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The Heats of Dilution of Atactic Polystyrene Solutions

By Akihiro KAGEMOTO, Sachio MURAKAMI and Ryoichi FUJISHIRO

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka

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The heats of dilution of atactic polystyrene ($\bar{P}=244$) - various solvent systems have been measured by using a micro-twin-calorimeter at 25°C. Toluene, anisole, ethyl methyl ketone, dioxane and ethyl acetate were used as the solvents. For the analysis of the experimental data obtained by each dilution process, the simple Van Laar formula has been used, and the apparent enthalpy parameter between the polymer and the solvent has been derived. Since these interaction parameters seemed to depend on the concentration, we tried to analyze the experimental data with a modified Van Laar formula which contained interaction parameters depending on the concentration. The interaction parameters obtained by these analyses are considerably dependent on the concentration in good solvents, while those in poor solvents depend hardly at all on the concentration. This dependence of the interaction parameters on the concentration has been explained by using the dilute solution theory of polymer solutions proposed by Flory and Krigbaum (*J. Chem. phys.*, **18**, 1086 (1951)). The interaction parameters in the dilute region have been compared with those obtained by other methods, and the agreement between our values and those obtained by other methods has been found to be fairly good.

The direct measurement of the heats of dilution of polymer solutions is very important in investigating the interaction parameter between the polymer and the solvent molecules. In spite of the fact that such measurement is accompanied by considerable difficulties, several reports[1-5] have been published in this field. We have now constructed a twin-calorimeter and, by using this apparatus, have attempted thermal measurements in order to study the behavior of atactic polystyrene using such solvents as anisole, toluene, ethyl acetate, dioxane and ethyl methyl ketone.

Experimental

Apparatus and Procedure.—The twin calorimeter which is shown in Fig. 1 was designed to measure the heats of dilution. It consists of two copper cell holders (A), a mixing cell (B_1) and a reference cell (B_2). Around the outside surface of the holders, a thirty-junction copper-constantan thermocouple (C) is wound. The heating coil, with a resistance of about 40 ohm is fixed with araldite cement around the mixing cell (D). The mixing cell is made of glass and consists of an outer cell (E) and an inner cell (F), as is shown in Fig. 2. The outer cell (E) is filled with the polymer solution, and the inner cell (F) is charged with the solvent by using a hypodermic syringe; each cell is then sealed, at G and H, with mercury.

The polymer solution and solvent are mixed by pulling up the lid of the inner cell through the manipulation of the wire (I) from the outside of the calorimeter chamber.

The solution is mixed by being stirred by a synchronous (30 r. p. m.) motor (J). The reference cell (B_2), containing only the solvent, is the same type of cell as the mixing cell and acts as the reference bath for the thermocouple.

The electronic circuit for the measurement of the heat of dilution is the same as that described in a previous

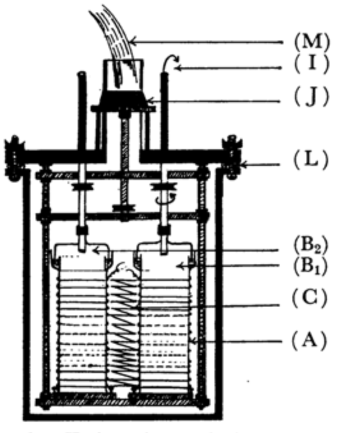

Fig. 1. Twin micro-calorimeter.

(A)	Copper cell holder
(B_1)	Mixing cell
(B_2)	Reference cell
(C)	Copper-constantan thermocouple
(L)	Rubber ring
(J)	30 r. p. m. motor
(M)	Lead wire
(I)	Wire for pulling up the lid

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1) H. Tompa, *J. Polymer Sci.*, **8**, 51 (1952).

2) G. H. Kabayama and H. Daoust, *Can. J. Chem.*, **36**, 556 (1958).

3) G. H. Schulz and H. Horbach, *Z. Physik Chem.*, **22**, 377 (1959).

4) M. Senez and H. Daoust, *Can. J. Chem.*, **40**, 734 (1962).

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

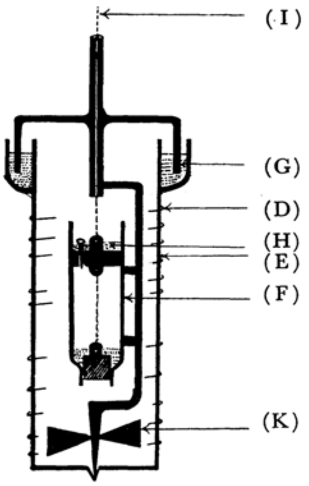

Fig. 2. Mixing cell.

