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Determination of equation of state parameters of poly(dimethylsiloxane)–benzene system by intrinsic viscosity

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The equation of state exchange energy (X_{12}) and entropy (Q_{12}) parameters and the ratio of contact sites (s_2/s_1) of the poly(dimethylsiloxane)–benzene system were determined using equation of state theory and intrinsic viscosity measurements. The values of X_{12} and Q_{12} parameters for $s_2/s_1=0.67$ are found to be 16.64 J cm^{-3} and -0.0394 J cm^{-3} K^{-1}, respectively.

(Keywords: thermodynamics; equation of state; intrinsic viscosity)

Introduction

The thermodynamics of many solvent–solvent and polymer–solvent pairs have been investigated by Flory and his collaborators using equation of state theory[1–8]. Three quantities, X_{12}, Q_{12} and s_2/s_1, were introduced in this theory. The parameters X_{12}, Q_{12} and s_2/s_1 are defined as the interchange energy upon formation of contacts between unlike molecules, the entropy erasing from interchange of neighbouring molecules, and the ratio of surface areas (or contact sites) for a polymer segment and solvent molecule, respectively.

The values of X_{12} and Q_{12} (especially Q_{12}) were chosen arbitrarily to fit the theory and experimental results by Flory and co-workers. The ratio of s_2/s_1 was estimated with either an approximation, where the solvent may be represented by a sphere whose volume is equal to the characteristic molar volume of the solvent V_1^* and the solute by a cylinder of volume V_1^*, or the sum of the surface areas of constituent groups given by Bondi[9].

Recently, a simple procedure based on intrinsic viscosity measurements has been proposed to estimate parameters X_{12} and Q_{12} of poly(4-chlorostyrene) in various solvents[10]. This procedure was developed to calculate the value of s_2/s_1 in our previous papers[11,12]. Q_{12}, X_{12} and s_2/s_1 were calculated for poly(ethyl methacrylate)–isopropyl alcohol and polystyrene–cyclohexane mixture using the abovementioned method[11,12]. It was shown that the results obtained by this procedure are in good agreement with literature values for the polystyrene–cyclohexane system[7].

In this study, the values of X_{12}, Q_{12} and s_2/s_1 for poly(dimethylsiloxane) solution in benzene were estimated using the equation of state theory from intrinsic viscosity measurements. Polymer–solvent interaction parameters (χ_1, χ_2) were determinated as a function of temperature from equation of state theory. Our results are compared with the result obtained from osmotic pressure experiments[8].

Theoretical background

The relation between intrinsic viscosity and molecular dimensions of a polymer chain in a solution is given by the following equations[13]:

$$\alpha_\eta^3=\frac{[\eta]}{[\eta]_\theta} \qquad (1)$$

$$K_\theta=\Phi(\langle r^2\rangle_0/M)^{3/2} \qquad (2)$$

$$\langle r^2\rangle_0=([\eta]_\theta M/\Phi)^{2/3} \qquad (3)$$

$$K_\theta=[\eta]_\theta/M^{1/2} \qquad (4)$$

The symbols in these equations are defined as follows: α_η^3 is the expansion factor; $[\eta]_\theta$ and $[\eta]$ are intrinsic viscosities at, respectively, theta and ordinary temperatures; K_θ is the unperturbed chain dimension constant; M is the molecular weight of polymer; $\langle r^2\rangle_0$ is the mean square end-to-end distance of the unperturbed coil; Φ is the universal viscosity constant (Flory–Fox constant) for the polymer chain and has a value of 2.5×10^{21} mol^{-1} if the intrinsic viscosity unit is dl g^{-1}.

α_η^3 is a function of the excluded volume parameter (z). The excluded volume parameter is related to the polymer–solvent interaction density (B), as given by:

$$\alpha_\eta^3=1+kz \qquad (5)$$

$$z=(3/2\pi)^{3/2}(B\Phi/K_\theta)M^{1/2} \qquad (6)$$

$$B=\bar{v}^2(1-2\chi_1)/V_1N_A \qquad (7)$$

where k is a constant with a value of 1.05–1.55 (ref. 14), $\bar{v}$ is the specific volume of polymer, χ_1 is the thermodynamic interaction parameter in infinitely dilute polymer solutions, V_1 is the molar volume of the solvent, N_A is Avogadro's number. The empirical relation in

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equation (5) is the best fit to the experimental data over the range $0 < \alpha_\eta^3 < 1.6$ (ref. 14).

