Heats of Dilution of Polystyrene Solutions. I

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Introduction

It is well known that entropy plays an important role in defining thermodynamical behaviours of high polymer solutions. Enthalpy has also a great significane as an interaction parameter between polymer and solvent.

Enthalpy can be obtained from the temperature dependence of osmotic pressure or vapor pressure of polymer solutions, and such experiments were reported by various authors[1,2,3,4,5], but the data calculated from their results are not accurate. Direct measurements of heat of dilution of polymer solutions were reported by a few authors[6,7,8] but their results had a considerable error in the range of concentrations where the heat changes are small.

It is thought that a more accurate measurement of heat of dilution of various polymer solutions has a great significance in explaining the thermodynamical behaviours of polymer solutions.

We constructed a calorimeter using thermister capable of measuring temperature change down to 0.5×10^{-4}°C (0.003 cal.) and measured the heats of dilution of three polystyrene solutions, using toluene, ethylbenzene and chloroform as solvents.

Experimental

Apparatus and Procedure.—The calorimeter. The calorimeter, similar to those described by Gee[6] and Meares[7], but different from them in using a thermister, was constructed and is shown in Fig. 1.

A is an unsilvered Dewar vessel 21 cm. long and 3.5 cm. in inner diameter. A double bulb, consisting of the inner bulb B and the outer bulb C, is the mixing bulb. The polymer solution S to be diluted was introduced into the outer bulb C from a pipette with a long delivery tube which reached to the bottom through the inner bulb B, and was separated by a pool of mercury F from the solvent S′ which is in the inner bulb B. To minimize the evaporation loss of the solvent from the outer bulb a rubber ring D which was fixed to the inner bulb was fitted tightly with the

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[1] G. Gee and W.J.C. Orr, *Trans. Faraday Soc.*, **42**, 507 (1946).

[2] M.J. Newing, ibid., **46**, 613 (1950).

[3] C.E.H. Bawn, R.F.J. Freeman and A.R. Kamaliddin, ibid., **46**, 677 (1950).

[4] M.J. Schick, P. Doty and B.H. Zimm, *J. Am. Chem. Sec.*, **72**, 531 (1950).

[5] C.E.H. Bawn and M.A. Wajid, *J. Polymer Sci.*, **12**, 109 (1954).

[6] J. Ferry, G. Gee and L.R.G. Treloar, *Trans. Faraday Soc.*, **41**, 340 (1945).

[7] P. Meares, ibid., **47**, 699 (1951).

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

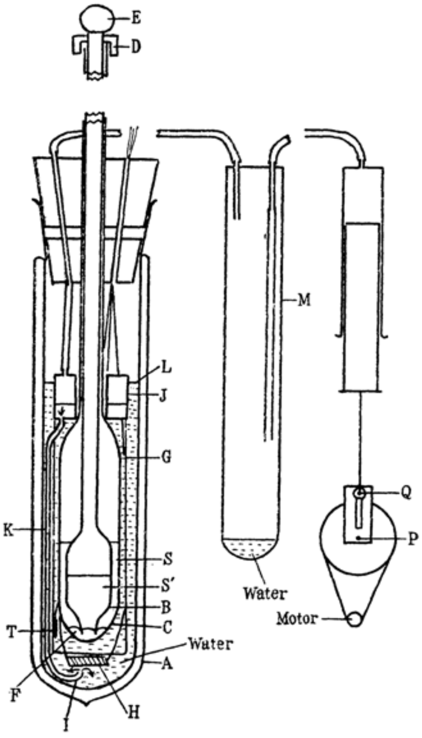

Fig. 1.

outer bulb. The inner bulb was closed by a rubber cap E at the top.

By raising the inner bulb and then moving it up and down in the solution, the solution was moved up and down through the aperture between the inner bulb and the outer bulb, and the mixing was performed. The polymer solution was fairly viscous, and sufficient mixing could not be achieved by only rotating the inner bulb.

The mixing bulb fitted centrally through a rubber bung into the Dewar vessel A filled with water up to the level L indicated in the diagram. A stirrer fitted with an injector was devised. The piston of the injector was connected to a rod R at Q which was rotated around the pivot P at a speed 20 r.p.m.. The volume of the air pumped in and out of the injector during a cycle was controlled by adjusting the distance between P and Q.