(D) Heating coil
(E) Outer cell
(F) Inner cell
(G)(H) Mercury seal
(I) Wire for pulling up the lid
(K) Stirrer

paper[5]. The calorimeter was immersed in a water thermostat kept at 25.00±0.01°C.

Materials.—An atactic polystyrene sample (degree of polymerization: 244) was supplied by Dr. T. Matuo of the Chemical Institute of Kyoto University. This sample was purified by dissolving it in toluene, precipitated with methanol, and then dried under a pressure of 1 mmHg until the solvent has been completely removed. The solvents used were anisole, toluene, dioxane, ethyl acetate and ethyl methyl ketone. These solvents were purified by the ordinary methods described in the literature[6] and finally distilled.

Results and Discussion

The heats of the dilution of atactic polystyrene were measured over the concentration range from a 0.2 to a 0.015 volume fraction of the polymer by the successive addition of 5- or 20-ml. portions of the solvent to a solution of a known concentration. The results obtained are shown in Table I.

Three systems, the solutions of anisole, toluene and ethyl acetate, are exothermic, while the other two systems, those of dioxane and ethyl methyl ketone, are endothermic.

Assuming that the heat of mixing is expressed by the simple Van Laar equation and following the method of treatment by Tompa,[1] the heat of dilution, $\Delta\overline{H}_d$, from the volume fraction ϕ_2 to the volume fraction ϕ_2' can be represented by;

$$\Delta\overline{H}_d=\boldsymbol{R}T\chi_{\mathrm{H}}\phi_2\phi_2'\Delta n_1 \tag{1}$$

where Δn_1 is the number of moles of solvent added and χ_{H} is the interaction parameter between the polymer and the solvent. Instead of Eq. 1, we can also obtain the equivalent expression:

$$\Delta\overline{H}_d=\boldsymbol{R}Txn_2(\phi_2-\phi_2')\chi_{\mathrm{H}} \tag{1'}$$

where n_2 is the number of moles of the structure unit and x the degree of the polymerization of the polymer.

By using the experimental data listed in Table I and Eq. 1 or 1′, the interaciion parameter, χ_{H}, can be obtained for each stage of the dilution process of each system; these parameters are given in the last column of the same table.

For the polystyrene-toluene system, we previously measured the heats of dilution in the concentrated solution and so derived the values of the interaction parameter, χ_{H}, values which were in the vicinity of -0.2. The χ_{H} values in this experiment are about -0.2 in the concentrated range, which is in good agreement with those obtained in the previous experiment; there is also a decrease in the absolute value in the fairly diluted region. The tendency for the χ_{H} parameter to depend on the concentration seems to be observed not only in the toluene system but also in other systems. To test this behavior, we plotted the heat of dilution, $\Delta\overline{H}_d$, against $\phi_2\phi_2'\Delta n_1$ or $xn_2(\phi_2-\phi_2')$ in Fig. 3.

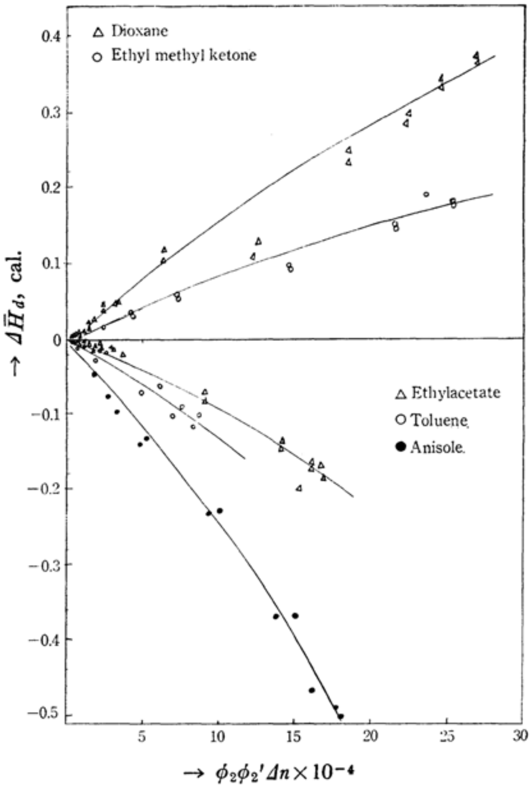

Fig. 3. The plot of the heat of dilution $\Delta\overline{H}_d$ against $\phi_2\phi_2'\Delta n_1$.

