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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[CONTRIBUTION NO. 204 FROM THE DEPARTMENT OF ORGANIC CHEMISTRY AND ENZYMOLOGY, FORDHAM UNIVERSITY]

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

BY F. F. NORD, M. BIER[2] AND SERGE N. TIMASHEFF

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 earlier[3] 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

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

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

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

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

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

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

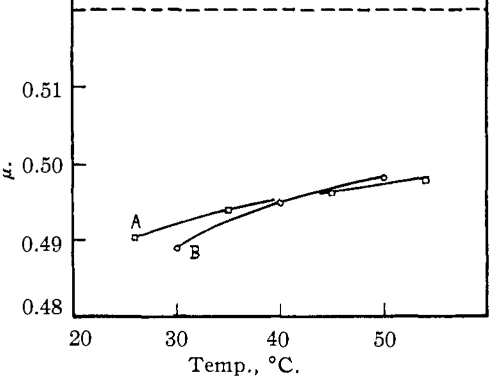

Fig. 1.—Comparison of $\mu_{\text{exptl.}}$ and particle weights at different temperatures of two samples of non-fractionated PVA–A: A, lot LB 76; B, lot JB 276.

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[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).

52-22).[6] Due to the negative partial molal heat of mixing[7] and in accordance with equation 3, the values of $\mu_{\text{exptl.}}$ increase with rising temperature, accompanied by an increase in average particle weight. It is of interest that two samples of PVA–A of the same grade, similar acetyl content (*ca.* 10–11%) and average particle weight were found to differ with respect to their rates of aggregation. This points to the fact that in such a polymer as PVA–A we have to take into consideration two types of polydispersity, with regard to the distribution of molecular weights and the degree of acetylation. Therefore, this study was made of the influence of these two factors on the thermal behavior of PVA–A.

PVA–A copolymers with an acetyl content of 15 to 20% are soluble in cold water but separate out of solution on heating over a wide temperature range. Such a polymer can be, therefore, fractionated according to the critical temperatures of phase separation of its various component fractions. Several such fractions were prepared and their acetyl content, degree of polymerization and of aggregation investigated.

Experimental

Fractionation.—Five hundred grams of PVA–A (du Pont Elvanol, Grade 31-31, lot 3K-636) was dissolved by continuous stirring in 10 l. of distilled water at 25°. The small amount of material which remained undissolved after 6 hr. of stirring was filtered off and discarded. The filtrate was placed in a thermostat at 85°, at which temperature a large portion of the polymer separated out of solution, depositing in a gelatinous layer at the bottom of the container. After 1 hour, the supernatant liquid was decanted and preserved as containing the fraction soluble above 85°.

The precipitated material was redissolved in cold water, filtered and placed into a thermostat at 35°. On standing overnight, the solution separated into two layers, the gelatinous layer on the bottom of the vessel containing the polymer fractions with critical temperatures of incipient phase separation in the range of 25 to 35°. From the supernatant solution, after decanting, by stepwise increases in temperature, further fractions were obtained. Each of these fractions was characterized by a temperature range, below the lower limit of which the entire fraction was completely soluble in water and above the upper limit of which the whole fraction precipitated. The fractions were 25-35°, 35-45°, 45-55°, 55-65° and 65-85°.

Each fraction was further refractionated by dissolving it at its lower temperature limit, any non-dissolved material, if present, being added to the next lower fraction. The remaining solution was then brought to the upper temperature limit, at which the fraction precipitated within a short time. This process was repeated five times, whereby it was observed that, with the progress of the purification of the fractions, the speed of phase separation considerably increased, with a simultaneous lowering of the critical temperature range. This effect was particularly pronounced in the first refractionation, causing the overlapping of some fractions. In order to assure a sharp lower critical temperature limit, each of the fractions was moreover repeatedly pressure filtered at that particular temperature through Seitz sterilizing filters, until a constant rapid rate of filtering was attained. The fractions were kept in solution in a refrigerator at 4° until used.

From fractions where sufficient material was available, an acetyl-free polyvinyl alcohol was prepared by hydrolysis with 0.02 *N* HCl[8] and subsequent dialysis of the solution.

Particle Weight Determination.—The particle weights of the fractions were determined by the light scattering method, using the previously described Tyndallometer and differential refractometer.[9] The actual procedure of measurement was similar to that already described.[1a,b] The scattering intensities at the 90° angle, dissymmetry ratios at 45 and 135° angles, and refractive index increments were determined at various temperatures, below the lower limit of the critical temperature range. At each temperature the corresponding particle weight was attained within 1 hour and did not change upon further standing. Therefore, in all measurements a 2-hour interval was chosen between increase in temperature and actual measurement.

