Viscosities of the Solutions of Polyvinyl Acetate in Acetone-Water Mixtures*

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The viscosities of the solutions of high molecular substances have been studied by many authors recently. It is generally said that the specific viscosity of the dilute solutions of flexible linear macromolecular substance is high in "good" solvents and low in "poor" solvents. Especially in the case of the solution in a mixture of "solvent" and "nonsolvent," the specific viscosity decreases gradually when the proportion of "nonsolvent" increases.(1) There appears a maximum in the specific viscosity of the solutions of polyvinyl acetate in methanol-water mixtures, which has been observed by Matsumoto.(2) In the present report, the results of the viscosity measurements on the dilute solutions of polyvinyl acetate in acetone-water mixtures, will be described.

Experimental

Polyvinyl Acetate.—The sample of polyvinyl acetate made by Dai-Nippon Celluloid Company has been used in the experiments. Insoluble polymer was removed from the sample by dissolving it in acetone and filtering carefully. After filtration the polymer was precipitated from the acetone solution by pouring it slowly into water, and the precipitated polymer was dried in vacuum. The same stock sample was used throughout the experiment. The osmotic molecular weight of the present sample was determined to be 155,000 by Endo.(3)

Acetone.—Ordinary material was boiled with potassium permanganate for some hours and then distilled with the addition of potassium carbonate. The distillate was dehydrated over calcium chloride and fractionated.

Solutions.—Solutions were prepared by dissolving polyvinyl acetate in acetone-water mixtures of varying proportions. The composition of the solvent varied from pure acetone to 25 vol.-% of water. The concentration was determined by evaporating the solution to dryness and expressed in grams of polymer per 100 cc. of solution.

Viscosity Measurement.—Viscosities were measured at 20±0.02° in the ordinary manner, by means of an Ostwald type capillary viscometer. The relative viscosities (η_r) were calculated according to the following formula(4)

$$\eta_r=\frac{t}{t_0}\frac{d}{d_0}\left\{1+\frac{Vd_0}{8\pi l\eta_0 t_0}\left(1-\frac{t_0^2}{t^2}\right)\right\}, \qquad (1)$$

where t_0 and t are the efflux times of solvent and solution respectively; d_0 and d are the corresponding densities; V is the volume of the "measuring bulb" in a viscometer; l is the length of the capillary; η_0 is the absolute viscosity of solvent. In equation (1), the term in brackets represents the kinetic energy correction, which amounted to about 1.3% in the worst case.

Results and Discussion

The resulting data are plotted in Fig. 1 as the specific viscosity ($\eta_{sp}=\eta_r-1$)-concentration (c) ratio against the concentration, with varying proportions of water. As is clear from Fig. 1, the concentration dependence of specific viscosity is well expressed by the following equation in low concentration range

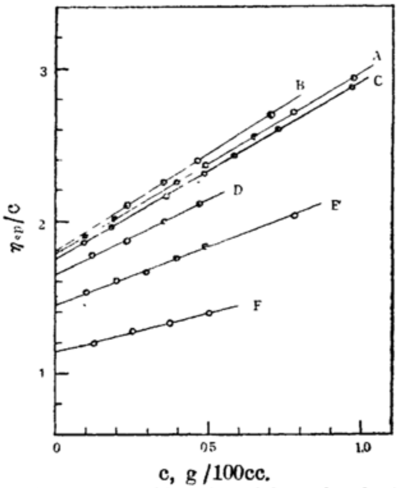

Fig. 1.—Specific viscosities of solutions of polyvinyl acetate in acetone-water mixtures at 20°. (A) Pure acetone; (B) Water 4.76%; (C) Water 10%; (D) Water 15.38%; (E) Water 20%; (F) Water 25%.

$$\eta_{sp}/c=[\eta]+Kc, \qquad (2)$$

where $[\eta]$ and K are constants. $[\eta]$ is the limiting value of η_{sp}/c at infinite dilution and usually called intrinsic viscosity. Equation (2) may also be expressed as follows

$$\eta_{sp}/c=[\eta]+k[\eta]^2c, \qquad (3)$$

where $k=K/[\eta]^2$ and is a dimensionless number.

$[\eta]$ and K are calculated by the method of least squares and given as function of solvent composition in Table 1, Fig. 2 and Fig. 3. In Table 1 is also given the value of k.

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* Read before the annual meeting of the Society on April 1, 1949.

(1) T. Alfrey, A. Bartovics and H. Mark, *J. Am. Chem. Soc.*, **64**, 1557, (1942); T. Alfrey, *J. Colloid Sci.*, **2**, 99, (1947).

(2) S. Matsumoto, *The Chemistry of High Polymer* (*Kobunshi Kagaku*), **6**, 179, (1949).

(3) K. Endo, *J. Chem. Soc., Japan*, **71**, 232, (1950).

(4) R. H. Wagner, *Anal. Chem.*, **20**, 155, (1948).

Table 1

Viscosities of Solutions of Polyvinyl Acetate in Acetone-Water Mixtures at 20°

Compn. of solvent (Vol. % of water)	[η]	K	k
0 (pure acetone)	1.785	1.184	0.37
4.76	1.800	1.273	0.39
10.00	1.746	1.171	0.38
15.38	1.654	0.967	0.35
20.00	1.454	0.746	0.35
25.00	1.140	0.505	0.39

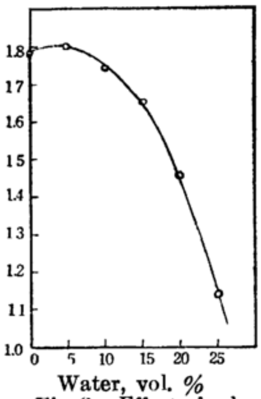

Fig. 2.—Effect of solvent composition on [η].

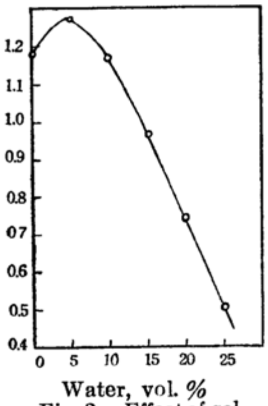

Fig. 3.—Effect of solvent composition on K.

For solvents containing up to about 10% water, the change of the intrinsic viscosity is small, and even a slight maximum is observed. From this experimental fact, it is supposed that the extension of polyvinyl acetate molecule in acetone is not appreciably changed by the addition of a small amount of water, in spite of its nature as typical nonsolvent. A similar result was obtained by Endo(3) from his osmotic measurements on the same system.

With a larger content of water, the intrinsic viscosity decreases as usual.

It is to be noted that k does not vary appreciably (i.e. $0.35 \sim 0.39$) as the amount of water increases, in spite of the remarkable change of K. Recently, Saito(4) and Ishihara(5) calculated theoretically the concentration dependence of specific viscosity, and found that $k=0.4$ as first approximation for spherical particles. This value is close upon the experimental data obtained by the present author.

Summary

Viscosities of the dilute solutions of polyvinyl acetate have been measured in acetone-water mixtures of varying proportions. The experimental results are well expressed by the following equation

$$\eta_{sp}/c=[\eta]+k[\eta]^2c.$$

The intrinsic viscosity ([η]) shows a slight maximum at about 5% of water content, and decreases gradually for larger content of water. The value of k is close upon 0.4 and does not vary appreciably.

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Chemical Institute, Faculty of Science,
the University of Tokyo.

(5) N. Saito, Lecture at the special meeting of the Physical Society of Japan, on May 1, 1949.

(6) A. Ishihara, Lecture at the special meeting of the Physical Society of Japan, on October 23, 1949.