concentration ratio vs. concentration for the solvent-polymer pairs: curve 1, polyacrylonitrile in dimethylformamide at 13.5°; curve 2 and 4, polyvinyl acetate G-25 and 2410, respectively, in benzene at 20°; curve 3, polyacenaaphthylene in benzene at 25°; curve 5, polyvinyl xylene VI/106 in benzene at 24°; curve 6, polyethyl methacrylate PM-1 in benzene at 16°. The curves were calculated by equation (1) using the parameters of Table II.

TABLE II
 OSMOTIC DATA OF MASSON AND MELVILLE⁵

Polymer designation	Masson and Melville	$(\pi/c)_0^a$	From Equation (1) ^b	Ratio	Nature of Masson and Melville extrapolation	Γ_2^b	Initial slope, $(\pi/c)_0 \times \Gamma_2$
Polyvinyl acetate in benzene at 20°							
G-25	2.73	2.68 ± 0.08	2.68 ± 0.08	0.98 ± 0.03	Non-linear	0.42 ± 0.05	1.13
1221	2.06	2.11 ± .08	2.11 ± .08	1.03 ± .04	Non-linear	.48 ± .02	1.01
G-45	1.77	1.93 ± .10	1.93 ± .10	1.09 ± .06	Non-linear	.48 ± .03	0.93
G-60	1.30	1.55 ± .07	1.55 ± .07	1.19 ± .05	Non-linear	.51 ± .05	.79
2410	1.17	1.34 ± .05	1.34 ± .05	1.15 ± .04	Non-linear	.61 ± .05	.82
Polyvinyl acetate in methyl acetate at 20°							
G-45	1.84	2.05 ± .07	2.05 ± .07	1.11 ± .04	Linear	0.52 ± .04	1.07
Polymethyl methacrylate in benzene at 16°							
PM-1	0.34	0.36 ± 0.02	0.36 ± 0.02	1.06 ± 0.06	Non-linear	1.00 ± 0.10	0.36
PM-2	.25	.244 ± .01	.244 ± .01	0.98 ± .04	Non-linear	1.45 ± .12	.35
PM-3	.14	.184 ± .01	.184 ± .01	1.33 ± .07	Non-linear	1.50 ± .20	.28
Polyvinyl xylene in benzene at 24°							
VI/106	0.96	0.97 ± 0.01	0.97 ± 0.01	1.01 ± 0.01	Linear	0.70 ± 0.03	0.68
VI/112	.80	.84 ± .02	.84 ± .02	1.05 ± .03	Linear	.77 ± .06	.65
VI/27	.57	.60 ± .05	.60 ± .05	1.05 ± .09	Linear	1.00 ± .15	.60
Polyacrylonitrile in dimethylformamide at 13.5°							
	7.2	6.93 ± .05	6.93 ± .05	0.96 ± .01	Non-linear	0.78 ± .01	5.4
Polyacenaphthylene in benzene at 25°							
	2.41	2.43 ± 0.02	2.43 ± 0.02	1.01 ± 0.01	Linear	0.25 ± 0.02	0.61

^a π in cm. of H₂O, c in g./100 cc. ^b The precision of the values of these parameters was estimated in each case by determining visually the limiting positions of the theoretical curve which represent the data within the experimental error in the latter.

wherein $(\pi/c)/(\pi/c)_0 < 3$. The data for toluene falling in this range are too few to permit comparison with equation (1); for methyl ethyl ketone the scatter of the data permits only an approximate determination of the parameters of this equation. The values of the parameters obtained here for these solvents are given in Table III. The $(\pi/c)_0$ values agree with those reported by the above authors. They fitted their data empirically to a three parameter equation, $\pi = RT(B_1c + B_2c^2 + B_3c^3)$, over much wider ranges in π/c than is legitimate for the application of equation (1), hence their second and third virial coefficients are not to be compared directly with the parameters of Table III. (Furthermore, the second and third virial coefficients reported by them appear to be unrelated to one another.) In Fig. 3 plots of $(\pi/c)/(\pi/c)_0 - (5/8)\Gamma_2^2c^2$ vs. c are shown for cyclohexane and ethyl acetate. The data when reduced in this way, employing the parameters of Table III, are well represented by the straight lines corresponding to equation (1).^{11,12}

According to the foregoing analysis of osmotic data, equation (1) is equally applicable to fractionated and unfractionated polymers. Thus, although the magnitude of Γ_2 should depend somewhat on heterogeneity,¹⁰ the form of the π/c vs. c relationship apparently is insensitive to heterogeneity, as was anticipated.¹⁰

(11) The present authors concur with the conclusion of Schick, *et al.*, that these data indicate a specific dependence of the entropy of dilution of polymer with solvent on the nature of the solvent. This observation, which is contrary to all previous assumptions, was arrived at independently from an investigation of the intrinsic viscosity-temperature relationships for polyisobutylene.¹²

(12) T. G. Fox, Jr., and P. J. Flory, in press.