Acetyl Content Determination.—The acetyl content of each fraction was determined by hydrolysis with dilute HCl. Fifteen ml. of PVA-A solution of known concentration was introduced into a round-bottom flask and 5 ml. of 0.1 *N* HCl was added. The solution was then heated under reflux at 90°. After 18 hours, in order to dissolve a ring of polymer which had formed in the flask at the level of the liquid, 10 ml. of distilled water had to be added and heating was continued for another 30 hours. At the end of this period the cooled clear solution was titrated with 0.05 *N* NaOH using phenolphthalein as an indicator.

Results

The light scattering data obtained on the various fractions of PVA–A at different temperatures are recorded in Table I. The extrapolated values of $(Hc/\tau)_{c=0}$, and the coefficients *B* and *D* have been calculated from the experimental points by the method of least square averages. In all instances, in the PVA–A fractions, a far reaching aggregation with increase in temperature is observed. The effect of temperature on the particle weight in these fractions (Fig. 2) is much more pronounced than in the non-fractionated PVA–A of lower acetyl content (Fig. 1). Moreover, whereas in non-fractionated PVA–A solutions a constancy of scattering intensities is established only in *ca.* 24 hours, the aggregation in fractionated solutions seems to be completed within 1 hour after change in temperature. The influence of the acetyl content of the copolymer on its thermal behavior is also evident from the analytical values presented in Table II.

Upon complete elimination of the acetyl residues by hydrolysis, no such temperature effect on state of aggregation is observed. Comparing the particle weights of the hydrolyzed fractions and the PVA–A fractions at the lowest measured temperatures, it can also be deduced that the PVA–A is not molecularly dispersed even far below the critical temperature of phase separation. Moreover, the small dissymmetries of scattering of the aggregated polymer, as compared to the hydrolyzed one, point to a densely coiled particle rather than to a gelification.

As can also be seen from Fig. 2, at any given temperature the average particle weights of the various fractions increase with the lowering of the critical temperature range. A similar relationship can also be observed in the acetyl-free polymers, Table I, thus indicating that the lowering of the critical temperature is due to both increase in the degree of polymerization and increase in acetylation.

Moreover, similarly to other systems which present an inverted phase diagram,[10] *i. e.*, possess a critical temperature below which they are perfectly miscible and above which they separate into two phases, PVA–A possesses also a second,

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(6) R. S. Stein and P. M. Doty, THIS JOURNAL, **68**, 159 (1946).

(7) K. H. Meyer, "Natural and Synthetic High Polymers," Interscience Publishers, New York, N. Y., 1942, p. 106.

(8) E. R. Blout and R. Karplus, THIS JOURNAL, **70**, 862 (1948).

(9) M. Bier and F. F. Nord, *Rev. Sci. Instruments*, **20**, 752 (1949).

(10) C. S. Hudson, *Z. physik. Chem.*, **47**, 113 (1904).

TABLE I

LIGHT SCATTERING DATA ON PVA-A FRACTIONS: (DENSITY OF PVA-A = 1.26)

