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The Heats of Dilution of the Oligomeric Ethylene Oxide—Benzene System

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ABSTRACT: In a previous paper,[1] we have reported the heats of dilution of the oligo-ethylene oxide—alcohol systems at 25°C. The interaction heat parameter χ_1 increases as the chain length of the alcohols increases. In order to obtain some further information about the behavior of the oligomer in solution, the heat of dilution of the oligo-ethylene oxide—benzene system has been measured at 25°C. The interaction heat parameter seems to be considerably dependent on the molecular weight of the oligomer; the results obtained show the opposite dependence to that found in the oligo-ethylene oxide—alcohol solutions.

KEY WORDS Oligomer / Ethylene Oxide / Benzene / Heat of Dilution / χ_1-Parameter /

As reported in a previous paper,[1] we have measured the heat of dilution of the oligomeric ethylene oxide—alcohol systems at 25°C. It was found that all the systems were endothermic in contrast with the exothermic values obtained for the aqueous solution of oligomeric ethylene oxide,[2] and that the interaction heat parameter, χ_1, between the oligomer and solvent increases as the chain length of the alcohols increases. Such behavior of the χ_1-parameter suggested that the attraction acting between the OH- and-O-groups of the oligomer and the HO-groups of the alcohol is compensated more or less by the repulsion operating between the HO-groups and CH_2-groups.

In this paper, in order to obtain some further information about the behavior of the oligomer in the solution, the heat of dilution of the oligomeric ethylene oxide—benzene system has been measured.

EXPERIMENTAL

Apparatus

The twin microcalorimeter used in this study was the same as that described in previous papers.[3,4]

Materials

The oligo-ethylene oxide used was purchased from Sanyo Kasei Co. Ltd., and was used without further purification.

The molecular weights of the oligo-ethylene oxides in this study were about 200, 300, 600, and 1000.

The solvent, benzene, was purified by the ordinary method.[5]

RESULTS AND DISCUSSION

The heat of dilution of oligo-ethylene oxide was measured by using the twin microcalorimeter at 25°C. The heat of dilution was measured over the concentration range from 1.00 to 0.128-volume fraction of the oligomer by successive additions of 5 or 10-cm^3 portions of the solvent to a solution of known concentration.

The results obtained are summarized in Table I. This system is endothermic. Assuming that the simple van Laar equation can be applied to an oligomer solution, we have the following equation for the heat of dilution, $\overline{\Delta H}_d$, from the initial volume fraction of polymer, ϕ_2, to the final one, ϕ_2',

$$\overline{\Delta H}_d/\Delta n_1 = RT\phi_2\phi_2'\chi_H \qquad (1)$$

where χ_H is the interaction heat parameter and Δn_1 is the number of moles of the solvent added.

Plots of $\overline{\Delta H}_d/\Delta n_1$ against $RT\phi_2\phi_2'$ are shown

Table I. Heats of dilution of the oligomeric ethylene oxide—benzene system at 25°C

	V, cm³	ϕ_2	V', cm³	ϕ_2'	Δn_1	$\Delta\bar{H}_d$, cal	χ_H
a) M_n=200							
	5	1.000	11	0.455	0.067	5.350	0.296
	6	1.000	13	0.462	0.078	6.404	0.299
	10	1.000	15	0.667	0.059	5.590	0.253
	15	0.667	22	0.455	0.078	6.452	0.458
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	17	0.588	25	0.400	0.090	5.889	0.472
	18	0.556	23	0.435	0.056	4.693	0.585
	23	0.435	29	0.345	0.067	4.053	0.679
	25	0.400	30	0.333	0.056	3.159	0.716
	29	0.345	33	0.303	0.045	2.462	0.890
	30	0.333	35	0.286	0.056	2.442	0.775
	30	0.333	36	0.278	0.067	2.442	0.664
b) M_n=300							
	10	1.000	15	0.667	0.056	4.850	0.219
	10	1.000	16	0.625	0.067	4.826	0.194
	15	0.667	22	0.455	0.078	4.730	0.336
	16	0.625	24	0.417	0.090	4.188	0.303
	16	0.625	27	0.370	0.123	4.485	0.266
	17	0.588	26	0.385	0.101	4.672	0.346
	22	0.455	31	0.323	0.101	4.692	0.535
	23	0.435	35	0.286	0.134	4.670	0.472
	26	0.385	34	0.294	0.090	2.566	0.427
	27	0.370	36	0.278	0.101	2.180	0.355
	27	0.370	36	0.278	0.101	2.983	0.486
	31	0.323	42	0.238	0.123	3.159	0.564
c) M_n=600							
	10	0.400	20	0.200	0.101	1.935	0.956
	17	0.588	25	0.400	0.090	4.903	0.393
	17	0.588	26	0.385	0.101	5.283	0.391
	20	0.200	28	0.143	0.090	0.373	0.248
	22	0.455	30	0.333	0.090	2.928	0.364
	24	0.167	34	0.118	0.112	0.571	0.412
	25	0.400	34	0.294	0.101	2.442	0.348
	26	0.385	34	0.294	0.090	1.672	0.279
	27	0.370	32	0.313	0.056	1.104	0.288
	28	0.143	33	0.121	0.056	0.198	0.345
d) M_n=1000							
	10	0.300	13	0.231	0.034	0.531	0.385
	10	0.303	16	0.189	0.067	1.202	0.528
	18	0.128	27	0.047	0.101	0.108	0.302
	19	0.159	27	0.059	0.090	0.172	0.345
	33	0.303	39	0.256	0.067	1.357	0.439
	33	0.303	40	0.250	0.078	1.334	0.380
	51	0.196	60	0.166	0.101	0.957	0.492

