

## The $P$ - $V$ - $T$ Relations of Poly(dimethylsiloxane) Solution in Benzene

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**ABSTRACT:** A new instrument for measuring accurate  $P$ - $V$ - $T$  relations of polymer solutions and liquid crystals and for observing their optical properties under pressure and microscope has been constructed. The  $P$ - $V$ - $T$  relations of a poly(dimethylsiloxane)-benzene system were measured in the range of 303.15–323.15 K and at a pressure up to 140 bar. The isothermal compressibilities ( $K_T$ ) and the thermal expansion coefficients ( $\alpha_p$ ) were determined from the  $P$ - $V$ - $T$  relations and then the composition dependence of  $K_T$  and  $\alpha_p$  was discussed. We determined that  $K_T$ -composition relations for this system were linear for each temperature within the experimental range and that the plots of  $\alpha_p$  against concentrations of poly(dimethylsiloxane) in benzene had a curvature with a positive deviation from linearity. The concentration dependence of the internal pressure,  $(\partial U/\partial V)_T$ , was also discussed.

**KEY WORDS** Polymer Solution / Poly(dimethylsiloxane) /  $P$ - $V$ - $T$  Relations /

In order to determine the thermodynamic properties of polymer solutions, it is important to obtain accurate thermodynamic derivatives of the system. Internal pressure, for example, gives information about the intermolecular forces of polymer solutions, and can be obtained by the isothermal compressibility ( $K_T$ ) and the thermal expansion coefficient ( $\alpha_p$ ).

Recently, a number of investigations have reported on the thermodynamic properties of poly(dimethylsiloxane) (PDMS); *i.e.*, the composition and temperature dependence of chemical potential at a constant pressure,<sup>1</sup> the second virial coefficients in several solvents up to 400 bar at various temperatures,<sup>2</sup> the internal pressures from 253.15 to 323.15 K,<sup>3</sup> the  $P$ - $V$ - $T$  relations in the range of 298.15 to 473.15 K up to 1 kbar,<sup>4</sup> and the calorimetric observation for solutions in many solvents.<sup>5</sup>

In this paper, we show a new instrument constructed for studying the accurate  $P$ - $V$ - $T$  relations of polymer solutions and measure the thermodynamic properties for a PDMS-benzene system in the range of 303.15 to 323.15 K up to 140 bar in order to determine the characteristics for this instrument. In addition, we discuss the concentration dependences

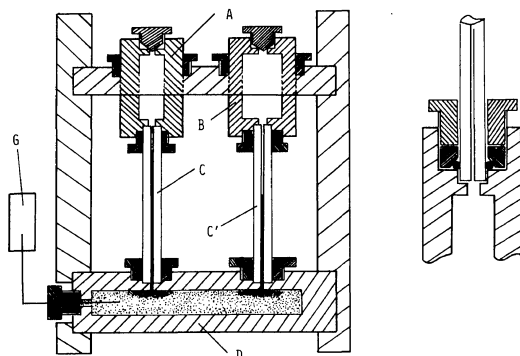
of  $K_T$ ,  $\alpha_p$  and the internal pressure,  $(\partial U/\partial V)_T$ , for this system. PDMS was chosen since it is a liquid polymer and has a large isothermal compressibility and thermal expansion coefficient.

### EXPERIMENTAL

#### *Apparatus and Procedure*

The instrument was constructed for observing optical properties under pressure by microscope. A detailed description of the apparatus is presented in Figure 1. A is a sample cell (about 2.7 cm<sup>3</sup>); B, a reference cell (about 1.5 cm<sup>3</sup>); D, a mercury container made of stainless steel; C and C', Pyrex glass capillary tubes of 1 mm (I.D.)  $\times$  8 mm (O.D.); and G, a pressure generator. Pyrex glass tubes were fitted to the cells A and B, and the mercury container D, as shown in Figure 1. The cells A and B were supported by a screw so as to get the best fit of the other end of Pyrex glass capillary tube with D, and then, D was fastened to a brass frame. All the O-rings were of Teflon, and were stored in benzene for about a week before use.

The inner diameter of capillary tube was calibrated by a usual weighing method, using the density and thermal expansion coefficient of mercury ob-



**Figure 1.** Apparatus for measurement of  $P$ - $V$ - $T$  relation of liquid: A, sample cell; B, reference cell; C and C', Pyrex capillary tube; D, mercury container; G, pressure generator.

tained from "International Critical Tables,"<sup>6</sup> and can be determined within an accuracy of 0.1%. The volumes of the cells A and B were determined by measuring the weight of mercury filled under vacuum ( $10^{-3}$  torr), and were determined with an accuracy of 0.3%. The volume change of a sample and the standard reference liquid were obtained from the displacement of the mercury meniscus in the capillary tubes C and C', and it was read as  $1 \times 10^{-4}$  cm<sup>3</sup>.