Concn. range, g./l.	Temp., °C.	$(Hc/\tau)_{c=0}$ $\times 10^7$	Intrinsic dissymmetry $(I_{45}/I_{135})_{c=0}$	Cor. fact.	M cor.	% incr.	$B \times 10^4$ cor., cm.³/g.²	$\mu_{\text{exptl.}}$	$\mu_{\text{crit.}}$	$3D \times 10^3$, cm.⁶/g.³
23-35° fraction										
0.5-12.9	14	27.9	1.27	1.19	426,000	...	−1.0	0.503	0.507	1.8
	17	23.8	1.19	1.14	480,000	12.7	−1.0	.503	.507	1.5
	20	20.7	1.11	1.08	522,000	22.5	−1.0	.503	.507	1.4
	23	18.3	1.10	1.07	584,000	37.1	−1.1	.503	.506	1.2
23-35° fraction, hydrolyzed										
0.3-5.2	20	65.0	1.26	1.19	183,000	...	4.5	.487	.511	...
	28	65.4	1.26	1.19	182,000	−0.5	4.3	.488	.511	...
35-45° fraction										
0.3-6.8	23	40.7	1.15	1.11	283,000	...	−3.3	.510	.509	7.5
	28	33.2	1.18	1.14	342,000	20.8	−2.7	.508	.508	5.4
	33	27.5	1.24	1.17	426,000	50.5	−2.5	.507	.507	4.8
	35	25.0	1.26	1.19	476,000	68.2	−2.8	.508	.507	4.2
35-45° fraction, hydrolyzed										
0.2-3.1	28	80.8	1.51	1.38	171,000	...	2.2	.494	.511	...
	38	81.8	1.51	1.38	169,000	−1.2	1.8	.495	.512	...
	48	81.8	1.51	1.38	169,000	−1.2	1.7	.495	.512	...
45-53° fraction										
0.4-7.0	23	49.9	1.25	1.18	236,000	...	−2.9	.508	.510	6.5
	28	42.7	1.29	1.22	284,000	20.3	−2.4	.507	.509	5.0
	33	36.4	1.31	1.23	338,000	43.2	−2.5	.507	.508	5.2
	38	31.8	1.38	1.28	402,000	70.3	−2.2	.506	.508	3.8
	43	27.0	1.34	1.26	467,000	97.9	−2.6	.507	.507	4.8
50-74° fraction										
0.4-20.3	23	52.3	1.09	1.06	203,000	...	−1.5	.504	.510	1.8
	33	39.5	1.07	1.04	264,000	30.0	−1.5	.504	.509	1.1
	43	28.3	1.06	1.03	364,000	79.3	−1.3	.504	.508	0.9
	48	25.2	1.03	1.02	405,000	99.5	−1.6	.505	.508	1.1
	50	23.1	1.02	1.01	437,000	115.3	−1.6	.505	.507	1.1
50-74° fraction, hydrolyzed										
0.1-2.7	28	96.5	1.27	1.19	123,000	...	4.2	.489	.514	...
	48	101.5	1.37	1.27	125,000	1.6	3.1	.491	.514	...

TABLE II

ACETYL CONTENT OF PVA-A FRACTIONS

Fraction	Acetyl, %
23-35°	19.90
35-45°	18.68
45-53°	18.08
50-74°	17.60
60-85°	16.28
Above 85°	10.55

higher critical temperature region, above which it becomes again perfectly soluble in water. Thus, when PVA-A solutions were heated in sealed capillaries, the visible turbidity caused by the precipitation of the polymer above its first critical temperature suddenly disappeared between 125 and 135°. This second critical temperature seems to be independent of the first, as all fractions redissolved in the above temperature interval. This solubilization is reversible and upon cooling turbidity reappeared between 133 and 128°.

Discussion

The demonstrated influence of the degree of acetylation of the polymer upon its aggregative properties is an example of a relation between the

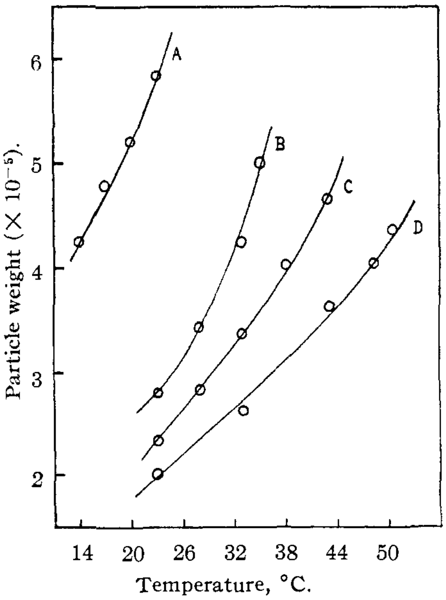

Fig. 2.—Particle weights of PVA-A fractions at different temperatures: A, 23-35° fraction; B, 35-45° fraction; C, 45-53° fraction; D, 50-74° fraction.

colloidal properties and chemical constitution of the compound. The chain of PVA–A contains a number of hydrophilic hydroxyl groups and hydrophobic acetyl groups, while, of course, the long basic hydrocarbon chain has a decided hydrophobic character. The hydrophilic groups will exert a strong attraction for the solvent molecules, *i. e.*, water, and the resulting hydration is a contributing factor in keeping the PVA–A in solution, the other factor being the gain in entropy. To the contrary, the hydrophobic groups tend to cluster together in the solvent, inducing possibly an aggregation. With rise in temperature the hydration will decrease, being exothermic. The clustering of the hydrophobic groups is thus enhanced and at each temperature an equilibrium between hydration and aggregation will be established.[11]