The exit of the injector was connected, through the water vapor saturator M, 270 cc. in volume, acting also as a temperature moderator, to a copper tube J in the Dewar vessel. J is a coaxial copper tube the inner tube of which was fitted loosely to C having holes at the upper and the bottom. To the hole at the bottom was connected a rubber tube K, the other end I of which reaches to the bottom of the Dewar vessel. By the motion of the piston of the injector the water in J going in and out through the rubber tube K and the water in the Dewar vessel was stirred.

To ensure immediate attainment of the thermal equilibrium, a piece of copper plate G, which almost covers the outer bulb C was connected to J. The calorimeter and the saturator were immersed in the water thermostat at 25°C kept constant to $\pm 1\times10^{-4}$°C.

The temperature changes were measured with a thermister T having about 400 KΩ in resistance and a temperature coefficient of -5.5 percent at 25°C. The heat capacity of the calorimeter was determined by introducing measured amounts of electrical energy through the constantan heater H having resistance of about 37 Ω. An electrical current passing through the heater was measured by a precision type m.A. meter, and the time during which the electrical current was passed was measured with a stop watch.

Various kinds of thermometer systems employing a thermister were tried. The most simple one, combining a low resistance thermister and a galvanometer was proved to be unsatisfactory because of the effect of self-heating of the thermister. The one employing a.c. Wheatstone bridge with a high resistance thermister and a.c. vacuum tube amplifier was quite satisfactory to eliminate the self-heating, but the adjustment of 2 components, namely resistance and capacitance was very cumbersome in the actual operation. The following was finally adopted.

The block diagram of the resistance measuring unit adopted is shown in Fig. 2. Unbalanced d.c. voltage across the Wheatstone bridge was converted to 30 c/s a.c. voltage by a converter driven by 30 c/s oscillator. The converter was made of a permanent dynamic speaker and was shown in Fig. 3. Converted signals were fed to a narrow band amplifier and to a phase sensitive detector. The output was detected by a μA meter and the resistance reading was performed by adjusting the resistance of the Wheatstone bridge so that the meter deflection returns to its zero point. The arms of the Wheatstone bridge were immersed in the thermostat except the 11.11 KΩ decade box.

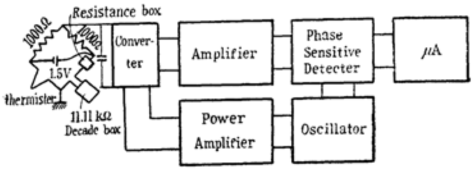

Fig. 2

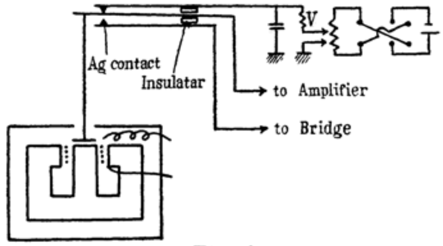

Fig. 3

The electrical circuits of the narrow band amplifier employing two twin-T. bridge is shown in Fig. 4. The phase sensitive detector is the same as that described by Schuster[9]. The oscillator and the driver of the converter are shown in Fig. 5 and Fig. 6 respectively.