If the isothermal compressibility of the standard reference liquid is known, the pressure applied to the system can be calculated by

$$\Delta P = (-1/K_T)(\Delta V/V_0) = -\pi R^2 \Delta L / K_T V_0$$

where  $V_0$  is the initial volume of the standard reference liquid (benzene in this study);  $R$ , the inner radius of the capillary tube C';  $\Delta V$ , the volume change caused by the pressure change;  $\Delta L$ , the displacement length of the mercury meniscus in C'. The pressure for obtaining the isothermal compressibility of the standard reference liquid was determined by Heise-Gauge whose accuracy is 0.1% of the entire scale. Pressure was applied to cells A and B at a slow rate enough to allow the heat of compression to be dissipated, and was raised approximately 1 bar per minute for all experiments. The temperature was controlled within a range of  $2 \times 10^{-3}$ – $3 \times 10^{-3}$  K.  $K_T$  (about  $1 \times 10^{-4}$  bar<sup>-1</sup> for PDMS and benzene) was determined within an accuracy of about 2%. By using a cathetometer, the difference in pressure could be read to the order of 0.1 bar for the whole pressure range. The concentration of the solution was determined by weighing the solution and polymer after measurement.

### Material

The poly(dimethylsiloxane) was commercial KF96 Silicone ( $\eta = 6000$  cSt,  $M_v \sim 5.1 \times 10^4$ ) obtained from Shinetsu Chemical Co. Benzene was of reagent-grade and was further purified before use.

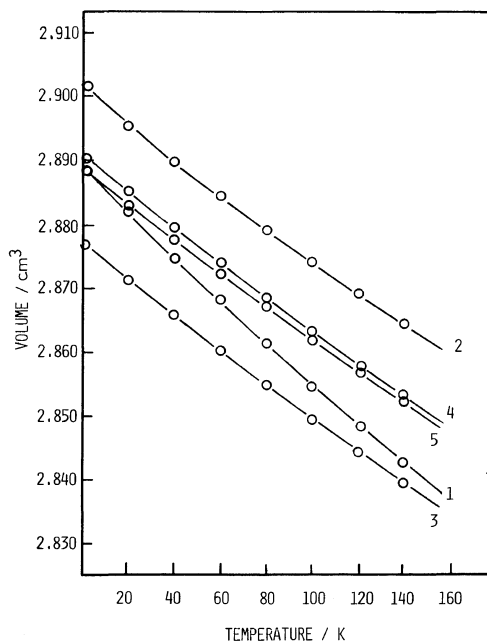
### RESULTS AND DISCUSSION

The empirical formulas of the  $P$ - $V$ - $T$  relations for the PDMS-benzene system were expressed in a polynomial equation, and then the isothermal compressibilities and the thermal expansion coefficients were obtained from this equation.

Pressure-volume relations for each composition at 303.55 K are plotted in Figure 2, and the isothermal compressibilities for this system are listed in Table I. The empirical formula of  $P$ - $V$  relation for PDMS and benzene were found as follows.

$$V = 2.8890 - 2.938 \times 10^{-4} P + 21.44 \times 10^{-8} P^2 \quad (\text{benzene}) \quad (1)$$

$$V = 2.8889 - 3.617 \times 10^{-4} P + 18.23 \times 10^{-8} P^2 \quad (\text{PDMS}) \quad (2)$$



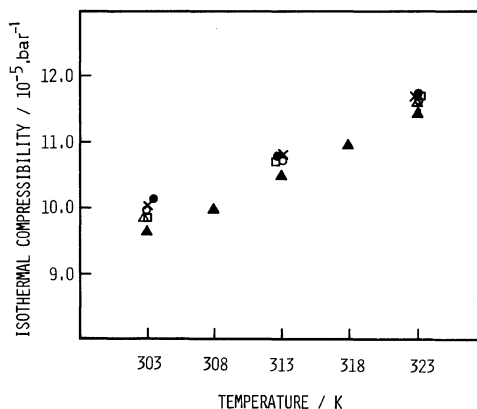
**Figure 2.** Pressure-volume relations of PDMS-benzene system at 303.15 K: 1, pure benzene; 2, 10.5 wt%; 3, 21.2 wt%; 4, 30.4 wt%; 5, pure PDMS. The same symbol is used in Figures 5, 6, and 8, 9.