In all PVA–A fractions a considerable curvature of the conventional light scattering plots is observable[1c] (Fig. 3). This curvature could be caused either by the quadratic term of equation 2 or also by an effect of concentration on aggregation.[12] However, in no case could any difference in the state of aggregation be observed whether the solutions were first diluted to the desired series of concentrations and allowed to reach constant turbidities at any given temperature, or if the most concentrated solution, after having reached constant turbidity at that temperature, and having been kept at the same temperature even for as long as 24 hours, was then diluted to the same series of concentrations. In the latter case the scattering intensities at the three angles of 45, 90 and 135° measured within 30 seconds after diluting, were found to be identical with the values obtained by the first procedure and did not change on further standing. A re-establishment of a concentration-depending aggregation, after dilution, could hardly be expected to be completed within the 30 seconds required for dilution, as it would have to involve a disaggregation and uncoiling of the polymer cluster.

The aggregation is rapid with increasing temperature and seems to follow closely the rate of heating, as constant and reproducible light scattering intensities are reached within 1 hour after a change in temperature. When, however, the temperature is lowered, the corresponding disaggregation proceeds slower and is not reproducible. Even after several hours, the values often did not return to those obtained originally at lower temperatures.

The system PVA–A being on the verge of precipitation, it would be expected (*cf.* eq. 2) that the slope $2B$ of equation 2 would be negative, or at most zero. The quadratic term of the light scattering equation, therefore, may take on a significant value already at low polymer concentrations causing a strong upward curvature of the Hc/τ *vs.* concentration plots, whereas any dependence of the aggregation on concentration with the slope $2B$ negative or zero could not cause such an upward curvature at higher concentration. Thus it seems that similarly to the case of the temperature-dependent aggregation of polyvinyl chloride and other polymers studied by Doty, *et al.*,[13] the concentration does not play a significant role in the aggregation of PVA–A.

Analyzing our results in this sense it was found that in all PVA–A fractions the slope $2B$ is negative, as recorded in Table I, column 8. In hydrolyzed, acetyl-free polymer fractions no curvature is observable, the slope $2B$ being positive (Fig. 4). The coefficients $3D$ of the quadratic term are recorded in Table I, column 11.

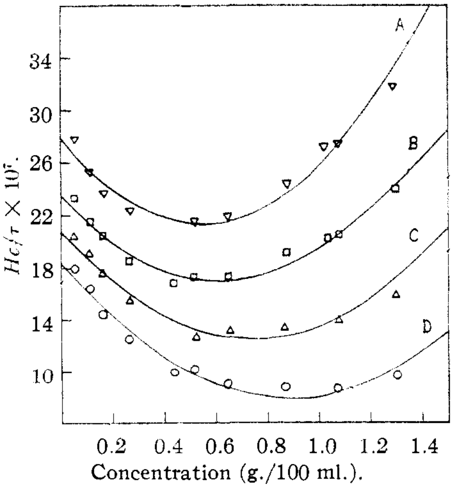

Fig. 3.—Hc/τ *vs.* concentration plots for the 23–35° fraction at various temperatures: experimental points: A, 14°; B, 17°; C, 20°; D, 23°. The curves were calculated from the experimental points by the method of least square averages.

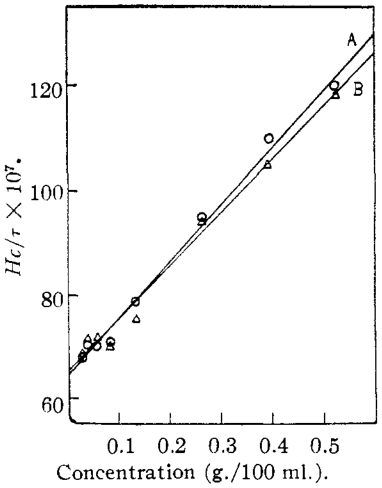

Fig. 4.—Hc/τ *vs.* concentration plots for the hydrolyzed 23–35° fraction: experimental points: A, 20°; B, 28°. The curves were calculated from the experimental points by the method of least square averages.

In many high polymer systems the separation of phases, either by change in temperature or by the addition of a precipitant occurs at a sharp

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[11] A similar chemical constitution is present also in partially methylated cellulose, the aqueous solutions of which exhibit an analogous reversible separation of phases on heating (Methocel, The Dow Chemical Co., 1949).

[12] C. Endoh, F. E. M. Lange and F. F. Nord, *Ber.*, **68**, 2009 (1935).