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[6] A. Weissberger and E. S. Proshauen, "Organic Solvent," Interscience Publishers, New York (1955).

TABLE I. HEATS OF DILUTION OF ATACTIC POLYSTYRENE SOLUTION AT 25°C

1. Polystyrene-Toluene

V, cc.	ϕ_2	V', cc.	ϕ_2'	$-\Delta\overline{H}_d$, cal.	χ_H
5	0.176	10	0.088	0.066	−0.15
10	0.088	15	0.058	0.029	−0.20
15	0.058	20	0.043	0.009	−0.14
5	0.166	10	0.083	0.074	−0.19
10	0.083	15	0.056	0.033	−0.25
15	0.056	20	0.042	0.014	−0.22
20	0.052	30	0.035	0.0134	−0.13
30	0.035	40	0.026	0.0044	−0.08
40	0.026	50	0.021	0.0016	−0.05
20	0.048	30	0.032	0.0087	−0.10
30	0.032	40	0.024	0.0035	−0.08
40	0.024	50	0.019	—	—
5	0.176	15	0.058	0.095	−0.16
5	0.176	20	0.043	0.104	−0.16
5	0.166	15	0.056	0.107	−0.20
5	0.166	20	0.042	0.121	−0.20
20	0.052	40	0.026	0.0178	−0.12
20	0.052	50	0.021	0.0194	−0.10
20	0.048	40	0.024	0.0123	−0.09

2. Polystyrene-Anisole

V, cc.	ϕ_2	V', cc.	ϕ_2'	$-\Delta\overline{H}_d$, cal.	χ_H
10	0.175	15	0.116	0.227	−0.42
15	0.116	20	0.087	0.153	−0.57
20	0.087	25	0.069	0.094	−0.59
25	0.069	30	0.058	0.036	−0.34
10	0.184	15	0.122	0.227	−0.38
15	0.122	20	0.091	0.148	−0.50
20	0.091	25	0.072	0.106	−0.61
10	0.175	20	0.087	0.380	−0.46
10	0.175	25	0.069	0.474	−0.49
10	0.175	30	0.058	0.510	−0.47
10	0.175	20	0.091	0.375	−0.42
10	0.184	25	0.072	0.481	−0.45

3. Polystyrene-Ethyl acetate

V, cc.	ϕ_2	V', cc.	ϕ_2'	$-\Delta\overline{H}_d$, cal.	χ_H
10	0.186	15	0.124	0.077	−0.11
15	0.124	20	0.093	0.066	−0.19
20	0.093	25	0.073	0.021	−0.10
25	0.073	30	0.060	0.013	−0.10
10	0.186	15	0.124	0.084	−0.12
15	0.124	20	0.093	0.063	−0.18
20	0.093	25	0.072	0.031	−0.15
25	0.072	30	0.060	0.014	−0.11
30	0.060	35	0.040	0.014	−0.20
20	0.050	40	0.025	0.0110	−0.073
40	0.025	50	0.020	0.0013	−0.046
50	0.020	60	0.016	0.0004	−0.023
60	0.016	70	0.014	—	—
20	0.059	40	0.029	0.0196	−0.095
40	0.029	50	0.024	0.0015	−0.039
10	0.186	20	0.093	0.141	−0.13
10	0.186	25	0.073	0.162	−0.13
10	0.186	30	0.060	0.175	−0.14
10	0.186	20	0.093	0.147	−0.14
10	0.186	25	0.072	0.178	−0.14
10	0.186	30	0.060	0.192	−0.15
10	0.186	35	0.040	0.206	−0.18
20	0.050	50	0.020	0.0123	−0.07
20	0.050	60	0.016	0.0127	−0.07
20	0.059	50	0.024	0.0212	−0.08

4. Polystyrene - Ethyl methyl ketone

V, cc.	ϕ_2	V', cc.	ϕ'_2	$\Delta\overline{H}_d$, cal.	χ_H
10	0.222	20	0.148	0.095	0.089
15	0.148	25	0.111	0.052	0.098
20	0.111	20	0.088	0.031	0.098
10	0.222	15	0.148	0.092	0.086
15	0.148	20	0.111	0.051	0.095
20	0.111	25	0.088	0.028	0.090
25	0.088	30	0.060	0.017	0.099
10	0.222	20	0.111	0.147	0.092
10	0.222	25	0.088	0.178	0.093
10	0.222	20	0.111	0.143	0.088
10	0.222	20	0.088	0.171	0.089
10	0.222	20	0.060	0.188	0.108

