Heats of Dilution of Polystyrene Solutions. II

By Kazuo AMAYA and Ryoichi FUJISHIRO*

(Received June 24, 1957)

The measurement of heat of dilution of polymer solutions is very significant for investigating the interaction power between polymer and solvent molecules. In the previous paper[1] we reported the heats of dilution in the solutions of polystyrene in toluene, ethylbenzene and chloroform. In this paper we shall report the heats of dilution in the systems of polystyrene-benzene, and polystyrene-cyclohexane. In both systems the heats have been directly measured by a few authors and in particular the results obtained in the former system seem not to be consistent with each other.

---

* Present address: Institute of Polytechnics, Osaka City University, Kitaku, Osaka.

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

Experimentals

Apparatus—The calorimeter used has been described in the previous paper[1].

Materials—A sample of polystyrene was the same as that used in the previous paper[1] and its degree of polymerisation was 275. The solvents were purified according to the method described in the literature and finally distilled.

Result and Discussion

The heat of dilution was measured by adding 5 cc. of solvent to the polymer solution having a definite concentration. The measurement was made at 25°C in the benzene system and at 30°C in the cyclohexane one, since at 25°C homogeneous solution could not be obtained for the latter.

The results obtained are shown in Table I. Both systems, solutions of polystyrene-benzene and polystyrene-cyclohexane, were endothermic. Assuming that the heat of mixing is represented by the formula of van Laar's type, and making a simple treatment described in the previous paper, the integral heat of dilution $\varDelta H_0$ from the volume fraction of polymer v_r to v_r' can be represented by

$$\varDelta H_0=\alpha(Vv_r-V'v'_r) \qquad (1)$$

where α is the interaction parameter between polymer and solvent, and V and V' are the volume of solutions before or after the dilution, respectively.

TABLE I

HEAT OF DILUTION OF POLYMER SOLUTION

1. Polystyrene-benzene system at 25°C.

Before dilution		After dilution		Heat absorbed	α
V cc.	v	V'	v'	cal.	cal/cc.
4.75	0.185	9.75	0.090	0.052	0.62
4.85	0.185	9.85	0.091	0.061	0.72
3.73	0.185	8.73	0.079	0.067	0.92
4.82	0.153	9.82	0.075	0.048	0.82
4.79	0.153	9.79	0.075	0.034	0.59

2. Polystyrene-cyclohexane system at 30°C.

Before dilution		After dilution		Heat absorbed	α
V cc.	v	V'	v'	cal.	cal/cc.
4.90	0.108	9.90	0.053	0.142	4.9
9.90	0.053	14.90	0.036	0.118	12
14.90	0.036	19.90	0.027	0.099	21
4.95	0.108	9.95	0.054	0.154	5.3
9.95	0.054	14.95	0.036	0.127	13
14.95	0.036	19.95	0.027	0.089	19

By the use of (1), the values of α can be calculated for both systems. They are shown in the last column of Table I. From Table I, it will be found that the values of α for the polystyrene-benzene system fluctuate considerably and those for the polystyrene-cyclohexane system increase anomally as the concentration of polymer decreases.

Considerable fluctuation of the values of α in the former case may be probably due to the experimental errors arising from stirring of the viscous solution on mixing, though the correction owing to stirring is made in each operation.

This could be understood, if it is considered that as the volume fractions of polystyrene are about two times higher in benzene than in cyclohexane and benzene is a better solvent than cyclohexane for polystyrene, the benzene solution is considerably more viscous than the cyclohexane solution and the former required much longer duration of stirring than the latter to make the solution homogeneous.

Even taking these experimental errors into consideration, the value of α in the benzene solution seems to be positive and is in the neighborhood of +0.7.

For the cyclohexane-polystyrene system, anormal increase of the values of α with the decrease of polymer concentration is difficult to explain. A tentative explanation may be as follows. Cyclohexane is a bad solvent for polystyrene and the critical temperature for the cyclohexane solution of polystyrene is in the neighborhood of 27°C**, though it is dependent on the molecular weight of polystyrene. The temperature at which the measurements were made is 30°C, being slightly higher than the critical temperature. Hence, it may be reasonable to suppose that in the solution at 30°C there will remain more or less the same aggregations of polymer as in the solution below the critical temperature. On dilution of such a solution it will be presumed that unusual heats are absorbed for separating these aggregations in the range of lower concentrations of polymer.

For the sake of comparison with the data for polymer solution, the heat of mixing and of dilution of ethylbenzene (which may be regarded as a monomer unit of polystyrene), with benzene and cyclohexane was also measured. The results are shown in Table II. From these data the values of α were calculated by the same procedure as in the polystyrene solution. These values are shown in the last column of Table II.

As in the previous paper, it will be found that the interaction parameter

---

** A. R. Shultz and P. J. Flory. *J. Am. Chem. Soc.*, **74**, 4760 (1952).

TABLE II

HEATS OF MIXING AND DILUTION OF ETHYLBENZENE SOLUTION AT 25°C.

