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Thermodynamic Properties of Solutions of *m*-Terphenyl in Benzene. I. The Vapor Pressures and the Related Thermodynamic Functions at 30 and 50°C[*1]

Sadao TAKAGI, the late Katsuya FURUKAWA and Ryoichi FUJISHIRO

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

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Vapor pressures of solutions of *m*-terphenyl in benzene were measured for the concentration less than 0.23 in mole fraction x of terphenyl at 30 and 50°C. Vapor pressures P mmHg obtained are represented by $\log_{10} P(30°)=2.076970-0.4343x-0.06569x^2-0.4340x^3$ and $\log_{10}$-$P(50°)=2.432100-0.4343x-0.14654x^2-0.3412x^3$. Chemical potentials observed were reproduced by the quasi-lattice theory for mixtures of molecules of different sizes. The Miller-Guggenheim expression ($r=3$, $z=6$—8) gives $w/\boldsymbol{k}=100\pm5°$, and the Flory-Huggins expression (r=molecular volume ratio) gives $\chi=0.272\pm0.004$ (30°) and $\chi=0.243\pm0.006$(50°). Partial molar heats of mixing are rather fitted by the regular solution theory similarly to the case for benzene+biphenyl, and the Flory-Huggins expression gives a concentration-dependent enthalpy parameter, $\chi_{\mathrm{H}}=(0.77_2+1.7_{16}\phi)\times10^2/T$, where ϕ means a volume fraction of terphenyl. The average value of χ_{H}, 0.39 agreed with a theoretical estimate from solubility parameters.

It is well known that the thermodynamic study of the monomer+oligomer solutions is quite significant for the investigation of the molecular size effect in the solutions of small molecules as well as in the polymer solutions. In these monomer+oligomer mixtures, the monomer+dimer mixtures have been thermodynamically studied by many authors. Of those the benzene+biphenyl system has been most extensively studied, and has shown that the results of both vapor-pressure and heat of dilution measurements behave like those predicted for mixtures of molecules of different sizes.1-6) Kortüm, *et al.* have shown, however, that the heats of mixing over the whole range of compositions at 71.6°C can not be fitted by the quasi-lattice model7) for mixtures of molecules of different sizes but can only be fitted using the model for mixtures of molecules of the same size, and that the experimental values of the excess partial molar entropy of mixing are strongly temperature-dependent and cannot be fitted by the formulae for athermal mixtures of molecules of

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[*1] Presented at the 15th Annual Meeting of the Society of Polymer Science, Japan, Nagoya, May, 1966, and the preliminary work was presented at the 14th Annual Meeting, Tokyo, May, 1965.

1) J. H. Baxendale, B. V. Enüstün and J. Stern, *Phil. Trans. Roy. Soc.*, **A243**, 169 (1951).

2) D. H. Everett and M. F. Penney, *Proc. Roy. Soc. (London)*, **A212**, 164 (1952).

3) D. H. Everett and M. L. McGlashan, Published in Ref. 1, p. 234.

4) a) H. Tompa, *J. Chem. Phys.*, **16**, 292 (1948); b) "Polymer Solutions," Butterworths Scientific Publications, London (1956), p. 127.

5) A. Bellemans and C. Colin-Naar, *J. Polymer Sci.*, **15**, 121 (1955).

6) I. Prigogine, "The Molecular Theory of Solutions," North-Holland Publishing Company, Amsterdam (1957), p. 368.

7) E. A. Guggenhiem, "Mixtures," Oxford at the Clarendon Press (1952).

different sizes.[8,9] In order to obtain further information about size effect, thermodynamic properties of benzene+terphenyl system were begun to measure.

Experimental

Materials. Commercial *m*-terphenyl (chemical grade, Tokyo Kasei Kogyo K. K.) was purified carefully by repeating fractional recrystallizations from the solutions first with trichlorobenzene and thereafter with ethanol.[10] The *m*-terphenyl obtained was further purified by chromatography on silica gel (for chromatography, E. Merck) with benzene as an elutant. Finally occluded benzene was removed by vacuum sublimation. Mp 86.5°C.*2 An ultraviolet absorption spectrum of the purified *m*-terphenyl in alcohol showed no trace of the isomeric impurities.

Benzene was purified by an ordinary method with concentrated sulfuric acid, and then fractionally distilled twice over phosphorus pentoxide through a 1-m column packed with helices of stainless steel. After having been passed through silica gel, benzene was fractionally distilled once again, and finally submitted to repeated fractional crystallization. The boiling point sample used was 80.1°C.