In this study, equations (1)–(7) were rearranged in the following form:

$$\chi_1 = 0.5 - \{(\alpha_\eta^3 - 1)V_1 N_A[\eta]_\theta / \Phi M \bar{v}^2 2k(3/2\pi)^{3/2}\} \tag{8}$$

If we say that

$$S = N_A / \Phi 2k(3/2\pi)^{3/2} \tag{9}$$

then a simple equation is obtained for calculation of χ_1:

$$\chi_1 = 0.5 - \{(\alpha_\eta^3 - 1)[\eta]_\theta S V_1 / \bar{v}^2 M\} \tag{10}$$

Polymer–solvent interaction parameter, χ, is a function of concentration and temperature. χ can be expanded in series with respect to volume fraction of polymer, v_2, at constant temperature[15]:

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \cdots \tag{11}$$

where χ_1, χ_2, χ_3, are the thermodynamic interaction parameters which are functions of temperature. The volume fraction of polymeric samples approaches zero at very dilute solutions. Therefore χ can be taken as equal to χ_1 with a good approximation. In this study, as the intrinsic viscosities were measured at very low concentrations, χ_1, which was calculated using equation (10), was assumed to be equal to χ_1 in equation (11).

In the equation of state theory, polymer–solvent interaction parameters are given by[15]:

$$\lim_{v_2 \to 0} \chi = \chi_1 = (p_1^* V_1^* / \tilde{v}_1 RT)[A^2 \alpha_1 T/2) + Y_{12}]$$
$$- V_1^* Q_{12}(s_2/s_1)^2/R \tag{12}$$

$$\chi_2 = \{2(1 - s_2/s_1)(Y_{12} + Z_{12}T)$$
$$+ [2Y_{12} + (1 - p_2^* T_1^* / p_1^* T_2^*)A]A\alpha_1 T$$
$$- (3 + 2\alpha_1 T + 2\alpha_1^2 T^2)(2\alpha_1 T A^3/9)\}(p_1^* V_1^* / \tilde{v}_1 RT) \tag{13}$$

where

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (s_2/s_1)X_{12}/p_1^* \tag{14}$$

$$Y_{12} = X_{12}(s_2/s_1)^2/p_1^* \tag{15}$$

$$Z_{12} = -Q_{12}(s_2/s_1)^2 \tilde{v}_1/p_1^* \tag{16}$$

Quantities appearing in these equations are defined as follows: V_1^*, p_1^* and T_1^* are, respectively, the characteristic molar volume, pressure and temperature of the solvent; p_2^* and T_2^* are the corresponding quantities for the polymer; R is the universal gas constant; α_1 is the thermal expansion coefficient of the solvent; $\tilde{v}_1 = (V_1/V_1^*)$ is the reduced volume; s_2/s_1 is the ratio of surface areas for a polymer segment and solvent molecule; X_{12} and Q_{12} are the exchange energy and entropy parameters of interaction, respectively. As shown in refs 10–12, if equation (12) is rearranged, a straight line equation is obtained which is given by the following equations for its slope (sl) and intercept (I):

$$sl = (s_2/s_1)^2 V_1^* X_{12} / \tilde{v}_1 R \tag{17}$$

$$I = p_1^* V_1^* \alpha_1 A^2 / 2\tilde{v}_1 R - Q_{12}(s_2/s_1)^2 V_1^*/R \tag{18}$$

Experimental

A sample of poly(dimethylsiloxane) (PDMS), having a viscosity-average molecular weight of about 2.8×10^4, was obtained from the Petrarch System Inc., Bristol, USA. A home-made modified Ubbelohde-type capillary viscometer was used for intrinsic viscosity measurements. The viscometer was immersed in a constant temperature bath controlled to ±0.02°C.

Intrinsic viscosities were calculated using the following relationship:

$$[\eta] = \lim_{c \to 0}(\eta_{sp}/c) \tag{19}$$

Polymer solutions were obtained in the viscometer by successive dilution of the initial PDMS solution. Intrinsic viscosity values were obtained by least-squares linear fitting of the experimental data. Detailed experimental procedures for viscometric measurements and calculations are given in ref. 16.

Results and discussion

The intrinsic viscosities of PDMS solution in benzene were performed in the temperature range of about 25–60°C. The intrinsic viscosity results of PDMS are given in *Table 1*. Thermal expansion factors, α_η, were determined by equation (1). In this calculation, $[\eta]_\theta$ was obtained as $0.132\,\mathrm{dl\,g^{-1}}$ from the K_θ value of methyl ethyl ketone by means of equation (4)[17]. Thermodynamic interaction parameters (χ_1) of PDMS in benzene were calculated from equations (1) and (10) by using the intrinsic viscosity data at the temperatures measured. The variation of χ_1 with reciprocal values of absolute temperature is shown in *Figure 1*.

