Heats of Dilution of Polyvinylalcohol Solution. I

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Introduction

The measurement of heats of dilution of polymer solutions is important for investigating the thermodynamical behavior of polymer solutions as well as for industrial purposes. Previously we reported the heats of dilution of several polystyrene solutions. In this paper we shall report the heats of dilution of polyvinylalcohol solutions using water as a solvent.

Experimental

Apparatus and Procedures.—The apparatus used was an older type though an improved one had been already described in the previous paper¹⁾. The former is different from the latter in two points, (1) using A.C. bridge instead of D.C. bridge combined with the converter, and (2) introducing the solution directly into the Dewar vessel as shown in Fig. 1. The thermister has resistance of about 33 KΩ at 30°C, and its temperature coefficient is about 5%. The resistance change of 0.1 Ω can be detected and this corresponds to about 0.005 cal. Fifteen or 20 cc. of solution was introduced with a pipet in the Dewar vessel and 5 or 10 cc. of water was taken into the solvent container. By raising the solvent container and pushing the rubber cap, mixing was performed. Stirring of the mixed solution was operated manually after mixing. Other procedures were the same as those described in the previous paper¹⁾.

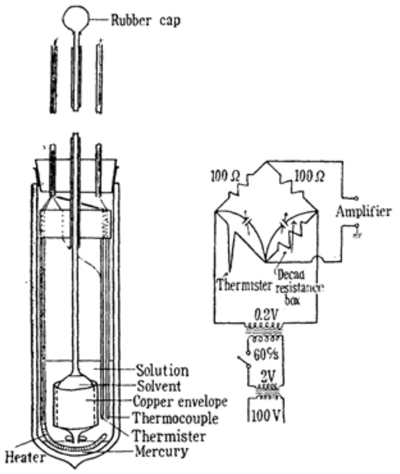

Fig. 1.

Samples*.—The degree of polymerization of polyvinylalcohol used in this experiment was 450 and 600. The content of acetyl radical of the latter sample was less than 0.3 mol. %, but that of the former one was 1.7 mol. %.

Results and Discussion

The heats evolved $-\Delta H$ when the polyvinylalcohol solutions are diluted successively with water at 30°C, are shown in Table I.

TABLE I

HEATS OF DILUTION OF P.V.A. SOLUTIONS

Exp. series	V* cc.	v_r*	v* cc.	v_r'*	$-\Delta H$* cal.	α	T_p* °C.
System I. Solution of P.V.A. of D.P. 450.							
	15	0.155	5	0.115	0.312	−4.3	30
	20	0.115	5	0.092	0.252		
	25	0.092	5	0.077	0.172		
System II. Solution of P.V.A. of D.P. 600.							
1	15	0.100	5	0.075	0.112	−3.2	70
	20	0.075	5	0.059	0.074		
	25	0.059	5	0.049	0.046		
	30	0.049	5	0.042	0.010		
2	20	0.143	5	0.114	0.192	−2.3	100
	25	0.114	5	0.094	(0.119)**		
	20	0.094	5	0.075	0.069		
	25	0.075	5	0.062	0.050		
	30	0.062	10	0.046	0.063		
	40	0.046	10	0.037	0.044		
3	25	0.114	5	0.094	0.120	−2.3	100
	30	0.094	5	0.081	0.090		
	35	0.081	5	0.071	0.078		
	40	0.071	5	0.063	0.046		
	45	0.063	5	0.056	0.037		

* These notations are as follows:
V: Volume of solution before dilution. v_r: Volume fraction of polymer before dilution. v: Volume of water added. v_r': Volume fraction of polymer after dilution. $-\Delta H$: Heat evolved. T_p: Pre-heating temperature.

** This value in the brace is the expected one owing to the failure of the experiment.

Both systems, solutions of P.V.A. of D.P. 450 and 600, proved to be exothermic.

Assuming that the heat of mixing is represented by the van Laar form, we find

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1) K. Amaya and R. Fujishiro, This Bulletin 29, 270 (1956).

* We are indebted to Dr. S. Matsumoto of the Kurashiki Rayon Company and Mr. H. Inagaki of Kyoto University for these samples.

easily that the integral heat of dilution ΔH_o from the volume fraction of polymer v_r to v_r' is given by

$$\Delta H_o = aV_r(v_r - v_r')$$

where α is a constant describing the interaction between polymer and solvent and V_r is the volume of polymer in the solution.