Apparatus. The measurements of vapor pressures were carried out by using a liquid-vapor equilibrium still of recirculation type which was appropriate for small sample size.*3 Auxiliary equipments for the control and measurement of pressure were essentially the same as those described by Scatchard *et al.*,[11] and dry nitrogen was used as confining gas. The heights of mercury in a precision manometer which was immersed in a water thermostat were read to 0.05 mm by means of a 1-m cathetometer. Equilibrium temperatures were measured with a Beckmann thermometer which was calibrated against a standard thermometer certified by National Research Laboratory of Metrology, Tokyo. The error in the temperature measurements was within 0.003°C relatively, and within 0.03°C absolutely.

Procedures. The vapor pressures of the *m*-terphenyl solutions were measured over the concentration range less than 0.23 in mole fraction of terphenyl at 30 and 50°C. After about three or four hour's recirculation, both the equilibrium pressure and temperature were measured thrice. In order to obtain the equilibrium pressure at the precisely definite temperature as a function of composition, the interpolation of the points of three sets of measurements were carried out. The interpolation was made by first plotting the values of $\log P$ against reciprocals of temperature, and next reading a value from the smoothed curve at a desired temperature. This procedure is illustrated in Fig. 1. As the differences in temperatures were very small, each equilibrium composition was thought to be unchanged. An equilibrium liquid sample was withdrawn into a weighing bottle from the liquid trap of the still. The weight of this solution and that of *m*-terphenyl crystal which was produced by slow evaporation*4 of benzene from this solution were measured. The composition of the solution was determined by these weights. In the range of dilute concentration, *i. e.*, less than 0.1 in mole fraction, the composition was also determined by the measurement

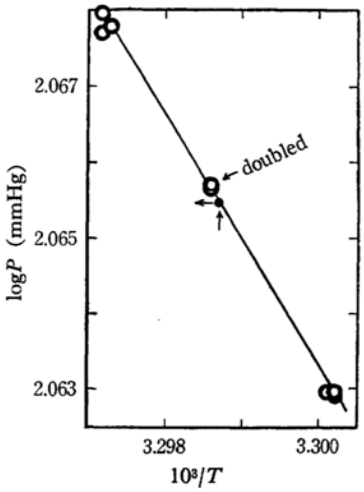

Fig. 1. Example of the determination of vapor pressure at 30.0°C. (x=0.0249)

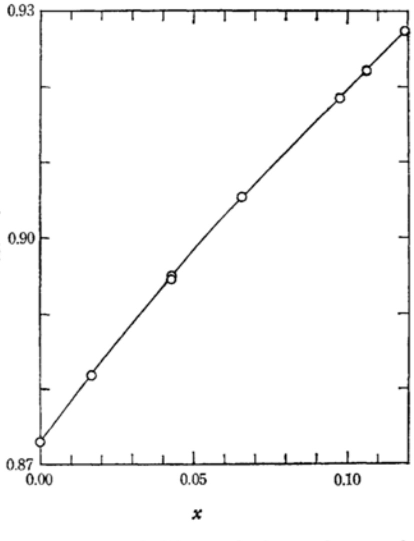

Fig. 2. Densities of dilute solutions of *m*-terphenyl in benzene at 25°C.

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[8] G. Kortüm, G. Dreesen and H.-J. Freier, *Z. Naturforsch.*, **8a**, 546 (1953).

[9] D. S. Adcock and M. L. McGlashan, *Proc. Roy. Soc. (London)*, **A226**, 266 (1954).

[10] S. Kato and H. Hashimoto, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **61**, 1265 (1958).

*2 The melting point was determined by the capillary method by us and was also kindly measured by Mr. M. Matsumoto by using a Cobble Automatic Thermoanalyzer, Type 201. Both results agreed each other.

*3 A detailed description of the design and the method of operation of the still will be published in this Bulletin in near future.

[11] G. Scatchard, C. L. Raymond and H. H. Gilmann, *J. Am. Chem. Soc.*, **60**, 1275 (1938).

*4 Evaporation of benzene from the solution was carefully carried out in a hot atmosphere at the temperature not higher than 55°C.

of the density with the aid of a calibration curve shown in Fig. 2. The values of the composition obtained by both methods agreed within the experimental error.