5. Polystyrene-Dioxane

V, cc.	ϕ_2	V', cc.	ϕ_2'	$\Delta\overline{H}_d$, cal.	χ_H
10	0.216	15	0.144	0.128	0.12
15	0.144	20	0.108	0.117	0.22
20	0.108	25	0.086	0.054	0.17
25	0.086	30	0.070	0.041	0.20
30	0.070	35	0.060	0.032	0.22
10	0.213	15	0.142	0.104	0.10
15	0.142	20	0.106	0.129	0.25
20	0.106	25	0.084	0.052	0.17
25	0.084	30	0.070	0.046	0.23
30	0.070	35	0.060	0.030	0.21
10.9	0.039	21.4	0.020	0.007	0.12
9.7	0.053	19.2	0.027	0.011	0.12
19.2	0.027	24.2	0.021	0.003	0.13
24.2	0.021	29.3	0.018	0.002	0.17
11.1	0.054	16.3	0.037	0.012	0.17
16.3	0.037	21.3	0.028	0.006	0.17
10	0.216	20	0.108	0.245	0.15
10	0.216	25	0.086	0.299	0.16
10	0.216	30	0.070	0.340	0.16
10	0.216	35	0.060	0.372	0.17
10	0.213	20	0.106	0.233	0.15
10	0.213	25	0.084	0.285	0.15
10	0.213	30	0.070	0.331	0.16
10	0.213	35	0.060	0.361	0.17
9.7	0.053	24.2	0.021	0.014	0.12
9.7	0.053	29.3	0.018	0.016	0.12

According to Eq. 1 a linear plot must be obtained, its slope giving the interaction parameter. However, as may be seen in Fig. 3, this plot is not linear, indicating that the interaction parameter depends on the concentration.

Assuming that the interaction parameter, χ_H, is expressed as:

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

and making the same derivation as that of Eq. 1 or 1′, we can obtain the following equation:

$$\Delta\overline{H}_d=\boldsymbol{R}T\phi_2\phi_2'\Delta n_1[\chi_1+\chi_2(\phi_2+\phi_2')/2] \qquad (2)$$

or

$$\Delta\overline{H}_d=\boldsymbol{R}Txn_2(\phi_2-\phi_2')[\chi_1+\chi_2(\phi_2+\phi_2')/2] \qquad (2')$$

where $\phi_2=xn_2/(n_1+xn_2)$

and $\phi_2'=xn_2/(n_1+\Delta n_1+xn_2)$.

In order to find χ_1 and χ_2, we tried to plot the $\Delta\overline{H}_d/\boldsymbol{R}T\phi_2\phi_2'\Delta n_1$ against $(\phi_2+\phi'_2)/2$ for each system of Fig. 4.

The experimental data, however, were too scattered for us to obtain accurate values. Therefore, we carried out the least-squares treatment of the data according to Eq. 2; this gave the values for χ_1 and χ_2 shown in Table II.

TABLE II. VALUES OF INTERACTION PARAMETER $\chi_H=\chi_1+\chi_2\phi_2$

Solvent	χ_1	χ_2
Toluene	−0.08	−0.94
Anisole	−0.60	−1.18
Ethyl acetate	−0.05	−0.66
Dioxane	0.16	−0.008
Ethyl methyl ketone	0.10	−0.08
Toluene[5]	−0.27	0.69

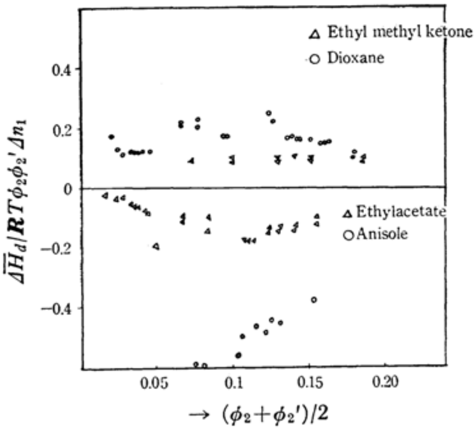

Fig. 4a. The variation of the apparent heat parameter with the average volume fraction of polystyrene-various solvents at 25°C.

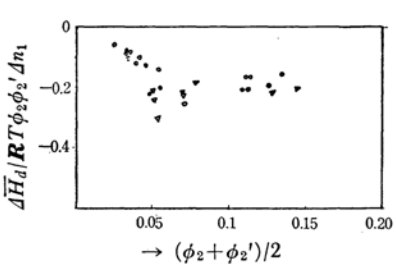

Fig. 4b. The variation of the apparent heat parameter with the average volume fraction of polystyrene-various solvents at 25°C.
Toluene, ○ $\overline{P}=244$, △ $\overline{P}=270$

By using the values of χ_1 and χ_2 listed in Table II, a $\Delta\overline{H}_d-\phi_2\phi_2'\Delta n_1$ curve has been calculated for each system; this curve, which is shown by the full line in Fig. 3, is in good agreement with the experimental data for each system.

