Heats of Dilution of Polyvinylalcohol Solutions. II

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Introduction

In the previous paper[1] we measured the heats of dilution of aqueous solution of polyvinylalcohol and found that the value of the interaction parameter is about -3 cal./cc., which is too small compared with that of ethylalcohol-water solution (-40 cal./cc.) and indicates considerable inter-segmental associations of polyvinylalcohol.

In order to make a further study about these facts, we measured the heats of mixing for the 1,3- or 1,4-butanediol and water system, and the heats of dilution for the polyvinyl-alcohol of different acetyl radical content and water systems.

These butanediols may be regarded as dimer molecules of polyvinylalcohol and it is expected that they play an important role as intermediate molecules between ethylalcohol and polyvinylalcohol. As the polyvinylalcohol has been thought to have a large number of inter-segmental hydrogen bondings, it is supposed that if a portion of hydroxyl radicals is substituted with acetyl ones, the formation of inter-segmental hydrogen bondings may be disturbed and there may occur some changes in the interaction parameter.

Experimental

The apparatus used was already described in the previous paper. Commercial 1,3- and 1,4-butanediol* were dehydrated under the pressure of about 1 mmHg for long time and then distilled with a long column under the reduced pressure.

Polyvinylalcohol samples** of the degree of polymerization 1200 were supplied by the Laboratory of the Mitsubishi Rayon Campany and the acetyl contents of these samples were 0.4, 7.8, 15.6 and 19.4 mol.% respectively.

Results and Discussion

The heats evolved, when the butanediol and water were mixed and then the solution was diluted successively with water or butanediol, were measured at 25°C. By integrating these heats evolved by mixing or dilution, the heats of mixing at various concentrations were obtained and are shown in Table I and II.

TABLE I

HEATS OF MIXING OF 1,3-BUTANEDIOL AND WATER

Weight of Diol, g.	Weight of Water, g.	Heat Evolved, cal.	$-\Delta H$, cal. / Unit Mole Solution	Unit Mole Fraction
1.973	16.130	52.6	56.1	0.046
1.973	8.131	45.7	92.3	0.088
1.973	4.125	36.5	134	0.161
1.973	2.061	24.4	154	0.277
1.921	2.045	25.7	165	0.273
3.884	2.045	30.0	150	0.432
7.711	2.045	34.3	120	0.601
1.748	11.96	44.7	63.3	0.055
1.748	5.982	39.6	106	0.104
1.748	3.988	34.9	134	0.149
1.748	1.994	24.2	162	0.259
1.970	1.994	25.1	162	0.282
3.980	1.994	30.4	153	0.442
5.990	1.994	32.3	133	0.544

TABLE II

HEATS OF MIXING OF 1,4-BUTANEDIOL AND WATER

Weight of Diol, g.	Weight of Water, g.	Heat Evolved, cal.	$-\Delta H$, cal. / Unit Mole Solution	Unit Mole Fraction
2.004	17.58	44.1	43.2	0.044
2.004	8.194	40.0	80.1	0.089
2.004	4.134	32.0	117	0.162
2.004	2.058	22.3	140	0.280
1.961	2.006	23.1	149	0.281
3.965	2.006	29.2	147	0.441
7.990	2.006	35.5	123	0.614

The accuracy of the measurement was not so satisfactory, because the butanediols are highly viscous and adhere to the wall of the mixing vessel. The accuracy may be estimated from the two measurements at nearly the same concentration (about 0.5 volume fraction), one with water in the inside bulb and butanediols in the outside bulb and the other the reverse.

As ethylalcohol and butanediol may be regarded as a monomer- and dimer-unit of polyvinylalcohol respectively, by considering the butanediol as two unit molecules the heats of mixing per unit mole of solution (which means that the number of water molecules

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[1] K. Amaya and R. Fujishiro, This Bulletin 29, 361 (1956).

* We wish to thank Mr. T. Wakabayashi of the Nippon Yushi Company for supplying these butanediols.

** We are indebted to Dr. H. Suyama of the Mitsubishi Rayon Company for these samples.

plus two times the number of butanediol molecules is equal to the Avogadro number) are calculated from the above data and plotted in Fig. 1 against the unit mole fraction of butanediol. For the sake of comparison, the heats of mixing per mole of the ethylalcohol-water solution[2] at the same temperature are shown in the same figure.