Experimental Results

The values of vapor pressures obtained are summarized in Table 1 where P is in standard mm of mercury and x is the mole fraction of terphenyl in the solution. The vapor pressure of pure *m*-terphenyl melt has been measured by Mandel *et al.*[12] in the high temperature range. These data are represented by the following expression[*5]

$$\log_{10}P(\text{mmHg}) = 7.68211 - 2814.37/(207.79 + t) \tag{1}$$

where t is temperature expressed in degree Celcius. By assuming that this expression holds at temperature below the melting point, the values of the vapor pressure of the super-cooled pure *m*-terphenyl melt at 30 and 50°C are estimated to be 7.0×10^{-5} and 5.8×10^{-4} mmHg, respectively. The partial pressures of terphenyl in the solutions investigated were thus quite negligible, compared with the values of the vapor pressures of benzene over the solutions.[*5]

TABLE 1. COMPOSITIONS OF LIQUID PHASE, EQUILIBRIUM VAPOR PRESSURES, AND DEVIATIONS FROM THE LEAST-SQUARES CALCULATION AT 30 and 50°C

(A) AT 30°C

x	P mmHg	$P-P_{\text{calc}}$ mmHg
0.000_0	119.3_9	—
0.002_6	119.0_9	$+0.0_1$
0.024_9	116.2_7	-0.1_8
0.033_6	115.2_9	-0.1_3
0.042_1	114.3_3	-0.1_0
0.047_3	113.8_4	$+0.0_1$
0.074_4	110.4_3	-0.2_7
0.100_1	107.7_0	-0.0_4
0.122_4	104.9_8	-0.2_2
0.132_8	103.8_3	-0.1_9
0.140_5	103.4_4	$+0.3_1$
0.148_3	102.2_9	$+0.0_3$
0.155_8	101.5_0	$+0.0_9$
0.193_6	97.6_1	$+0.5_2$
0.205_6	95.3_6	-0.3_9
0.216_4	94.4_6	-0.0_6

(B) AT 50°C

x	P mmHg	$P-P_{\text{calc}}$ mmHg
0.000_0	270.4_6	—
0.018_7	265.4_4	$+0.0_2$
0.046_1	257.9_2	-0.1_5
0.082_0	248.6_3	$+0.1_4$
0.108_1	241.3_1	-0.2_4
0.132_6	235.3_2	$+0.2_8$
0.140_0	233.0_7	0.0_0
0.188_6	219.9_3	-0.2_0
0.205_6	215.6_8	$+0.0_8$
0.226_5	210.0_4	$+0.0_2$

Usually, for a solution composed of a solvent and a non-volatile solute whose molecular sizes are not so different each other, the vapor pressure of the solvent can be expressed as

$$P=P^\circ(1-x)\exp(\alpha x^2+\beta x^3+\cdots)$$

or

$$\log_{10}P = \log_{10}P^\circ - 0.4343x + cx^2 + dx^3 + \cdots \tag{2}$$

where x is the mole fraction of the solute, P° the vapor pressure of the pure solvent at the same temperature with the solution, and $\alpha, \beta, \cdots$, or $c, d, \cdots$, adjustable parameters. A least-squares treatment of our data according to Eq. (2), neglecting higher terms than the fourth power of x, gave

TABLE 2. VALUES OF THE SECOND VIRIAL COEFFICIENTS OF BENZENE, MOLAR VOLUMES OF THE LIQUIDS, AND VOLUME RATIO OF THE COMPONENTS

t °C	B [a] cm^{3}mol^{-1}	V_1° [b] m*l* mol^{-1}	V_2° [c] m*l* mol^{-1}	$r=V_2^\circ/V_1^\circ$
25	—	89.44	213.94	2.39_2
30	−1366	89.99	214.35	2.38_2
40	—	91.12	215.26	2.36_2
50	−1194	92.28	215.17	3.33_2

a Calculated with the expression:
$B=70-13.2\times10^7/T^2$[cm^{3}mol^{-1}].[13]

b Molar volume of benzene:
calculated with Eq. (5).[14]

c Molar volume of super-cooled *m*-terphenyl; estimated from the data reported by Opdycke *et al.*[15] by extrapolation below the melting point.

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[12] H. Mandel, F. Silvey and K. Koda, *U. S. At. Energy Comm.*, **NAA-SR-5128**, 25 (1964).

[*5] Constants in Eq. (1) were determined by a least-squares analysis of the smoothed values reported.[12] A plot of $\log P$ *vs.* $1/T$ showed significant deviation of lowest two values from others, so that these two values were omitted. If all values were used, Eq. (1) would be replaced by

$$\log_{10}P = 8.42379 - 3908.11/(326.8 + t),$$

from which the vapor pressures at 30 and 50°C were computed at 0.003 and 0.011 mmHg, respectively. We can safely regard the observed pressures over the dilute solutions as the vapor pressures of benzene.