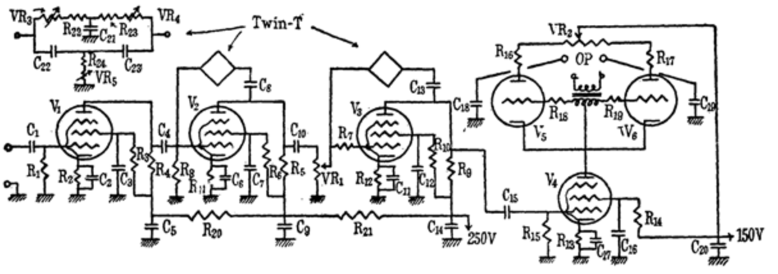

Fig. 4

R_1	100 KΩ	R_{16}	20 KΩ	C_2	100 μF	C_{16}	10 μF
R_2	2 KΩ	R_{17}	20 KΩ	C_3	2 μF (oil)	C_{17}	100 μF
R_3	1 MΩ	R_{18}	30 KΩ	C_4	0.1 μF	C_{18}	20 μF
R_4	500 KΩ	R_{19}	30 KΩ	C_5	20 μF	C_{19}	20 μF
R_5	500 KΩ	R_{20}	100 KΩ	C_6	100 μF	C_{20}	20 μF
R_6	1 MΩ	R_{21}	100 KΩ	C_7	3 μF	C_{21}	0.04 μF
R_7	2 MΩ	R_{22}	250 KΩ	C_8	0.1 μF	C_{22}	0.02 μF
R_8	2 MΩ	R_{23}	250 KΩ	C_9	20 μF	C_{23}	0.02 μF
R_9	500 KΩ	R_{24}	125 KΩ	C_{10}	0.1 μF	V_1	6SH7
R_{10}	1 MΩ	VR_1	1 MΩ	C_{11}	100 μF	V_2	6SH7
R_{11}	2 KΩ	VR_2	10 KΩ	C_{12}	3 μF	V_3	6SH7
R_{12}	2 KΩ	VR_3	100 KΩ	C_{13}	0.1 μF	V_4	6SH7
R_{13}	150 Ω	VR_4	100 KΩ	C_{14}	20 μF	V_5	1/2 6SN7
R_{14}	50 KΩ	VR_5	50 KΩ	C_{15}	0.1 μF	V_6	1/2 6SN7
R_{15}	500 KΩ	C_1	0.1 μF				

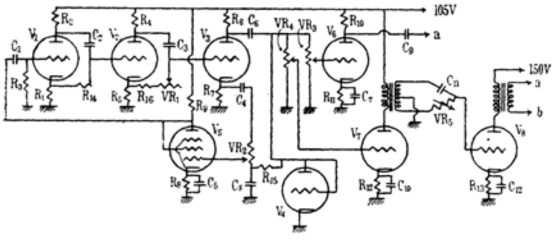

Fig. 5

R_1	1 KΩ	C_1	0.1 μF
R_2	1 KΩ	C_2	0.05 μF
R_3	1 MΩ	C_3	0.05 μF
R_4	2 KΩ	C_4	0.1 μF
R_5	2 KΩ	C_5	100 μF
R_6	20 KΩ	C_6	0.1 μF
R_7	4 KΩ	C_7	100 μF
R_8	300 Ω	C_8	2 μF
R_9	100 KΩ	C_9	0.1 μF
R_{10}	50 KΩ	C_{10}	100 μF
R_{11}	1 KΩ	C_{11}	0.02 μF
R_{12}	1 KΩ	C_{12}	100 μF
R_{13}	1 KΩ	V_1	1/2 6SL7
R_{14}	130 KΩ	V_2	1/2 6SL7
R_{15}	1 MΩ	V_3	1/2 6SL7
R_{16}	100 KΩ	V_4	1/2 6SL7
VR_1	50 KΩ	V_5	6BD6
VR_2	1 MΩ	V_6	1/2 6SN7
VR_3	500 KΩ	V_7	1/2 6SN7
VR_4	500 KΩ	V_8	6J5
VR_5	500 KΩ		

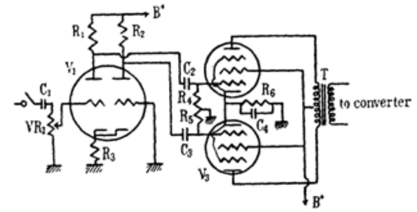

Fig. 6

R_1	100 KΩ	C_1	0.1 μF
R_2	100 KΩ	C_2	0.1 μF
R_3	1 KΩ	C_3	0.1 μF
R_4	250 KΩ	C_4	100 μF
R_5	250 KΩ	V_1	6SL7
R_6	210 Ω	V_2	UZ42
VR_1	500 KΩ	V_3	UZ42

1 Ω change in resistance can be detected. The resistance of the thermister is about 400 KΩ and the temperature coefficient is about −5.5 percent at 25°C and thus it corresponds to about $1/2\times10^{-4}$ degree.