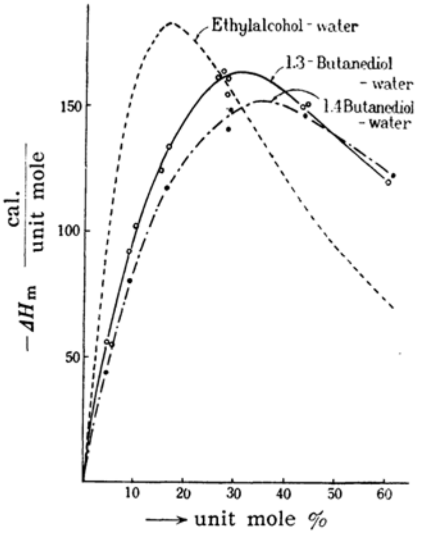

Fig. 1

The remarkable features which appeared in this figure are the lowering of the maximum of the curve and the shift of the maximum position to the higher concentration of butanediol. The former may be easily explained as the intra-molecular association of the two hydroxyl groups of the butanediol molecule which decreases the apparent interaction of the butanediol with the solvent molecule. The magnitude of lowering of the maximum is more in 1, 4-butanediol than in 1, 3-butanediol and this is consistent with the fact that 1, 4-butanediol is apt to form the intra-molecular hydrogen bonding from the steric standpoint in comparison with 1, 4-butanediol.

Generally the maximum in the heats of mixing per unit volume of mixture of two kinds of normal liquids where there is no specific interaction will be at the equi-volume concentration. In the mixture where the two normal liquids have the same molecular volume, the maximum in the heats of mixing per mole of the mixture will be at the equi-molar concentration. But in the mixture of two normal liquids having different molecular volumes, the maximum in the heats of mixing per mole of the mixture will be shifted to the $(\sqrt{x}-1)/(x-1)$ mole fraction, where x is the ratio of molecular volume of the two liquids.

In a case when one or both liquids have specific groups of interaction, the position of the maximum may shift more or less from the normal value $(\sqrt{x}-1)/(x-1)$. Ethylalcohol-water system is such a typical example and the maximum shifts to a lower value of the mol. fraction of ethylalcohol such as 0.18, to be compared with the nomal value 0.36 calculated by using $x=3$ for this system.

In the butanediol-water systems the observed values of the maximum point are 0.30 and 0.35 for 1, 3- and 1, 4-butanediol respectively, and these values are compared with the normal one 0.40 which is evaluated by using the value 2.4 for the ratio of molecular volume of monomer-unit of both butanediols to that of water.

Hence it is shown that the maximum point approaches considerably to a normal one for both butanediol-water systems compared with that for the ethylalcohol-water system.

It may be supposed to be natural that this will be due to the intra-molecular association of butanediol which decreases the specific interaction power per unit molecule.

From the fact above mentioned, the more the number of units in a molecule, the smaller the magnitude of the maximum for the solution containing the molecule and the more the maximum point may approach to the normal value.

This indicates a remarkable lowering of the heats of mixing and thus a remarkable decrease of the magnitude of the interaction parameter in the polyvinylalcohol-water solution.

In order to get the quantitative explanation, the conventional interaction parameter which is the quantity per cc. of solution, is evaluated and plotted in Fig. 2 against the

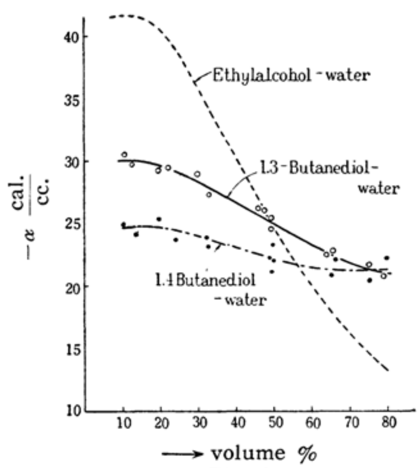

Fig. 2

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[2] E. Bose, *Z. physik. Chem.*, 58, 587 (1907).

volume fraction of ethylalcohol or butanediols respectively. Here the equation used for the evaluation of the interaction parameter is the following van Laar's,

$$\Delta H_{\mathrm{m}} = \alpha V v_{\mathrm{o}} v_{\mathrm{r}}$$

where v_{o}, v_{r} are the volume fractions of solvent (water) and ethylalcohol or butanediols respectively, V the total volume of the solution, ΔH_{m} the heats of mixing of such solution and α the interaction parameter per cc.

In Fig. 2 it is found that in the ethylalcohol-water system the value of $-\alpha$ decreases sharply as the volume concentration of ethylalcohol increases, but not in the butanediol-water one. In the previous paper it was in the volume fraction less than 0.2 where the heats of dilution of polyvinylalcohol solution were measured.