in Figure 1. According to eq 1, $\overline{\Delta H}_d/\Delta n_1$ should vary linearly with $RT\phi_2\phi_2'$, but these plots are not linear, indicating that the interaction heat parameter depends on the concentration of oligomer.

Let us assume that the interaction heat parameter, χ_H, is expressed by:

$$\chi_H=\chi_1+\chi_2\phi_2$$

where χ_1 is the heat parameter at infinite dilution corresponding to κ_1 and χ_2 is a heat parameter depending on the oligomer concentration. Making the same derivation as that of eq 1, we can obtain the following equation:

$$\overline{\Delta H}_d/\Delta n_1=RT\phi_2\phi_2'[\chi_1+\chi_2(\phi_2+\phi_2')/2] \quad (2)$$

In order to obtain χ_1 and χ_2, the least square treatment of the data was carried out according to eq 2 and the results obtained are shown in Table II. As seen in Table II, the interaction heat parameter in dilute solution depends on the molecular weight of the oligomer, as shown in Figure 2 which includes other values from previous papers.[1,2]

Each χ_1 parameter seems to be considerably dependent on the molecular weight of the oligomer in the opposite manner to that found in the oligo-ethylene oxide—alcohol solutions.

In the previous results,[1] the χ_1 parameter increased with the chain length of the alcohols for each oligomer solution, indicating that the CH_2-groups of an alcohol molecule play a hydrophobic role. We suggested that the attraction acting between the HO- and -O- groups of the oligomer, and the HO-groups of the alcohols is compensated more or less by the repulsion operating between the HO-groups and CH_2-groups. However, the χ_1 parameter of the oligo-ethylene oxide—benzene system seems to be considerably dependent on the molecular weight of oligomer in the opposite manner to that found in the oligoethylene oxide—alcohol solutions.

It may be shown that the attraction acting between the HO-groups of the oligomer and the benzene molecule is larger than the repulsion operating between the -O- groups of the oligomer and the benzene molecule as the chain length of the oligo-ethylene oxide increases. This is the same dependence as in the usual

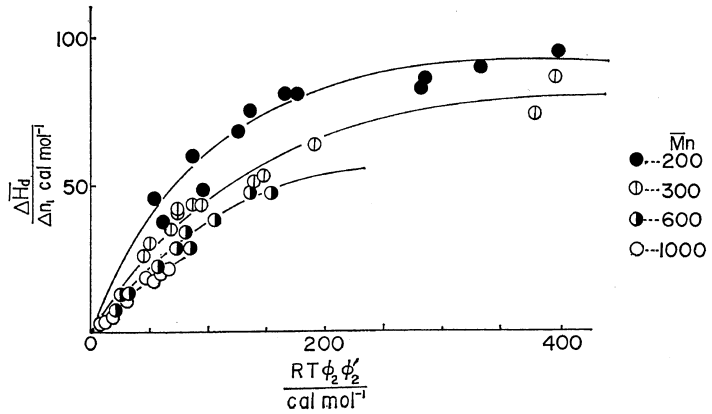

Figure 1. Heats of dilution per mole of solvent *vs.* the concentration of the oligomeric ethylene oxides—benzene system at 25°C.