Very little amounts of polarization in the thermister, probably due to the ions present, were observed. But the experiments were not affected, for the measurements were carried out after the polarization had been saturated. Thermoelectromotive force in the bridge circuit was cancelled by adjusting a variable resistor V in Fig. 3. Methods of Operation. After setting the calorimeter in the thermostat regulated at $25\pm1\times10^{-4}$°C, temperature of the calorimeter was adjusted

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9) N.A. Schuster, *Rev. Sci. Inst.*, **22**, 254 (1951).

almost equal to that of the thermostat by heating. It was then left for three to five hours in order to establish the thermal equilibrium.

The resistance reading was started after the calorimeter had reached thermal equilibrium. After mixing the solution and the solvent, the resistance reading was taken at an interval of one minute for about twenty minutes and a cooling curve was constructed. The heat change was always complete in two or three minutes. The heat capacity was determined for each run by introducing a certain amount of electrical energy which produces approximately equal resistance change to that in the mixing. The mixed solution was stirred manually by moving the inner bulb up and down from 10 times to 30 times according to the viscousness of the mixed solution until no inhomogeneity of the solution was observed. A stirring correction for the mixing was obtained by stirring the already mixed solution by the same standard technique as that employed in the mixing.

During the stirring, heat was developed and was quite reproducible in the cases of toluene and ethylbenzene, both having fairly low vapor pressure at 25°C. In the case of chloroform, however, reproducibility was not so satisfactory. This may be as-cribed to the fact the latter solvent has a fairly high vapor pressure at 25°C, and evaporates during the stirring and its amount is irregular because of the manual operation.

Materials.—A sample of Polystyrene* was prepared by polymerizing the monomer in carbon tetrachloride. This sample was purified by dissolving in benzene and precipitating with methanol. The same procedure was repeated twice and dried for about a week under the pressure of 1 mmHg.

The solvents used were purified according to the method described in the literature and finally distilled. Toluene, ethylbenzene** and chloroform used were fractions having boiling point 110.8–111.2°C, 135.5–136.0°C and 61.1–61.2°C respectively.

Results and Discussion

The heat of dilution was measured by adding 5 or 10 cc. of solvent successively to the solution of a definite concentration. The results obtained are shown in Table I.

Assuming that the heat of mixing is represented by the van Laar form, the heat of mixing H_m of solvent of volume V_0 and polystyrene of volume V_r can be represented as:

$$H_m=\alpha V_0 V_r/(V_0+V_r), \tag{1}$$

where α is a constant describing the interaction between solute and solvent. Accordingly, when the solvent of volume dV_0 is added to this solution, its heat of dilution is given by:

$$dH_d=(\partial H_m/\partial V_0)_p dV_0=[\alpha V_r^2/(V_0+V_r)^2]\cdot dV_0. \tag{2}$$

Thus, the integral heat of dilution ΔH_0 obtained when the solvent of the volume ΔV_0 is added to this solution is given by:

$$\Delta H_0=\int dH_d=\int_{V_0}^{V_0+\Delta V_0}[\alpha V_r^2/(V_0+V_r)^2]dV_0. \tag{3}$$

Assuming that α is constant within a small

TABLE I

HEAT OF DILUTION OF POLYMER SOLUTION

	Before dilution		After dilution		Heat evolved cal.	$-\alpha_d$	$-\alpha_{av}$	$-\mu$
	V cc.	v_r	V' cc.	v_r'				
1. Polystyrene-toluene system.								
1	4.70	0.189	9.70	0.092	0.099	1.14	1.37	0.24
	9.70	0.092	14.70	0.060	0.035	1.26		
	14.70	0.660	19.70	0.045	0.025	1.82		
2	4.70	0.170	9.70	0.083	0.106	1.51	1.51	0.27
	9.70	0.083	14.70	0.055	0.037	1.64		
	14.70	0.055	19.70	0.041	0.014	1.29		
3	9.70	0.083	14.70	0.055	0.037	1.64	1.51	0.27
	14.70	0.055	19.70	0.041	0.016	1.41		
2. Polystyrene-chloroform system.								
1	4.75	0.275	9.75	0.134	0.234	1.28	1.36	0.17
	9.75	0.134	14.75	0.088	0.122	1.29		
	14.75	0.088	19.75	0.066	0.046	1.58		
2	4.70	0.171	9.70	0.083	0.081	1.11	1.13	0.14
	9.70	0.083	14.70	0.055	0.028	1.25		
3. Polystyrene-ethylbenzene system.								
	4.75	0.194	9.75	0.081	0.002	0.02	0.00	0.00
	9.75	0.081	14.75	0.053	−0.002	−0.07		