[13] P. W. Allen, D. H. Everett and M. F. Penney, *Proc. Roy. Soc. (London)*, **A212**, 149 (1952).

[14] "International Critical Tables," Vol. 3, p. 29 (1928).

[15] J. Opdycke, J. P. Dawson, R. K. Clark, M. Dutton, J. J. Ewing and H. H. Schmidt, *J. Phys. Chem.*, **68**, 2385 (1964).

TABLE 3. SMOOTHED VALUES OF VAPOR PRESSURE P, EXCESS CHEMICAL POTENTIAL DIVIDED BY $\boldsymbol{R}T$, $\log_{10}\gamma_1=\mu_1{}^{\mathrm{E}}/2.3026\boldsymbol{R}T$, PARTIAL MOLAR EXCESS ENTROPY $\overline{S}_1{}^{\mathrm{E}}$, AND PARTIAL MOLAR EXCESS HEAT $\overline{H}_1{}^{\mathrm{E}}$ OF BENZENE IN SOLUTION AT 30 AND 50°C

x	30°C			30—50°C	50°C		
	P mmHg	$10^5 \log\gamma_1$	$\overline{S}_1{}^{\mathrm{E}}$ e. u.	$\overline{H}_1{}^{\mathrm{E}}$ cal/mol	P mmHg	$10^5 \log\gamma_1$	$\overline{S}_1{}^{\mathrm{E}}$ e. u.
0.06	112.3_5	$73._4$	0.009_6	$3._9$	254.3_5	55.8	0.009_7
0.09	108.9_0	137.7	0.013_9	6.1	246.3_6	110.4	0.014_0
0.12	105.4_8	217.3	0.033_1	$13._0$	238.3_9	159.1	0.033_1
0.15	102.0_7	307.2	0.058_0	$21._8$	230.4_1	$209._7$	0.058_0
0.18	98.6_6	$404._7$	0.088_2	$32._3$	222.4_3	$260._4$	0.088_2
0.21	95.2_5	$506._4$	0.12_2	$44._0$	214.4_2	$310._1$	0.12_2

TABLE 4. $\log_{10}\gamma_1$ FOR THE MIXTURES AND TERMS WHICH MAKE UP $\log_{10}\gamma_1$ AT 30 AND 50°C

x	$\log_{10}\dfrac{P}{P^\circ(1-x)}$	$-\dfrac{B(P^\circ-P)}{2.3026\boldsymbol{R}T}$	$\dfrac{V_1{}^\circ(P^\circ-P)}{2.3026\boldsymbol{R}T}$	$\log_{10}\gamma_1$
	30°C			
0.06	0.0004987_3	0.00022_1	0.0000145_5	0.00073_4
0.09	0.001026_3	0.000329_1	0.0000216_8	0.001377_1
0.12	0.001707_8	0.000436_6	0.0000287_6	0.002173_1
0.15	0.002492_2	0.000543_6	0.0000358_1	0.003071_7
0.18	0.00335_4	0.000650_5	0.0000428_5	0.00404_8
0.21	0.00425_7	0.000757_6	0.0000499_0	0.00506_4
	50°C			
0.06	0.0001118_9	0.000414_3	0.0000320_3	0.000558_3
0.09	0.0004358_2	0.000619_9	0.0000479_2	0.001103_7
0.12	0.0007021_2	0.000825_2	0.0000637_2	0.001591_1
0.15	0.0009869_0	0.00103_0	0.0000796_5	0.00209_7
0.18	0.001272_8	0.00123_6	0.0000955_3	0.00260_4
0.21	0.001548_1	0.00144_2	0.000111_5	0.00310_1

$$\log_{10}P = 2.076970 - 0.4343x - 0.06569x^2 - 0.4340x^3 \text{ at } 30^\circ\mathrm{C}$$

and

$$\log_{10}P = 2.432100 - 0.4343x - 0.14654x^2 - 0.3412x^3 \text{ at } 50^\circ\mathrm{C} \tag{3}$$

The calculated values of vapor pressure by using Eq. (3) are seen to be in good agreement with the observed ones, as shown in the last column of Table 1, suggesting that Eqs. (3) are adequate expressions for representing the vapor pressure of the benzene solutions of *m*-terphenyl at both temperatures.

