The Heats of the Dilution of *cis*-Polybutadiene Solutions in Benzene and Toluene

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In a previous paper,[1] we measured the heats of the dilution of the atactic polystyrene solution and found that the interaction parameter, χ_H, between the polymer and the solvent depends on the concentration. In order to confirm this fact for other polymer solutions, the heats of dilution of which have not been directly determined, we measured the heats of the dilution of *cis*-polybutadiene, using toluene and benzene as a solvent.

The calorimeter used in this study has been described in the previous paper.[1] The *cis*-polybutadiene sample, the molecular weight of which was about 200000, was supplied by Dr. Toshio Yoshimoto of the Bridgestone Tire Co., Ltd.

The heats of the dilution of *cis*-polybutadiene solution were measured over the concentration range from 0.36 to 0.05 in a volume fraction of polymer at 25.0±0.01°C for the benzene solution, and at 26.0±0.01°C for the toluene solution, by adding the solvent in successive 10- or 20-ml. portions to a solution of a known concentration. The data obtained are shown in Table I. The *cis*-polybutadiene - toluene system is exothermic, while the benzene system is endothermic.

As was shown in the previous paper,[1] the heat of dilution, $\Delta\overline{H}_d$, is related to the initial volume fraction of the polymer, ϕ_2, and the final ϕ'_2 value as follows:

1) A. Kagemoto, S. Murakami and R. Fujishiro, This Bulletin, **39**, 15 (1966).

either $$\Delta\overline{H}_d = RT\chi_H\phi_2\phi'_2\Delta n_1 \quad (1)$$

when the interaction parameter, χ_H, is not dependent on the concentration,

or $$\Delta\overline{H}_d/RT\phi_2\phi'_2\Delta n_1 = \chi_1+\chi_2(\phi_2+\phi'_2)/2 \quad (2)$$

when χ_H depends linearly on the concentration, in conformity with the equation that $\chi_H=\chi_1+\chi_2\phi_2$. In these equations, Δn_1 is the number of moles of the solvent added.

By using the experimental data presented in Table I and Eq. 1, the interaction parameter has been obtained for each dilution process of each system; these values are given in the last column of the same table.

According to Eq. 1, $\Delta\overline{H}_d$ must linearly vary

Table I. Heats of dilution of *cis*-polybutadiene solution

I. *cis*-Polybutadiene - Toluene at 26°C

V, cc.	ϕ_2	V', cc.	ϕ'_2	$-\Delta\overline{H}_d$, cal.	χ_H
20	0.318	30	0.212	0.154	−0.048
30	0.212	40	0.159	0.062	−0.032
40	0.159	50	0.127	0.040	−0.034
20	0.318	40	0.159	0.246	−0.042
20	0.318	50	0.127	0.286	−0.041
16	0.367	26	0.225	0.179	−0.038
26	0.225	46	0.127	0.070	−0.025
16	0.367	46	0.127	0.245	−0.032
50	0.127	70	0.091	0.049	−0.037
20	0.318	70	0.091	0.335	−0.040
15	0.318	25	0.190	0.080	−0.023
15	0.235	25	0.144	0.045	−0.024
25	0.141	55	0.064	0.037	−0.024
15	0.235	55	0.064	0.081	−0.024
55	0.064	85	0.041	0.010	−0.023
15	0.235	85	0.041	0.092	−0.023
25	0.134	35	0.096	0.021	−0.028

II. *cis*-Polybutadiene - Benzene at 25°C

V, cc.	ϕ_2	V', cc.	ϕ'_2	$\Delta\overline{H}_d$, cal.	χ_H
20	0.242	30	0.161	0.098	0.038
30	0.161	40	0.121	0.054	0.042
40	0.121	50	0.097	0.033	0.042
20	0.242	40	0.121	0.153	0.040
20	0.242	50	0.097	0.186	0.040
10	0.265	20	0.133	0.102	0.043
20	0.133	30	0.088	0.035	0.045
10	0.265	30	0.088	0.137	0.045
10	0.361	20	0.181	0.160	0.037
20	0.181	30	0.121	0.061	0.042
30	0.121	40	0.090	0.029	0.040
10	0.361	30	0.121	0.222	0.039
10	0.361	40	0.090	0.250	0.039
20	0.115	40	0.056	0.031	0.037
40	0.056	60	0.038	0.010	0.035
20	0.115	60	0.038	0.042	0.036
20	0.318	50	0.127	0.107	0.040
15	0.318	25	0.190	0.148	0.037
50	0.064	80	0.040	0.018	0.036

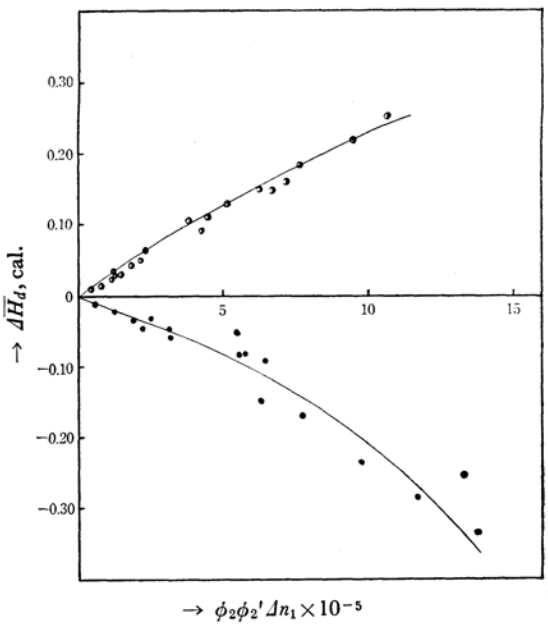

Fig. 1. $\Delta\overline{H}_d$ versus $\phi_2\phi_2'\Delta n_1$ data for *cis*-polybutadiene solution in benzene -◑- at 25°C and in toluene -●- at 26°C.

The curves are drawn according to Eq. 2 with the parameter of Table II.

Table II. Values of interaction parameter $\chi_H=\chi_1+\chi_2\phi_2$

Solvent	χ_1	χ_2
Toluene	−0.019	−0.067
Benzene	0.039	−0.005

with the $\phi_2\phi'_2\Delta n_1$ value. However, as is shown in Fig. 1, those plots are not linear, indicating that χ_H depends on the concentration.

In order to obtain the dependence of the χ_H parameter on the concentration, a least-square analysis of the data were carried out according to Eq. 2; this gave the values of χ_1 and χ_2 summarized in Table II.

By using the values of χ_1 and χ_2 listed in Table II, the $\Delta\overline{H}_d-\phi_2\phi'_2\Delta n_1$ curve has been calculated for each system; this curve, shown by the full line in Fig. 2, is in good agreement with the experimental data for each system.

As is shown in Table II, the χ_H parameter in a good solvent (an exothermic system) is considerably dependent on the concentration, while in a poor solvent (an endothermic system) it depends hardly at all on the concentration.

Such a tendency was also seen in the polystyrene solution and explained by the use of the dilute solution theory.

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