**Table I.** The various thermodynamic functions at a given temperature for PDMS-benzene system

Sample <sup>a</sup>	Temp, K	$K_T$ $10^{-6} \text{ bar}^{-1}$	$\alpha_P$ $10^{-3} \text{ K}^{-1}$	$(\partial S/\partial V)_T$ $\text{bar K}^{-1}$	$(\partial U/\partial V)_T$ $\text{cal cm}^{-3}$
$\text{C}_6\text{H}_6$	303.55	101.5	1.229	12.1	87.7
	312.55	107.8	1.237	11.4	85.1
	318.15	112.3	1.242	11.0	83.6
	323.15	116.4	1.250	10.7	82.9
$X=10.5$	303.55	103.6	1.197	11.6	84.0
	312.55	110.3	1.213	11.0	82.1
	318.15	115.5	1.225	10.6	80.5
	323.15	120.5	1.236	10.2	79.1
$X=21.2$	303.55	105.4	1.174	11.1	80.5
	312.55	112.9	1.197	10.6	79.0
	318.15	117.7	1.207	10.3	78.2
	323.15	122.7	1.219	9.9	75.2
$X=30.4$	303.55	108.1	1.156	10.7	77.5
	312.55	116.6	1.174	10.0	75.2
	318.15	120.0	1.188	9.9	75.1
	323.15	126.2	1.205	9.5	74.2
PDMS	303.55	125.4	0.915	7.2	52.8
	312.55	134.0	0.919	6.8	51.1
	318.15	139.5	0.921	6.6	50.2
	323.15	145.6	0.925	6.3	50.0

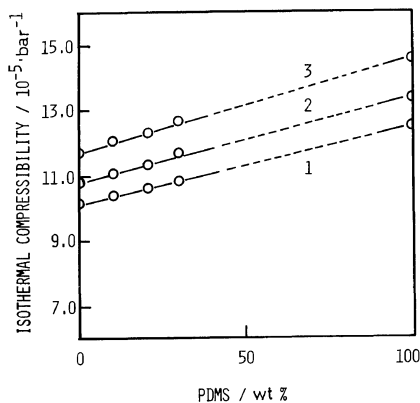
<sup>a</sup>  $X$  is the concentration (wt%) of PDMS in benzene.

The isothermal compressibilities for benzene reported by other workers<sup>7-11</sup> were compared with ours in Figure 3. The results obtained in this work agree well with those of others within error. The isothermal compressibility for PDMS in our study at 303.55 K under atmosphere is  $1.254 \times 10^{-4} \text{ bar}^{-1}$  and is in good agreement with Weessler's<sup>12</sup>  $1.22_1 \times 10^{-4} \text{ bar}^{-1}$  at 303.15 K (for low molecular weight about 3000) and Flory and Shih's<sup>1</sup>  $1.232 \times 10^{-4} \text{ bar}^{-1}$  at 303.15 K (for molecular weight of about  $10^5$ ). The isothermal compressibility is plotted as a function of the concentration of PDMS temperature is greater than that for benzene. This may be due to the fact that PDMS is more compressible than benzene since  $-\text{Si}(\text{CH}_3)_2-$  group in the molecular structure of PDMS retain a comparatively large space, and the  $-\text{Si}-\text{O}-$  chain is extremely flexible owing to the absence of substituents on the oxygen atom.<sup>13</sup> Beside,  $K_T$ -compression relations for the PDMS-benzene system are linear for each temperature within the experimental range.

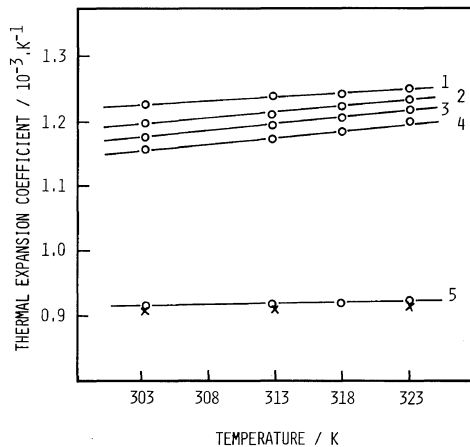


**Figure 3.** Comparison of the isothermal compressibility of benzene at  $P=1$  bar; ●, this work; ○, Tryer<sup>7</sup>; ×, Stavelly, Tupman, and Hart<sup>8</sup>; △, Freyer, Hubbard, and Andrews<sup>9</sup>; □, Holder and Whally<sup>10</sup>; ▲, Gibson.<sup>11</sup>