Then the activity coefficients of the solvent were obtained at every 3 mol per cent for each temperature by making use of Eq. (3) and the following equation including the correction due to the gas imperfection,

$$\log_{10}\gamma_1 = \log_{10}\frac{P}{P^\circ(1-x)} - \frac{B(P^\circ-P)}{2.3026\boldsymbol{R}T} + \frac{V_1{}^\circ(P^\circ-P)}{2.3026\boldsymbol{R}T} \tag{4}$$

where B is the second virial coefficient of pure benzene in the gaseous state and $V_1{}^\circ$ the molar volume of pure benzene. Values used for B's are evaluated from the expression given by Allen *et al.*,[13] which are tabulated in Table 2 as well as the values of $V_1{}^\circ$ used. The molar volume of benzene at t°C are calculated from the density,[14]

$$d = 0.90005 - 1.0636\times10^{-3}t - 0.0376\times10^{-6}t^2 - 2.213\times10^{-9}t^3, \quad (\pm2\times10^{-4}). \tag{5}$$

Numerical values of $\log_{10}\gamma_1$ thus obtained are listed in Table 3. The deviations from the ideal solutions are positive. The relative contribution of each of the terms in Eq. (4) to the total $\log_{10}\gamma_1$ is illustrated in Table 4 which shows the importance of the term involving the second virial coefficient B.

From $\log_{10}\gamma_1$'s, the excess partial molar enthalpy and entropy of benzene are derived by the following thermodynamic relationships;

$$\overline{H}_1^{\mathrm{E}} = \partial(\overline{G}_1{}^{\mathrm{E}}/T)/\partial(1/T) = 2.3026\boldsymbol{R}[\Delta\log_{10}\gamma_1/\Delta(1/T)] \tag{6}$$

$$\bar{S}_1{}^{E} = \bar{H}_1{}^{E}/T - 2.3026\boldsymbol{R}\log_{10}\gamma_1 \tag{7}$$

and are also summarized in Table 3.

Discussion

For a solution which consists of N_1 monomers and N_2 r-mers, Guggenheim[16] has derived the theoretical formula, according to which the activity coefficient of solvent (monomer) is written in the zeroth approximation as follows:

$$\begin{aligned}\log_{10}\gamma_1 = &-\log_{10}(1-x) + \log_{10}[N_1/(N_1+rN_2)] \\ &+ (z/2)\log_{10}[(N_1+rN_2)/(N_1+qN_2)] \\ &+ (1/2.3026)[qN_2/(N_1+qN_2)]^2 w/\boldsymbol{k}T \end{aligned} \tag{8}$$

where z is the co-ordination number, $zq(=rz-2r+2)$ is the number of the nearest neighbor contacts around a r-mer molecule, w is the free energy parameter of interaction between monomer and r-mer molecules, and $\boldsymbol{k}$ is the Boltzmann constant. Assuming that terphenyl is a trimer of benzene ($r=3$), and z lies between 6 and 8,*6 one can calculate the values of $w/\boldsymbol{k}$ by substitution of the observed values of $\log_{10}\gamma_1$ into the Miller-Guggenheim expression, Eq. (8), as shown in Table 5.

TABLE 5. VALUES OF INTERACTION PARAMETER OBTAINED WITH THE ZEROTH APPROXIMATION OF GUGGENHEIM

x	$10^{-2}w/\boldsymbol{k}$, [deg^{-1}]			
	$z=8$		$z=6$	
	30°C	50°C	30°C	50°C
0.06	1.0_3	1.03	0.97	0.96
0.09	1.02	1.03	0.98	0.99
0.12	1.02	1.02	0.99	0.98
0.15	1.03	1.02	1.00	0.98
0.18	1.04	1.02	1.01	0.99
0.21	1.05	1.02	1.02	0.99

The constancy in the values of $w/\boldsymbol{k}$ irrespective of the mole fraction of terphenyl in the solution seems to suggest that Eq. (8) is adequate to the system such as benzene+m-terphenyl solution. The constant value of about 100° for $w/\boldsymbol{k}$ may be reasonable, compared with 76° or 77° found for the benzene solution of biphenyl which is regarded as a dimer ($z=6$).[3,4b)]