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* We are indebted to Prof. T. Matsumoto of the Faculty of Technology of our University for this sample.

** We wish to thanks Dr. H. Yoshida of the Government Industrial Research Institute, Osaka, for supplying purified ethylbenzene.

concentration range (of course it is generally concentration dependent), we can express (3) as follows:

$$\Delta H_0 = -\alpha[V_r^2/(V_0+\Delta V_0+V_r) - V_r^2/(V_0+V_r)] \quad (4)$$

If we introduce the quantities V, V', v_r and v_r' defined as:

$V_0+V_r=V$ (Total volume of solution before dilution),
$V_0+\Delta V_0+V_r=V'$ (Total volume of solution after dilution),
$v_r=V_r/(V_0+V_r)$ (Volume fraction of polymer before dilution),
$v_r'=V_r/(V_0+\Delta V_0+V_r)$ (Volume fraction of polymer after dilution),

the above expression can be written as follows:

$$\Delta H_0 = \alpha(Vv_r^2 - V'v_r'^2). \quad (5)$$

The amount of polystyrene in the solution is the same before and after the dilution. Then (5) can be written as:

$$\Delta H_0 = \alpha V_r(v_r - v_r'). \quad (6)$$

Plotting ΔH_0 obtained from the experiment as ordinate and v_r as abscissa for each of three systems, we obtain a straight line in each case in the concentration range from 0.2 to 0.05 volume fractions. As an example, $H_0 - v_r$ diagram of the polystyrene-toluene system is shown in Fig. 7.

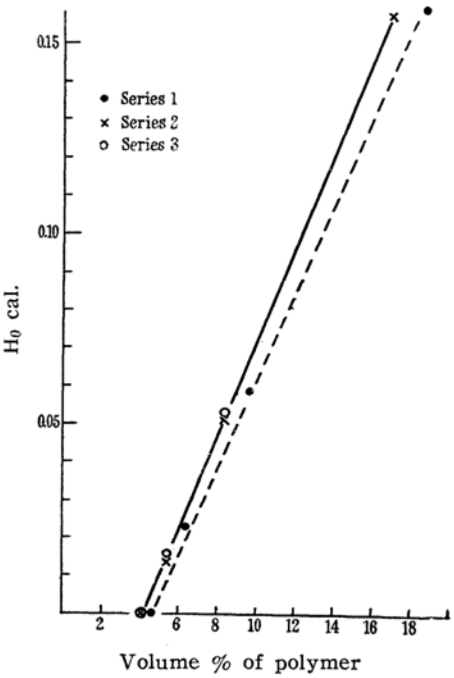

Fig. 7. Polystyrene—Toluene Solution.

α can be obtained from the tangent of the straight line in the diagram and its value for each system is given in Table I as α_{av}. Using (5), α at each concentration can be evaluated and the values thus obtained are represented as α_d. From these α values, μ can be derived by the equation, $\mu=\overline{V}\alpha/RT$, where $\overline{V}$ is the partial molal volume of the solvent, and shown in Table I.

For the sake of comparison with these data, the heat of mixing and the heat of dilution of ethylbenzene, which may be regarded as a monomer unit of polystyrene, with toluene and chloroform were also measured and the results are shown in Table II. From these data α values were calculated by the same procedure as in the polystyrene under the assumption that the equations (1) and (5) can also be applied. These values are shown in Table II as α_m and α_d respectively.