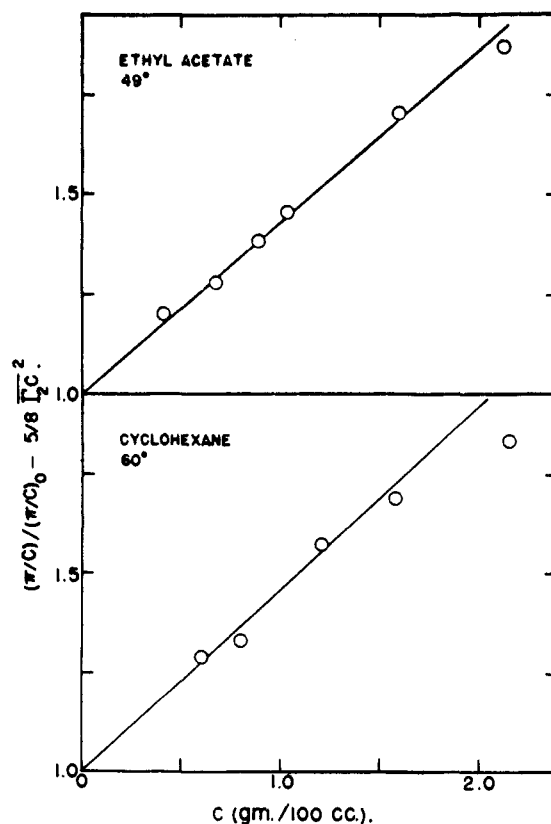


Fig. 3.—A plot illustrating the linearity of the $(\pi/c)/(\pi/c)_0 - 5/8(\Gamma_2^2)c^2$ vs. c relationship for dilute solutions of polystyrene in various solvents.⁸ The circles represent the experimental data; the straight lines correspond to equation (1). The values of $(\pi/c)_0$ and Γ_2 are from Table III.

TABLE III
OSMOTIC DATA OF SCHICK, DOTY AND ZIMM⁶ ON POLYSTYRENE OF \bar{M}_v , 540,000

Solvent	T, °C.	$(\pi/c)_0^a$	Γ_2
Cyclohexane	49	0.522	0.26
	60	.539	.46
Ethyl acetate	27	.486	.39
	49	.522	.43
Methyl ethyl ketone ^b	27	.486	.68
	49	.522	.52

^a π in g./sq. cm., c in g./100 cc. ^b The values for the parameters for methyl ethyl ketone are approximate in nature.

Turbidities of Dilute Polystyrene Solutions.—The polystyrene employed in the present light scattering investigations was obtained by the

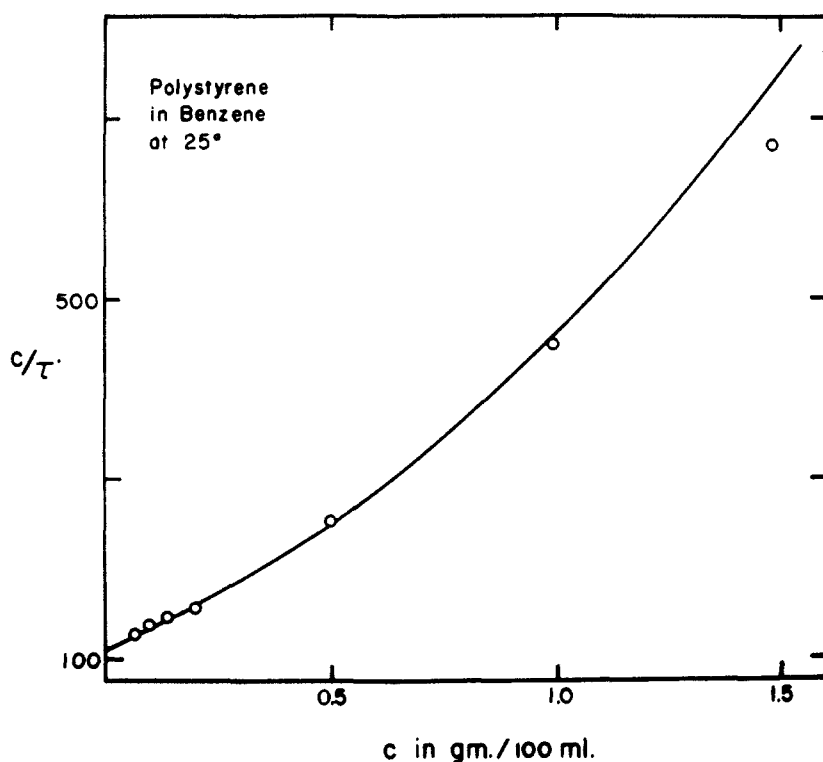


Fig. 4.—A plot of c/τ vs. c for a polystyrene fraction of $\bar{M}_v = 290,000$ in benzene at 25°. The curved line was calculated by equation (2) using values of $(c/\tau)_0$ and Γ_2 of 114 and 0.85, respectively.