It is well known that the Miller-Guggenheim formula becomes the Flory-Huggins expression when the co-ordination number z reaches infinity. The Flory-Huggins expression for activity coefficient of a solvent (monomer) is

$$\begin{aligned}\log_{10}\gamma_1 = &\log_{10}[(1-\phi)/(1-x)] \\ &+ (1/2.3026)(1-1/r) + (1/2.3026)\chi\phi^2\end{aligned} \tag{9}$$

where ϕ is the volume fraction of solute (r-mer), r the volume ratio of r-mer to monomer, and χ the free energy parameter of interaction between solvent and solute. By using Eq. (9), the free energy parameters χ were evaluated and values obtained are summarized in Table 6 where the corresponding value for the case of benzene+biphenyl is cited from the literature for comparison, and are plotted in Fig. 3. The numerical values of volume ratios r used are shown in Table 2. Figure 3 shows a slight tendency of the concentration-dependence of the parameters, which decrease with the volume fraction of terphenyl at 50°C and increase with the concentration at 30°C. The reasons for these behaviors, however, have not been discussed here, because there is no information about the excess volumes at those temperatures. The average values of χ at 30 and 50°C, $\chi=0.272_3$ and 0.243_1, correspond to $w/\boldsymbol{k}=83$ and 79°, respectively when r is chosen to be the volume ratio. The corresponding value for benzene+biphenyl mixture is $w/\boldsymbol{k}=63°$. Figure 4 shows that the Flory-Huggins expression, as well as the Miller-Guggenheim expression, represents the experimental values of free energy of mixing.

TABLE 6. FLORY-HUGGINS FREE-ENERGY AND ENTHALPY PARAMETERS

Benzene + m-Terphenyl mixture				
x	χ		χ_H	
	30°C	50°C	30°C	50°C
0.06	0.274_5	0.248_3	0.38	0.37
0.09	0.269_1	0.248_7	0.28	0.27
0.12	0.269_3	0.242_9	0.36	0.35
0.15	0.271_2	0.240_7	0.41	0.40
0.18	0.273_7	0.240_1	0.46	0.44
0.21	0.276_3	0.237_7	0.49	0.47
mean	0.272_3	0.243_1	0.40	0.38
Benzene + Biphenyl mixture[a]				
$\chi(65°\text{C})=0.185$,		$\chi_H(25°\text{C})=0.194$ $\chi_H(50°\text{C})=0.158$		

[a] Cited from Ref. 4b.

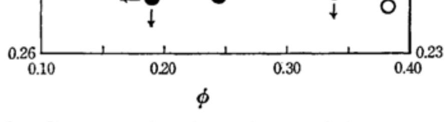

Fig. 3. Concentration-dependence of free energy parameters at 30°C (filled circles) and 50°C (open circles).

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16) E. A. Guggenheim, "Mixtures," *l. c.*,[7)] Chapt. XI.

*6 For the sake of comparison with the case of benzene+biphenyl, 6 and 8 are used as z after Everett and McGlashan.[8)] If $z=10$ are used, a little larger values of $w/\boldsymbol{k}$ will be obtained.

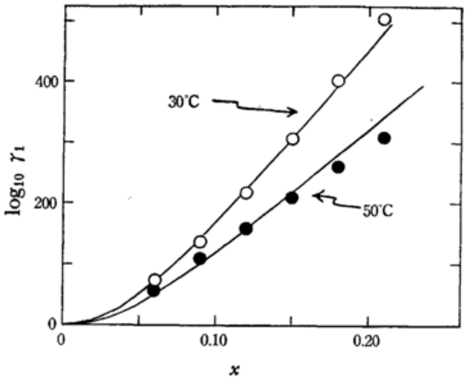

Fig. 4. $\log_{10}\gamma_1$ as a function of x.
○ or ● Experimental
—— Thpeoretical curves calculated by the Flory-Huggins expression by using $\chi = 0.272_3$ (at 30°C) and 0.243_1 (at 50°C).

The enthalpy parameter χ_H calculated through Eq. (10) at each temperature are also given in

$$\chi_H = H_1{}^E/\boldsymbol{R}T\phi^2 \tag{10}$$

Table 6. Their composition dependence at 30 and 50°C is given as a linear function of the volume fraction of terphenyl, Eq. (11), by a least-squares calculation.