Before dilution		After dilution		Heat absorbed	α
V cc.	v	V cc.	v	cal.	cal./cc.
1. Ethylbenzene-benzene system					
5	1.000	10	0.500	2.450	0.98
10	0.500	15	0.333	0.792	0.97
15	0.333	20	0.250	0.351	0.96
2. Ethylbenzene-cyclohexane system					
5	1.000	10	0.500	9.04	3.0
10	0.500	15	0.333	1.918	2.8
15	0.333	20	0.250	1.491	2.9
20	0.250	25	0.200	0.824	2.9

between polymer and solvent has the same sign as that between the monomer unit of polymer (ethylbenzene) and the solvent for each system. The interaction parameter in the benzene-polystyrene system is a little smaller than that in the monomer unit-benzene system. This may be easily understood, as it is supposed that there may be more chances of the self-contacts between polymer segments in the polymer solution, as Meares pointed out[2]. On the other hand, the values of α for the polystyrene-cyclohexane system are higher than for the monomer unit-cyclohexane system. This may be explained if it is considered that there remain more or less the aggregations of polymers in the cyclohexane solution as mentioned above.

Our results are compared with the data obtained by other authors. Tompa[3] found that the value of α for the benzene solution was $-0.7\sim-1.6$ cal./cc. from the direct measurement of heats of dilution. (Here the value of α is recalculated from the value of μ obtained by Tompa according to the equation, $\mu = V_0\alpha/kT$, where V_0 is the partial molar volume of benzene in the polymer solution) Tompa's value of α is contradictory to our result in sign.

As for this system there have been no other reports on direct measurement of heat of dilution to be compared with ours. But here we shall discuss, making use of the results of heats of mixing between polystyrene and benzene obtained by Hellfritz[4]. According to Hellfritz, the heat of solution of polystyrene in benzene is -3.69 cal. per gram of polystyrene, which seems to be favorable for explaining Tompa's data.

The measurement of density of polystyrene by Boyer and Streeter[5], however, showed that the specific volume of polystyrene is considerably smaller in the dilute solution than in the solid state and it is constant independent of the concentration in the former state. Hence, the solid state of polymer may be supposed to have a glassy and loose structure containing many vacant holes and to be a metastable state, as Jenckel and Gorke pointed out[6]. The state of polymer having the same specific volume as in the dilute solution will probably be the one in equilibrium.

Thus, the process of solution will be divided into two parts. The one is the transformation of polymer from a glassy state to a stable one or the occupation of many holes in polymer by solvent molecules, and this may be expected to occur in the range of higher concentrations and decrease the specific volume of polymer considerably. The other is the process of normal dilution or of mixing between polymer in equilibrium state and solvents. This will occur in all concentration ranges and is detectable only in the dilution of solution having a lower concentration, because of the dominancy of the first process in the higher concentrations.

Hence, the heat of solution will be given as the sum of the heat of two processes. The heat of the first is calculated as that arising from the condensation of solvent into holes of polymer. As the specific volumes of polystyrene in a solid state and in a dilute solution are 0.956 and 0.905 cc. respectively and the heat of vaporization per cc. of benzene is 80.9 cal., the energy of condensation of benzene in 0.051 cc. (0.956—0.905 cc.) of vacant holes of polystyrene will amount to -4.21 cal.. Combining this value with the heat of solution, we can obtain 0.52 cal. for the value of the heat arising only from infinite dilution of a gram of polystyrene with benzene.

Taking 0.52 cal./g. as the heat of infinite dilution and using Eq. (1) we can obtain the value of α of 0.6 cal./cc., which may be consistent with our result both in sign and in magnitude.

Similar treatments can be applied to other solutions of polystyrene. The values of α thus obtained are shown in Table III. The values of α thus calculated from the heat of solution seems to be consistent

---

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

[3] H. Tompa, *J. Polymer Sci.*, **8**, 51 (1953).

[4] H. Hellfritz, *Makromol. Chem.*, **7**, 191 (1951).

[5] D. J. Streeter and R. F. Boyer, *Ind. Eng. Chem.*, **43**, 1790 (1951).

[6] E. Jenckel and K. Gorke, *Z. Electrochem.*, **60**, 579 (1956).

TABLE III
INTERACTION PARAMETER CALCULATED FROM THE HEATS OF SOLUTION

Solvent	Chloroform	Toluene	Benzene	Cyclohexane
Heat of solution of polymer[4]. cal./g.	−4.4	−3.99	−3.69	0.59
Spec. vol. of polymer in solid[5]. cc.	0.957	0.957	0.957	0.957
Spec. vol. of polymer in dil. soln[5]. cc.	0.908	0.914	0.905	0.933***
Decrease of volume polymer cc.	0.049	0.043	0.052	0.024
Heat of vaporization of solvent[7]. cal/cc.	79.7	74.4	80.9	60.8
Heat of condensation of solvent into vacant sites of polymer. cal./g.	−3.91	−3.20	−4.21	−1.46
Net heat of dilution cal./g.	−0.49	−0.79	0.52	2.05
α cal./cc.	−0.54	−0.86	0.57	2.20
α observed. cal./cc.	−1.1∼−1.3	−1.4∼−1.5	0.5∼0.9	5∼20

in sign with our results, though in magnitude some deviations are seen.

Summary

The heats of dilution in the systems of polystyrene - benzene and polystyrene-cyclohexane were measured and the values of interaction parameters were derived. The heat of mixing of ethylbenzene, which may be regarded as the monomer unit of polystyrene, with the same solvents was also measured and it was found that the interaction of polymer solutions has the same sign as those of the corresponding monomer unit solutions.

We would like to express our gratitude to Professor A. Kotera of Tokyo University of Education for his valuable suggestions.

Department of Chemistry
Faculty of Science, Kobe University
Higashinada-ku, Kobe

---

[7] J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes", Reinhold, 1950.

*** Since there is no data in cyclohexane, the value in dioxane which is considered to be similar to cyclohexane, is indicated.