fractionation of a polymer of viscosity average molecular weight (\bar{M}_v) of 250,000, which was polymerized in bulk from styrene at 60° in the presence of 0.1 mole per cent. benzoyl peroxide. The fractionation was made at 30° from methyl ethyl ketone wherein the initial concentration of the polymer was 2.0 g./100 cc., employing methanol as the precipitant. Six fractions were separated and the third of these, representing about 15% of the whole polymer and having a viscosity average molecular weight of about 290,000, was employed in the experiments here described. Solutions of this fraction in benzene were prepared individually and each was filtered through a fine sintered glass frit to remove extraneous sources of turbidity insofar as possible. Turbidity meas-

urements were made on these at room temperature with the 90° scattering instrument described by Debye.¹³ The data obtained when plotted as c/τ vs. c (Fig. 4) exhibit curvature as predicted. The curved line in this figure was calculated by equation (2), using values of 114 and 0.85 for $(c/\tau)_0$ and Γ_2 , respectively, where c is expressed as g./100 cc. These data indicate the adequacy of the theory in the range when $(c/\tau)/(c/\tau)_0 \leq 4$, which should correspond to $(\pi/c)/(\pi/c)_0 \leq 2.3$. The molecular weight calculated from $(c/\tau)_0$ is 288,000¹⁴ which compares favorably with the \bar{M}_v value of 290,000. The fact that the Γ_2 value obtained in the present case is higher than those for the solvents listed in Table III, even though the latter were obtained for a polystyrene of higher molecular weight ($\bar{M}_n = 540,000$), is indicative of the fact that thermodynamically benzene is a better solvent for polystyrene.

The various experimental results on the osmotic pressures of solutions of fractionated polyisobutylenes⁴ and of unfractionated polystyrene⁶ and on the turbidity of benzene solutions of a fractionated polystyrene exhibit negative deviations from the extrapolations of equations (1) and (2) to higher concentrations. These equations should not be employed for data obtained at high concentrations.

Conclusions

The osmotic pressure expression, equation (1), obtained from the recent theory of dilute polymer solutions adequately represents the π/c vs. c relationship for a variety of polymer-solvent combinations including both homogeneous and heterogeneous polymers. The equation applies only in dilute solutions where $(\pi/c)/(\pi/c)_0 < 3$. This success in analysis of experimental results over wide molecular weight ranges, including examples wherein the initial slope and curvature of the π/c vs. c plots are small as well as cases where these are pronounced, is indicative of the validity of the form of equation (1) where the third virial coefficient is related to the square of the second. Accurate confirmation of the numerical coefficient (5/8), on the other hand, will require further precise data.

As predicted, the initial slope and curvature of these plots vary with molecular weight of the

(13) P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575 (1949).

(14) This represents a molecular weight corrected for the small dissymmetry (1.2) based on the turbidity of the Cornell-Dow Styron sample of 3.57×10^{-3} . This value for the standard turbidity is somewhat higher than the value of 2.74×10^{-3} found using the "absolute camera." If the latter value is used, the molecular weight becomes 221,000.

polymer and with the nature of the polymer-solvent combination. Although the values of $(\pi/c)_0$ obtained by other extrapolation methods where the molecular weight is low do not differ substantially from those obtained through the use of equation (1), this difference does become important as M increases. Finally, data on the c/τ vs. c relationship for dilute solutions of polystyrene in benzene indicate curvature, and these

are adequately represented by the theoretical expression, equation (2), in the range where $(c/\tau)/(c/\tau)_0 \leq 4$. In view of these observations, general use of equations (1) and (2) is recommended for the evaluation of molecular weights and of thermodynamic parameters Γ_2 from osmotic and/or light scattering data on dilute solutions of polymers.

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Investigations on Proteins and Polymers. IV.¹ Critical Phenomena in Polyvinyl Alcohol-Acetate Copolymer Solutions

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Introduction

In a previous communication it has been reported that the state of aggregation of polyvinyl alcohol-acetate copolymers (PVA-A) in aqueous solutions depends upon their thermal history.^{1b} Using the light scattering method of investigation it was shown that an increase in temperature is followed by an aggregation of the polymer, while a decrease in temperature induced the polymer to disaggregate. These findings thus extend earlier³ observations that subfreezing temperatures affect the state of aggregation of this and other colloids.