$$10^{-2}T\chi_H = 0.77_2 + 1.7_{16}\phi \tag{11}$$

In the case of benzene+biphenyl mixtures heat of dilution measured are compatible to both the quasi-lattice theory for mixtures of molecules of different sizes and the regular solution theory with the same degree of accuracy within the experimental error,[4b,9)] and the heat of mixing of benzene and molten biphenyl can not be expressed by other than the regular solution theory.[8)] In our case of *m*-terphenyl also the regular solution theory can reproduce the partial molar heats of mixing of benzene as shown in Fig. 5. Figure 6 shows the systematic deviation of the experimental points from the Flory-Huggins equation. If the Flory-Huggins equation holds, the experimental points would lie on a straight line through the origin. The quasi-lattice theory which contains the molecular size effect reproduces the experimental values only when the composition dependence of the parameter χ_H is considered. The average value of the parameter is $\chi_H=0.39$ (at 40°) which corresponds to $zu/\boldsymbol{k}=122°$ and $\boldsymbol{N}zu=242._7$ cal/mol, on the other hand those reported[4b)] for benzene+biphenyl mixture are $zu/\boldsymbol{k}=58°$ and $\boldsymbol{N}zu=114._9$ cal/mol at 25°C and $zu/\boldsymbol{k}=51°$ and $\boldsymbol{N}zu=101._5$ cal/mol at 50°C.

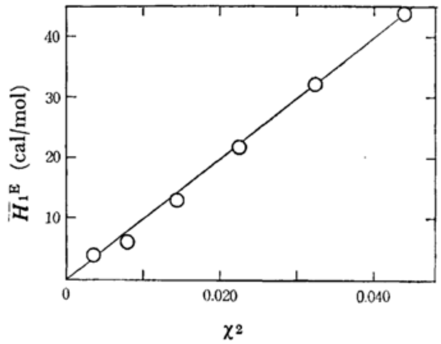

Fig. 5. Regular solution plot of the partial molar heat of mixing of benzene at 40°C.
○ Experimental

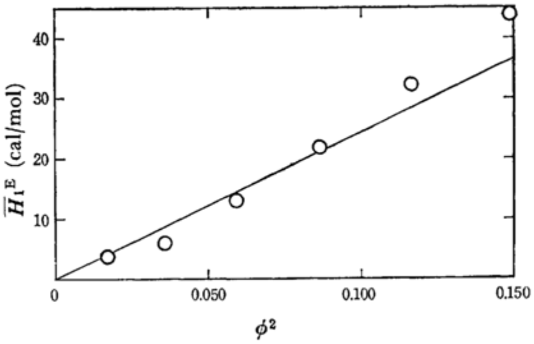

Fig. 6. Flory-Huggins plot of the partial molar heat of mixing of benzene at 40°C.
○ Experimental
—— $\boldsymbol{R}T\chi_H\phi^2$ when $\chi_H=0.39$.

The χ_H parameter can be estimated by using Eq. (12) based on the zeroth approximation of mixtures of molecules of different sizes,

$$\chi_H = (\overline{V}_1/\boldsymbol{R}T)(\delta_1 - \delta_2)^2 \tag{12}$$

where $\overline{V}_1$ is the partial molar volume of benzene and δ's are the solubility parameters which are defined by

$$\delta^2 = (\varDelta H^V - \boldsymbol{R}T)/V \tag{13}$$

$$= n^{-1}(\partial E/\partial V)_T \tag{14}$$

where $\varDelta H^V$ is the heat of vaporization, V the molar volume, $(\partial E/\partial V)_T$ the internal pressure, and n the parameter which is slightly greater than 1.0 for non-polar liquids.[17)] The internal pressure can be computed directly from the thermal pressure coefficient or from the coefficient of expansion α and the isothermal compressibility β_T. The external pressure P is negligibly small, compared to the thermal pressure term in a condensed phase under atmospheric pressure.

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P$$
$$\simeq T(\partial P/\partial T)_V = T(\alpha/\beta_T) = T\gamma \tag{15}$$

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17) J. H. Hildebrand and R. L. Scott, "The Solubility of Noneletrolytes," 3rd Edition, Dover Publications, Inc., New York, N. Y. (1964), p. 97.

Since there is the experimental evidence of constancy of the quantity $TV^2\gamma$ over a range of temperature,[18-20] once it is known at an appropriate temperature it is possible to deduce the internal pressure at any desired temperature by using only the knowledge of the molar volume at that temperature.