[13] (a) P. M. Doty, H. Wagner and S. Singer, *J. Phys. Colloid Chem.*, **51**, 32 (1947); (b) P. M. Doty and E. Mishuck, THIS JOURNAL, **69**, 1631 (1947).

critical point. In other cases, however, the critical phenomena are extended over a critical region rather than being confined to a point.[14]

It seems that in the case of PVA–A the critical phenomena are extended over a wide temperature range, an aggregation preceding the phase separation. Although in the thermodynamics of phase separation such a possibility was not considered, the theory may be applied. From data presented in Table I, columns 9 and 10, it can be seen that the values of $\mu_{\text{exptl.}}$ of the aggregating fractions are near to the values of $\mu_{\text{crit.}}$, calculated for a monodisperse polymer of uniform chain composition and of molecular weight equal to our average observed values. As aggregation proceeds, the difference between the two becomes smaller, chiefly due to the decrease of the calculated values of $\mu_{\text{crit.}}$. Contrary to the case of the unfractionated polymer (Fig. 1), in the above fractions there is no well defined change in $\mu_{\text{exptl.}}$, *i. e.*, slope $2B$ with temperature. The actual incipient separation of the phases would occur when the values of $\mu_{\text{exptl.}}$ and $\mu_{\text{crit.}}$ coincide, in the present case meaning that the particle weight approaches infinity. The gradual approach of conditions of phase separation with increasing temperature can be demonstrated also graphically.

In Fig. 5 the turbidity data of the 50–74° fraction are presented in terms of partial molal free energies using the relationship obtained on integration of equation 2, and compared with the theoretical curves for a system approaching phase separation according to equation 1. The curves for lower temperatures do not present evidence of any inflection point, $-\Delta\bar{F}_1$ increasing continuously with polymer concentration. At higher temperatures, a gradual inflection becomes observable, which is characteristic of the approach to the critical point of phase separation. Thus, a close relation between aggregation and phase separation is established.

Acknowledgment.—This work has been carried out under the auspices of the Office of Naval Research. The synthetic high polymers used were obtained through the courtesy of E. I. du Pont de Nemours and Co., Inc., Electrochemicals Division, New York, N. Y.

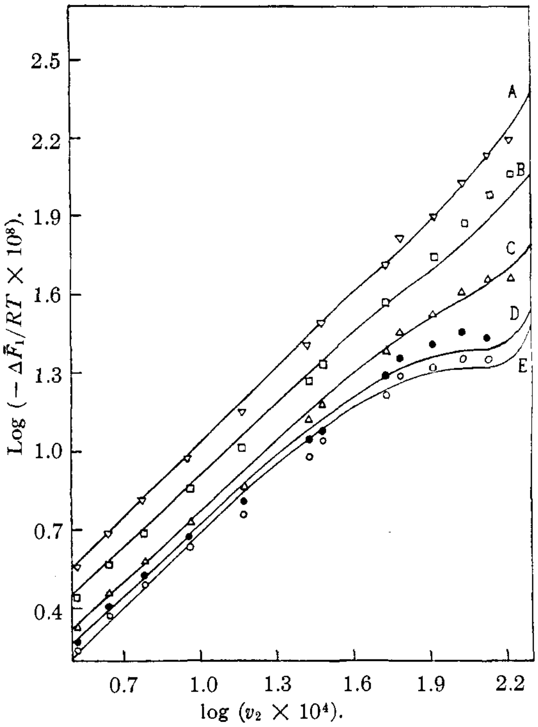

Fig. 5.—Partial molal free energy *vs.* volume fraction of polymer for the 50–74° fraction at various temperatures (log–log presentation): experimental points: A, 23°; B, 33°; C, 43°; D, 48°; E, 50°. The curves are drawn according to equation 1 using data of Table I.

Summary

Polyvinyl alcohol–acetate copolymers with an acetyl content of 15–20% were separated into fractions possessing narrow temperature ranges of incipient phase separation. In every fraction a far reaching aggregation was observed already far below the critical temperature of phase separation. The lowering of the critical temperature is caused by an increase in degree of acetylation and degree of polymerization of the fractions. The polymer possesses also a second, higher critical temperature of phase separation, above which it becomes again miscible with the solvent. These properties of the polymers are analyzed in the light of thermodynamics of polymer solutions.

NEW YORK 58, N. Y. RECEIVED JANUARY 9, 1950

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[14] O. K. Rice, *Chem. Revs.*, **44**, 69 (1949).