TABLE II

HEAT OF DILUTION OF MONOMER-UNIT (ETHYLBENZENE) SOLUTION

	Before dilution		After dilution		Heat evolved	$-\alpha_m$	$-\alpha_d$
	V cc.	v_r	V' cc.	v_r'			
1. Ethylbenzene-toluene system.							
1	5	1.000	10	0.500	0.206	0.08	
	10	0.500	15	0.333	0.098	0.09	0.20
	15	0.333	20	0.250	0.070	0.10	0.17
2	3	1.000	6	0.500	0.124	0.08	
	6	0.500	9	0.333	0.074	0.10	0.15
2. Ethylbenzene-chloroform system.							
	2	1.000	4	0.500	5.619	5.62	
	4	0.500	6	0.333	2.030	5.74	6.09
	6	0.333	8	0.250	1.135	5.86	6.81
	8	0.250	10	0.200	0.653	5.90	6.53
	10	0.200	12	0.167	0.243	5.81	3.65
	12	0.167	17	0.116	0.343	5.68	3.47

It is interesting that the interaction parameters between polymer and solvents have the same signs as those between monomer unit of polymer (ethylbenzene) and that the polymer-monomer unit system is athermal. That the polymermonomer unit system is athermal was confirmed by Meares[7] in the polyvinylacetateethylacetate system.

It is expected that α or μ for the polymer-solvent system is smaller in magnitude than that for the monomer unit-solvent system owing to the self-contact between polymer segments. But for the polystyrene-toluene system the reverse was observed. From this fact it is expected that there are some anomalous phenomena which might be explained by measuring the volume change or the changes of other physical properties on mixing for this system.

TABLE III

COMPARISON WITH THE DATA OBTAINED BY VARIOUS METHOD

1. Polystyrene-toluene system.

Observer	Method	$-\mu$	Temperature °C	Volume fraction	D.P.
Tompa[8]	a	0.10–0.17	25	0.25–0.40	17–30
Bawn et al[3]	b	0–0.01	25–55	0.003–0.009	$(1.5-3)\times10^3$
Doty et al[4]	b	0.17–0.04	27–69	0.01–0.08	540
Schulz[10]	b	0.09–0.05	15–40	0.01–0.03	90
Schulz et al[11]	b	0.03–0.04	20–42	0.03	$(2.3-5.8)\times10^3$
This experiment	a	0.24–0.27	25	0.04–0.19	275
2. Polystyrene-chloroform system.					
Bawn et al[3]	b	0	25–55	0.2–0.6	$(1.5-3)\times10^3$
Schulz et al[11]	b	0.02	20–42	0.03	$(2.3-5.8)\times10^3$
This experiment	a	0.14–0.17	25	0.05–0.27	275

Method a: Direct measurement.
b: From the temperature dependence of osmotic pressure or vapor pressure.

Our results are compared with the previous data obtained by various methods, and shown in Table III. For the chloroform-polystyrene system, it is found that the μ value is negative and large. This is consistent with the fact that chloroform is a good solvent for polystyrene. That the μ value obtained by Bawn and Wajid[5] from the temperature dependence of vapor pressure was zero, is in marked contrast to our result.

A direct measurement of heat of dilution for the toluene-polystyrene system was carried out by Tompa[8]. His value was the same in sign but different in magnitude. The degree of polymerization of the sample used by him was from 17 to 30, but our sample had a degree of polymerization of about 275. From the μ values obtained for various samples of different polymerization degree, ($\mu = -0.27$ for D.P. = 275, -0.17 for 17 to 30, -0.03 for 1) it seems that an apparent correlation exists between the μ value and the polymerization degree. But for a definite conclusion, further investigation will be needed.

Summary

A calorimeter equipped with a thermister capable of measuring the temperature change down to 0.5×10^{-4}°C was constructed. By this apparatus the heats of dilution of three polystyrene solutions were measured and the values of interaction parameters were derived. The μ values for toluene solution and chloroform solution were both negative and large, but that for ethylbenzene solution was zero.

In order to compare with the polymer solution, the heat of mixing of ethylbenzene, which may be regarded as the monomer-unit of polystyrene, with same solvents were also measured and it was found that the interaction parameters of polymer solutions have the same signs as that of the corresponding monomer-unit solutions.

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[11] G. V. Schulz und H. Hellfritz, *Z. Elektrochem.*, 57, 835 (1953).