The internal pressures of benzene were calculated from the data given by Stavely *et al.*[18] The comparison with the cohesive energy density[21] gave 1.06 as a numerical value of n at 25°C which agreed very well with the value obtained at 20°C ($n=1.06$).[22] Thus, $n=1.06$ has been used for both components at 30 and 50°C. The internal pressures of *m*-terphenyl were estimated from the solubility parameter at 90°C given by Clark and Schmidt,[23] under the assumption that $TV^2\gamma$ is constant over the range of temperature. The solubility parameters obtained are given in Table 7. The values of χ_H calculated through Eq. (12) are 0.3_9 and 0.3_2 at 50 and 30°C, respectively, on the assumption that the partial molar volume of benzene is approximately equal to the molar volume in pure state, $V_1°$. Taking account of the assumptions made in the calculation, agreement between the values of χ_H obtained by the experiment and those calculated by using Eq. (12) is satisfactory as shown in Table 7. After the present measurements had been completed, the studies of this system by gas-liquid partition chromatography were presented by Clark and Schmidt.[23] They reported that the heat of solution at infinite dilution for benzene in *m*-terphenyl ($x\to1$) at 90°C is 180±50 cal/mol. It corresponds to 0.25±0.07 as χ_H which is consistent with the present experimental values obtained at 50 and 30°C.

TABLE 7. PREDICTION OF χ_H FROM THE SOLUBILITY PARAMETERS

t °C	δ_1	δ_2	χ_H Eq. (12)	Expt.
50	8.8_5	10.5_0	0.3_9	0.38
30	9.0_8	10.5_4	0.3_2	0.40

The partial molar excess entropies of mixing of benzene are described by the Flory-Huggins formula as follows,

$$\overline{S}_1{}^E = \overline{S}_1{}^E(\mathrm{I}) + \overline{S}_1{}^E(\mathrm{II}) \tag{16}$$

$$\overline{S}_1{}^E(\mathrm{I}) = -\boldsymbol{R}\{\ln[(1-\phi)/(1-x)] + (1-1/r)\phi\} \tag{17}$$

$$\overline{S}_1{}^E(\mathrm{II}) = -\boldsymbol{R}\chi_S\phi^2 \tag{18}$$

where $\chi_S=\chi-\chi_H$. In Fig. 7 the experimental partial molar excess entropies and the athermal contributions for those, given by Eq. (17), are plotted against the volume fraction of terphenyl, where the curves have been drawn by hand through the origin of the co-ordinate. Figure 7 shows that the contribution for the excess entropy from the non-athermal term, Eq. (18), seems to be significant,[*7] although the detailed studies on the physical meanings of the χ_S must be postponed until the excess volumes and compressibilities at the temperatures where present experiments were undertaken become available.

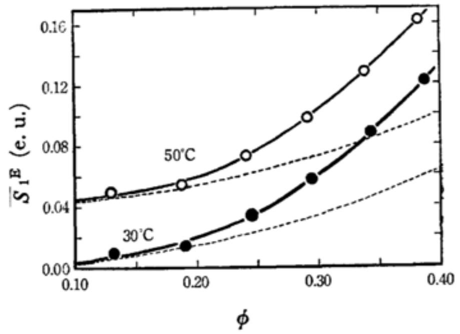

Fig. 7. Excess partial molar entropies of benzene (plots for 50°C is shifted upwards by 0.04 in e. u.).

——: $\overline{S}_1{}^E$, Experimental

- - -: $\overline{S}_1{}^E(\mathrm{I})$, Calculated

Since calculations of the excess thermodynamic functions in terms of the average potential, corresponding states theory of polymer mixtures extended by Prigogine implicitly, include the effects of volume changes on mixing,[24] the experimental results have been compared with the predictions by this theory. Explicit expression derived for excess Gibbs energy of mixing at vanishing pressure agreed with that given by Clark *et al.*[23] In this case, however, it was not able to predict the thermodynamic properties obtained by the measurements.

Finally we conclude that the thermodynamic behavior of benzene+*m*-terphenyl solution is similar to that of benzene+biphenyl solution.

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[18] L. A. K. Staveley, W. I. Tupman and K. R. Hart, *Trans. Faraday Soc.*, **51**, 323 (1955).

[19] J. H. Hildebrand and J. M. Carter, *J. Am. Chem. Soc.*, **54**, 3592 (1932).

[20] W. Westwater, H. W. Frantz and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928).

[21] G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).

[22] G. Allen, G. Gee and G. J. Wilson, *Polymer*, **1**, 456 (1960).

[23] R. K. Clark and H. H. Schmidt, *J. Phys. Chem.*, **69**, 3682 (1965).

[*7] If we evaluate $\overline{S}_1{}^E(\mathrm{I})$ by using the Miller-Guggenheim formula, difference of $\overline{S}_1{}^E$ and $\overline{S}_1{}^E(\mathrm{I})$ becomes larger, because the Flory-Huggins formula ($z=\infty$) gives the largest athermal entropy of mixing.

[24] I. Prigogine, Chapt. XVII of Ref. 6.