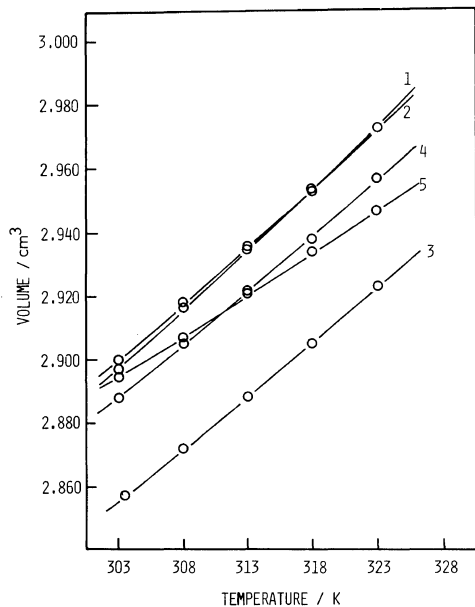
Temperature-volume relations under atmosphere were plotted in Figure 5. Thermal expansion



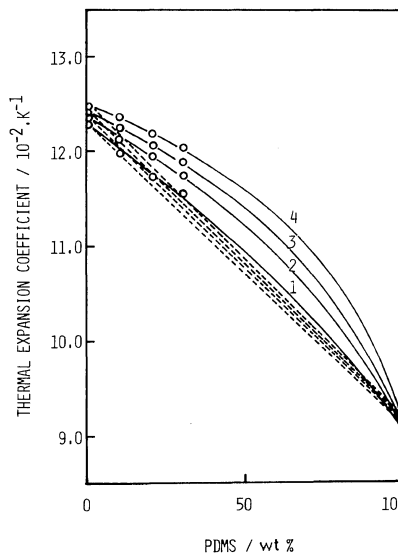
**Figure 4.** Plots of  $K_T$  for PDMS-benzene system at various temperatures and  $P=1$  bar against the concentrations of PDMS in benzene: 1, 303.55 K; 2, 312.55 K; 3, 323.15 K.



**Figure 6.** Thermal expansion coefficient-temperature relations of PDMS-benzene system under atmosphere.  $\times$ , Flory's results for PDMS.



**Figure 5.** Temperature volume relations of PDMS-benzene system under atmosphere.



**Figure 7.** Plots of  $\alpha_p$  for PDMS-benzene system at various temperatures and  $P=1$  bar against the concentrations of PDMS in benzene: 1, 303.55 K; 2, 312.55 K; 3, 318.15 K; 4, 323.15 K.

coefficients are listed in Table I, and are plotted as a function of temperature in Figure 6. The polynomial equations of the  $T$ - $V$  relation for PDMS and benzene were found as follows.

$$V = 2.1452 + 1.37 \times 10^{-3}T + 3.58 \times 10^{-6}T^2 \text{ (benzene)} \quad (3)$$

$$V = 2.2731 + 1.44 \times 10^{-3}T + 1.98 \times 10^{-6}T^2 \text{ (PDMS)} \quad (4)$$

where  $T$  is the absolute temperature. The thermal expansion coefficients for PDMS and benzene obtained from eq 3 and 4 agree well with those of other workers.<sup>1,6-8,14</sup> The plots of  $\alpha_p$  against concentrations of PDMS in benzene have a curvature convex upwards as shown in Figure 7.

$$\left(\frac{\partial S}{\partial V}\right)_T \text{ was calculated by} \\ \left(\frac{\partial S}{\partial V}\right)_T = -(\partial V/\partial T)_P/(\partial V/\partial P)_T = \alpha_p/K_T$$

The results are summarized in Table I. Figure 8 show the plots of  $(\partial S/\partial V)_T$  vs. temperature under atmosphere for various concentrations of PDMS in benzene.  $(\partial S/\partial V)_T$  decreases with increasing temperature for each composition and with an increase in the concentration of PDMS in benzene at constant temperature. This behavior may be explained by the increase of randomness in the polymer segments or solvent molecules with temperature or concentration of PDMS in benzene. As the temperature is increased, the arrangement of molecules in liquid becomes more random and the intermolecular distance is increased.<sup>17</sup> The value of  $(\partial S/\partial V)_T$  is linear for each composition over the temperature range of 303.15 to 323.15 K. Our results for PDMS and benzene are in good agreement with the results of Hamada, *et al.*,<sup>18</sup> in the same experimental range. They reported that the value of  $(\partial S/\partial V)_T$  was nonlinear for each composition over a temperature

range of 283.15 to 333.15 K.