Plotting ΔH_o or $\Delta H_o/V_r$ as ordinate and V_r as abscissa for each series, we obtain straight lines as shown in Fig. 2 and this result suggests that the assumption mentioned above is satisfied. In the figure we adopt the integral heat of dilution per unit volume of polymer $\Delta H_o/V_r$, as ordinate for the sake of convenience. The values of α can be derived from the tangent of the straight lines in the figure and these values from each series are given in Table I.

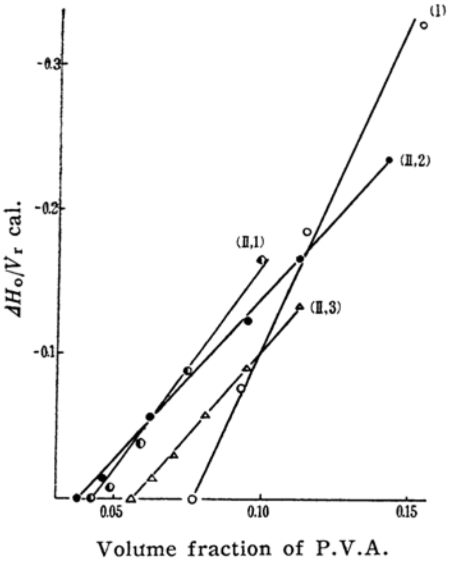

Fig. 2.

As ethanol may be regarded as a monomer-unit of P. V. A., the value of α obtained from the heat of mixing of ethanol solution may be compared with that of P. V. A. solution. Using the data in the literature[2], we find that the value of α for the ethanol-water system is about $-40 \sim -20$ cal./cc. in the equal concentration range. This value is the same in sign as that of our experiment, but its magnitude is remarkably larger. According to G. Gee[3] and P. Meares[4], the value of α for the polymer solution is said to be 70–80% of that of the corresponding monomer-unit solution, owing to the increase of polymer-polymer contacts in the polymer solution. But the value of α for the P. V. A.-water system is only 10% of that of the ethanol-water system. This suggests that the strong intersegmental hydrogen bonds in P. V. A. exist and the apparent interaction between P. V. A. and water decreases considerably.

In the system I the solution was introduced into the Dewar vessel after warming to about 30°C. But in the system II before being introduced into the calorimeter, solutions were warmed to about 70°C or 100°C respectively, corresponding to series 1 or 2 and 3. From the values of α of both systems the effects of pre-heating was observed. In other words the absolute magnitude of α is in the inverse relation to the temperature of pre-heating.

It may be considered that the P. V. A.-water system being exothermic the polymer-water contact is energetically more stable than the polymer-polymer contact and therefore, by raising the temperature, the number of polymer-polymer contacts having higher energy increases owing to intersegmental associations of P. V. A.. This state produced by heating is expected to be maintained to some extent even after cooling the solution to 30°C. The higher the temperature of heating, the more the number of polymer-polymer contacts increases and the more that of polymer-water contacts decreases. Thus the number of polymer-water contacts is the most in the system I, next in the series 1 of the system II and the least in the series 2 and 3 of the same system. Consequently on dilution the change in these numbers may be in the same order.

The fact that high degree of intersegmental association by hydrogen bonding is present is more confirmed by other experimental facts. The one is the heats of solvation for lower polyalcohol homologues which were measured by S. Seki and K. Suzuki[5]. They showed that the more the number of hydroxyl radicals in a molecule, the stronger the intramolecular hydrogen bonds are and the apparent interaction between solute and solvent per unit hydroxyl radical decreases considerably even for lower alcohols. Their results seem to be consistent with our ones that the values of α for the polymer solutions are remarkably lower than that for the ethanol solution. Secondly, according to our unpublished data[6], the value of α increases by substituting a fraction of hydroxyl radicals with acetyl. This may be due to the hindrance of intersegmental hydrogen bonds

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[2] E. Bose, *Z. physik. Chem.*, **58**, 585 (1907).

[3] G. Gee and W. J. C. Orr, *Trans. Faraday Soc.*, **42**, 507 (1946).

[4] P. Meares, *Trans. Faraday Soc.*, **47**, 699 (1951).

[5] S. Seki and K. Suzuki, This Bulletin, **26**, 63 (1953).

[6] To be published in the forthcoming paper.

by acetyl radicals and seems to support our interpretation.

Summary

The heats of dilution of P. V. A. solutions were measured and the interaction parameter α between P. V. A. and water was found to be in the range of $-2\sim-4$ cal./cc. That these values are remarkably lower than that of ethanol solution suggests the presence of strong intersegmental hydrogen bonds of P. V. A.. The effect of pre-heating was also observed. It may be attributed to the increase of intersegmental associations by heating.

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