As may be seen in Table II, the χ_H parameter in good solvents (exothermic systems) are considerable concentration-dependent, while those in poor solvents (endothermic systems) do not depend on the concentration. These tendencies indicate that the absolute values of the χ_H parameter in the dilute solution are considerably lower than those in the moderate concentration range in good solvents, while the values of the χ_H parameter in poor solvents hardly change.

According to the dilution theory of the polymer solution proposed by Flory,[7] the second virial coefficient, A_2, is expressed as:

$$A_2\propto(\psi_1-\kappa_1)F(X)$$

where: $X=2(\alpha^2-1)$,

$$F(X)=1-X/2!\cdot 2^{-3/2}+\cdots$$

An approximate treatment gives the interaction parameter as $\kappa_1F(X)$, which is an apparent interaction parameter in the dilute region. Now we may assume that Flory's formula also applies to the solution of good solvents, though this formula has hitherto been considered to be correct only in poor-solvent systems. Therefore, in good solvents α is greater than 1 and $F(X)$ is considerably less than 1. The apparent interaction parameter, $\kappa_1F(X)$, in the dilute region is, therefore, considerably smaller than that in the moderate concentration in terms of absolute value. On the other hand, in poor solvents the expansion factor α is nearly equal to 1, and $F(X)\simeq 1$, suggesting that the interaction parameter may be independent of the concentration.

The interaction parameter is usually studied by other methods, such as the temperature dependence of the osmotic pressure of the solution. The values for the interaction parameter obtained by various

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[7] P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

TABLE III. VALUES OF THE INTERACTION PARAMETER OBTAINED BY VARIOUS AUTHORS

Solvent	χ_1 (a)	χ_1 (b)	χ_1 (c)	χ_1 (d)	χ_1 (e)	χ_1 (f)	χ_1 (g)	χ_1 (h)
Toluene	−0.030	−0.101	0.06	0.06	−0.10 ∼−0.17	−0.008	−0.27	−0.08
Ethyl methyl ketone	−0.001		0.00	0.00		0.04		0.10
Ethyl acetate	0.019	0.025	0.02					−0.05
Dioxane			0.07					0.16

(a) See Ref. 8, osmotic pressure
(b) See Ref. 9, osmotic pressure
(c) See Ref. 10, viscosity
(d) See Ref. 11, viscosity
(e) See Ref. 1, *direct* measurement
(f) See Ref. 12, osmotic pressure
(g) See Ref. 5, direct measurement
(h) This paper, direct measurement

authors[1,5,8−12] using these methods are listed in Table III. Since these measurements have been carried out in a dilute solution, those of our values of the interaction parameter to be compared with those in Table III must also be in a dilute solution, that is, the χ_1 values, which are the concentration-independent terms in χ_H as determined by our experiment and shown in the last column in Table III.

The agreement between our parameters and those obtained by other methods may be fairly good in terms of absolute value, though there remain some questions concerning their signs.

Summary

We have constructed a twin calorimeter with a thirty-junction thermocouple in order to measure the slight temperature-change of a polymer solution. By using this apparatus, the heats of the dilution of atactic polystyrene ($\overline{P}=244$) have been measured, and from them the interaction parameters have been derived according to Van Laar's simple formula. Since the interaction parameters seemed to depend on the concentration, we tried to analyze the experimental data with a modified Van Laar formula which contained the interaction parameter depending on the concentration.

We found that the interaction parameters are considerably concentration-dependent in good solvents, while those in poor solvents do not depend on the concentration.

The authors wish to thank Dr. T. Matuo of the Chemical Institute of Kyoto University for supplying the sample to them.

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8) G. H. Schulz and H. Hellfritz, *Z. Elektrochem.*, **57**, 835 (1953).

9) M. J. Schik, P. Doty and B. H. Zimm, *J. Am. Chem. Soc.*, **72**, 530 (1953).

10) L. H. Cragg and T. E. Dumitro, ibid., **74**, 1997 (1952).

11) T. G. Fox and P. J. Flory, ibid., **73**, 1915 (1952).

12) G. E. H. Bawn and M. A. Wajid, *J. Polymer Sci.*, **12**, 109 (1954).