Internal pressure,  $(\partial U/\partial V)_T$ , was calculated by the relation  $(\partial U/\partial V)_T = T \cdot \alpha_P / K_T - P$ , in which  $U$  is the internal energy. The values of  $(\partial U/\partial V)_T$  were summarized in Table I, and are plotted as a function of temperature for each composition in Figure 9. Allen<sup>3,15</sup> found  $(\partial U/\partial V)_T$  for benzene as 85.2 cal cm<sup>-3</sup> at 293.15 K, and Gee<sup>13</sup> reported 52.5 cal cm<sup>-3</sup> at 303.15 K for PDMS. Their results for PDMS and benzene are in good agreement with ours. As is shown in Figure 9, the internal pressure decreases with increasing temperature and for solutions at a given temperature, it lies between the values of the polymer and solvent. If we neglect the kinetic energy compared with the potential energy which is the sum of the attractive and repulsive energy between polymer and/or solvents, and assume that the average potential energy for the polymer solution is expressed as  $\langle \phi(r) \rangle = \alpha \langle r^{-\delta} \rangle - b \langle r^{-\gamma} \rangle$ , then

$$U(V) \propto \langle \phi(r) \rangle \quad (5)$$

where  $\langle r \rangle$  is the mean distance between polymer and/or solvents, and  $\langle \phi(r) \rangle$  the average potential energy for the polymer solution. Assuming that the average potential energy is predominated only by the attractive term,  $V \propto r^3$ , the internal energy can be represented by the relation,<sup>16</sup>

$$U(V) \propto \langle \phi(r) \rangle = -b \langle r^{-\gamma} \rangle = -b V^{-\langle \gamma \rangle/3} \quad (6)$$

Therefore,

$$(\partial U/\partial V)_T \propto V^{-\langle \gamma \rangle/3 + 1} = U_{\text{vap}}/V \quad (7)$$

$U_{\text{vap}}/V$  is the energy of vaporization per unit volume and is equal to the internal pressure. As shown in Figure 9, the internal pressure decreases at each composition as the temperature increases. This is explained as a result of the increase in the intermolecular distance with increase in temperature. The internal pressure for a solution at each temperature is linear with concentration for each temperature within the experimental range. The internal pressure is related to the parameter  $\langle \gamma \rangle$  in eq 7. If the parameter  $\langle \gamma \rangle$  depends on the concentration, the internal pressure should change with concentration of the solution. Thus, the concentration dependence of the internal pressure for a polymer solution may be explained in terms of the change of the parameter  $\langle \gamma \rangle$  with the concentration.

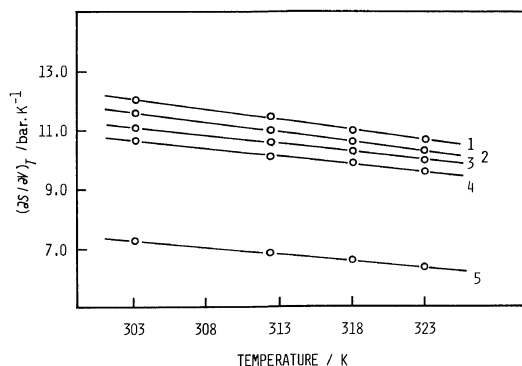


Figure 8.  $(\partial S/\partial V)_T$ -temperature relations of PDMS-benzene system under atmosphere.

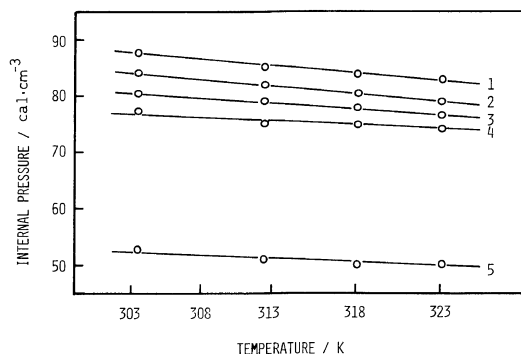


Figure 9. Internal pressure-temperature relations of PDMS-benzene system.

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