Table II. The interaction heat parameter of the oligomeric ethylene oxide—benzene system

Molar weight, M_n	Interaction heat parameter	
	χ_1	χ_2
200	1.09	−1.08
300	0.64	−0.56
600	0.40	−0.19
1000	0.30	−0.51

vinyl polymer solutions;[2] the χ_1 parameter decreases as the molecular weight of oligomer increases.

This dependence of the interaction heat parameter on the molecular weight has been theoretically derived by Huggins.[6] But our results can not be quantitatively compared with his theory because of the lack of information concerning the chain configuration in the polymer solution.

Our results can also be qualitatively explained

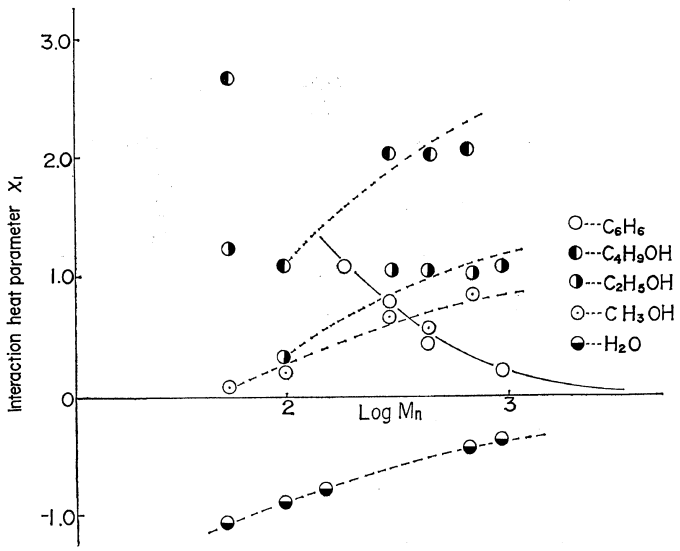

Figure 2. Interaction heat parameter, χ_1, *vs.* the logarithm of the molecular weight of oligomeric ethylene oxides in various solvents.

by application of Flory's polymer solution theory.[7]

We can consider a random coil with a radius of gyration ($\bar{s}_0$) for a polymer which is formed from a number of segments (n). The volume of a polymer solution (V) with a radius of gyration and expansion factor (α) is expressed as follows:

$$V=\tfrac{4}{3}\pi\bar{s}_0^{\,3}\alpha^3 =\tfrac{3}{4}\pi(\tfrac{1}{6})^{3/2}n^{3/2}a^3\alpha^3 \qquad (3)$$

where a is the distance between one segment and the next segment of the polymer. If the expansion of the polymer is due to the volume of the solvent, the number of solvent particles (n_s) in the volume of polymer solution is expressed as follows:

$$n_s=(\tfrac{2}{3})^{3/2}\alpha^3n^{3/2}-n \qquad (4)$$

The contact number (N_{sp}) between segments of polymer and solvent in the polymer solution is

$$N_{sp}=\frac{Z(Z-2)nN_s}{ZN_s+(Z-2)n} \qquad (5)$$

where Z is the number of coordination of the solvent or polymer segment.

The interaction heat parameter χ_1 is expressed as a function of the contact number (N_{sp}) and the solvent number (n_s) by

$$\chi_1=\frac{\Delta wN_{sp}}{RTn_s} \qquad (6)$$

where Δw expresses the interaction energy given by Hildebrand and Scott[8] as follows:

$$\Delta w=w_{sp}-\tfrac{1}{2}(w_{ss}+w_{pp})$$

From eq 3, 4, and 5, the interaction heat parameter is expresses as,

$$\chi_1=\frac{A}{\alpha^3n^{1/2}} \qquad (7)$$

where A is $(Z(Z-2)\Delta w)/(RTZ(\frac{2}{3})^{3/2})$. As the number of segments (n) is identical with the ratio of the molecular weight of the polymer (M) to that of the polymer unit (M_0), the interaction heat parameter χ_1 is:

$$\chi_1=\frac{A'}{\alpha^3M^{1/2}} \qquad (8)$$

where A' is $(Z(Z-2)\Delta wM_0^{1/2})/(RTZ(\frac{2}{3})^{3/2})$. As seen in eq 8, the interaction heat parameter, χ_1, decreases as molecular weight of the polymer increases. But definite information cannot be obtained due to the lack of the expansion factor for the chain conformation in the polymer solution in eq 8. Even allowing for such uncertainty, our results seem to be qualitatively explained by using eq 8.

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