In the same concentration range, the value of α of the ethylalcohol solution is -40 cal./cc. and those of the 1, 3- and 1, 4-butanediol solutions are -30 and -25 cal./cc. respectively.

A large decrease in magnitude of the interaction parameter is seen in transfer from monomer to dimer.

Such a decrease may probably be expected successively as the molecules become larger. Thus it may stand to reason that in the polyvinylalcohol solution the value of α has such small value as -3 cal./cc.

The heats of dilution of polyvinylalcohol which contains different acetyl contents were also measured and shown in Table III.

TABLE III

HEATS OF DILUTION OF POLYVINYLALCOHOL WITH DIFFERENT ACETYL CONTENT

	Before Dilution				
Acetyl Content Mole %	Volume of Solution cc.	Volume Fraction of P.V.A.	Volume of Water Added cc.	Heat Evolved, cal.	$-\alpha \frac{\text{cal.}}{\text{cc.}}$
0.4	9.00	0.099	10	0.145	3.1
0.4	9.51	0.109	10	0.177	3.0
7.8	9.57	0.077	10	0.167	5.7
7.8	8.57	0.077	10	0.151	5.5
15.6	9.91	0.052	10	0.040	2.9
15.6	9.94	0.052	10	0.041	3.0
19.4	9.86	0.038	10	0.017	2.4
19.4	9.94	0.038	10	0.015	2.1

By use of the van Laar equation, the values of the interaction parameter are calculated. The order of magnitude of α is found to be in good agreement with that of the previous paper. These values of α are plotted in Fig. 3 against the acetyl content in the polyvinylalcohol.

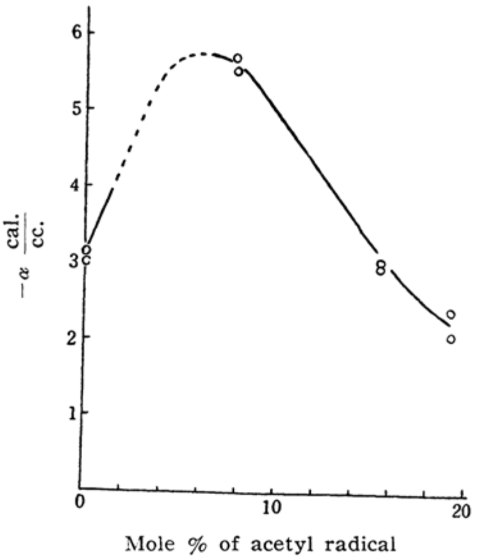

Fig. 3

In Fig. 3 the absolute value of the parameter α seems to show maximum between 0 to 10 mole % of acetyl radicals.

If some of hydroxyl radicals in the polyvinylalcohol are substituted by acetyl ones, two main effects may appear.

First, as it is supposed that there is no strong interaction between acetyl group and water molecule, these interactions may be repulsive and decrease the absolute value of α. Secondly, the substitution of hydroxyl radical with acetyl will disturb intra-molecular or inter-segmental hydrogen bonding in the polyvinylalcohol and consequently increase the hydroxyl radicals which do not form hydrogen bonding with each other. This means the increase of the absolute value of α.

Thus, these two effects may change the value of α in the reverse way as the acetyl content increases.

But it will be supposed that the effect of disturbing hydrogen bonding by substitution is considerable in the small acetyl content and saturated in the more concentrated fraction, while the interaction between acetyl radical and water increases linearly with acetyl content.

Consequently, in the small acetyl content the effect of disturbing inter-segmental hydrogen bonds is predominant compared with the first, and the absolute value of the interaction parameter may increase as the acetyl content increases.

But in the range of larger acetyl content the second effect may exceed the first.

So, it will be reasonable to assume that the absolute value of α increases at first, passes through a maximum and decreases as the acetyl content increases.

Summary

Heats of mixing of 1, 4- and 1, 3-butandiols with water and heats of dilution of polyvinylalcohol of different acetyl contents were measured.

The results obtained for the two butanediols and water system were compared with the results for ethylalcohol-water system and for polyvinylalcohol-water system (reported in the previous paper) and it was found that the apparent interaction parameter of these substances with water decreases and becomes more normal as the degree of polymerization becomes larger. The interaction parameter for polyvinylalcohol of different acetyl content with water first increases and then (through max.) decreases as the content of acetyl radical increases.

All these results are consistently explained from the standpoint of intra-molecular or inter-segmental association.

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