This property of the polymer can be analyzed in terms of thermodynamics of polymer solutions and phase separation. According to the early Flory-Huggins theory, the partial molal free energy of the solvent, $\Delta\bar{F}_1$, may be expressed^{4,5} as a function of the volume fraction of the polymer, v_2 , by

$$-\Delta\bar{F}_1 = RTv_2[1/x + (1/2 - \mu)v_2 + v_2^2/3 + \dots] \quad (1)$$

where x , the degree of polymerization, is defined as \bar{V}_2/\bar{V}_1 , i.e., the ratio of the partial molal volumes of solute and solvent. Moreover, it is known that the turbidity, τ , of a solution can be correlated to the partial molal free energy by

$$Hc/\tau = -\frac{1}{RT\bar{V}_1} \frac{\partial(\Delta\bar{F}_1)}{\partial c} = 1/M + 2Bc + 3Dc^2 + \dots \quad (2)$$

where the coefficients B and D have been previously defined.^{1c}

The shape governing factor of equation 1 is the second term $(1/2 - \mu)$, where

$$\mu = \beta + (\alpha/RT) \quad (3)$$

(1) For previous communications of this series see: (a) M. Bier and F. F. Nord, *Proc. Natl. Acad. Sci.*, **35**, 17 (1949); (b) S. N. Timasheff, M. Bier and F. F. Nord, *ibid.*, **35**, 364 (1949); (c) S. N. Timasheff, M. Bier and F. F. Nord, *J. Phys. Colloid Chem.*, **53**, 1134 (1949).

(2) Some of the material discussed here is abridged from a part of the dissertation submitted to the Graduate Faculty of Fordham University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1950.

(3) (a) F. F. Nord, *Science*, **75**, 54 (1932); (b) F. F. Nord, *Ergebn. Enzymforsch.*, **2**, 23 (1933); (c) H. Leichter and F. F. Nord, *Biochem. Z.*, **295**, 226 (1938); (d) L. Holzapfel and F. F. Nord, *Biodynamica*, **3**, No. 57 (1940); (e) L. D. Rampino and F. F. Nord, *THIS JOURNAL*, **63**, 2745 (1941).

(4) (a) M. L. Huggins, *THIS JOURNAL*, **64**, 1712 (1942); (b) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942); **44**, 431 (1943).

(5) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **13**, 453 (1945).

β being the empirical entropy contribution factor, and α/RT the heat of dilution term. When the term $(1/2 - \mu)$ is positive, $-\Delta\bar{F}_1$ increases continuously with polymer concentration, the solvent and polymer being miscible in all proportions. When this term becomes sufficiently negative, the curve of partial molal free energy will pass through minimum and maximum values, the solution separating into two phases. The condition for incipient separation of phases is given by

$$\mu_{\text{critical}} = (1 + \sqrt{x})^2/2x \quad (4)$$

the free energy curve passing by a point of inflection. Equation 4, of course, applies strictly only in a monodisperse polymer solution.

In Fig. 1 the values of the average particle weight and $\mu_{\text{exptl.}}$, calculated in the usual manner,^{6,1c} are plotted against temperature for two different samples of PVA-A (du Pont Elvanol, Grade

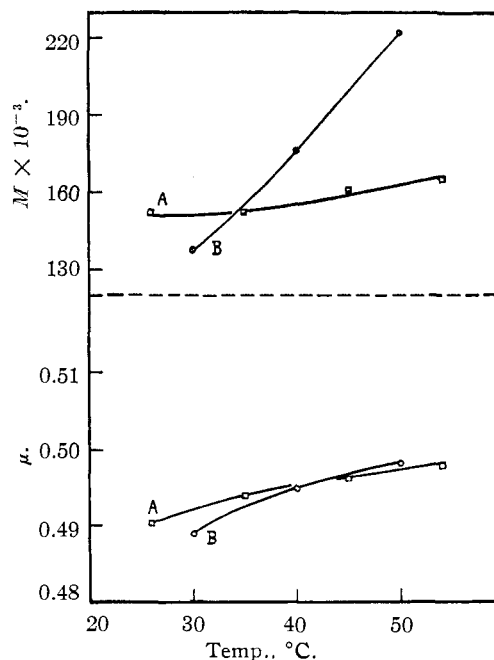


Fig. 1.—Comparison of $\mu_{\text{exptl.}}$ and particle weights at different temperatures of two samples of non-fractionated PVA-A: A, lot LB 76; B, lot JB 276.