By use of equations (12)–(16) and from the slope and intercept of *Figure 1*, a number of curves at various conditions have been simulated. The value of equation

Table 1 Intrinsic viscosity values for poly(dimethylsiloxane)–benzene mixtures at various temperatures

T (°C)	25	35	45	50	55	60
$[\eta]$	0.179	0.184 0.189	0.189 0.196	0.192	0.205	0.193

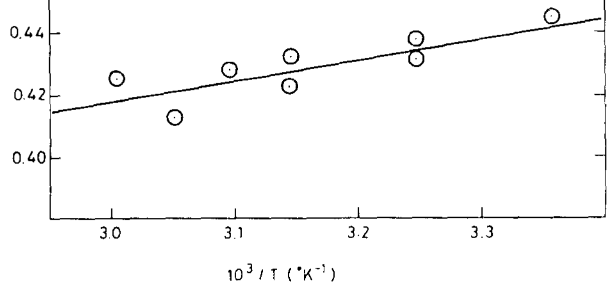

Figure 1 Polymer–solvent interaction parameter χ_1 obtained from experimental measurement results of intrinsic viscosity for the PDMS–benzene plotted against reciprocal values of absolute temperature

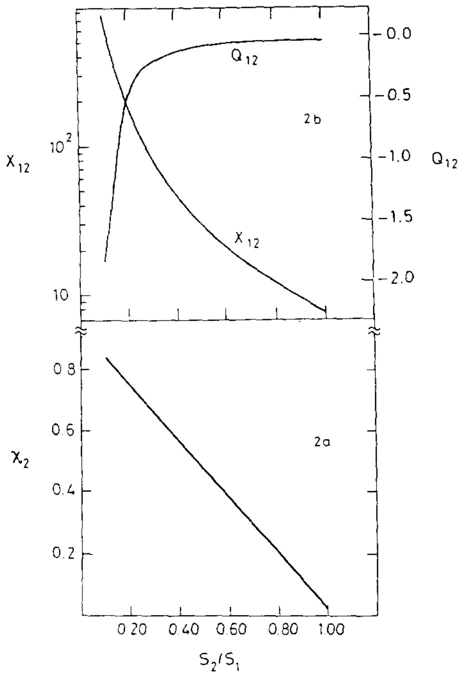

Figure 2 (a) Variation of χ_2 with the ratio s_2/s_1 at the theta point for the PDMS–benzene system. (b) Variation of X_{12} (left ordinate) and Q_{12} (right ordinate) with the ratio s_2/s_1 at the theta point for the PDMS–benzene system

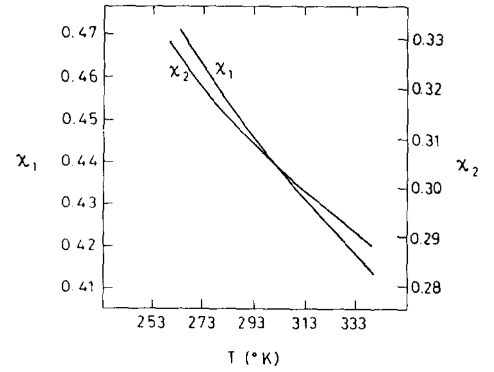

Figure 3 Value of χ_1 (left ordinate) and χ_2 (right ordinate), calculated according to the equation of state theory, plotted as functions of temperature for the PDMS–benzene system. In this calculation values of X_{12}, Q_{12} and s_2/s_1 were taken as 16.64 J cm^{-3}, -0.0394 J cm^{-3} K^{-1} and 0.67, respectively

of state exchange energy (X_{12}) and entropy (Q_{12}) parameters and the ratio of s_2/s_1 for the PDMS–benzene system were calculated. Values of parameters used for calculation for the PDMS–benzene system were taken as, $V_1^* = 95.84\,\mathrm{cm^3\,mol^{-1}}$, $T_1^* = 4709$ K, $T_2^* = 5528$ K, $\alpha_1 = 1.223 \times 10^{-3}\,\mathrm{K^{-1}}$, $\tilde{v}_1 = 1.2917$, $p_1^* = 628\,\mathrm{J\,cm^{-3}}$, $p_2^* = 341\,\mathrm{J\,cm^{-3}}$, at 25°C (ref. 18). As discussed in the previous papers[5,11,12], it was shown that the equation of state contribution of χ_1 is insensitive to the ratio s_2/s_1, but χ_2 is sensitive to this ratio. In this study, the theta point (-7°C) was taken as reference to perform these calculations[19]. It is known that theoretical and experimental values of χ_2 are in the order of 1/3 at the theta point[15].

The variation of χ_2, X_{12} and Q_{12} values with s_2/s_1 ratios at the theta point is shown in *Figure 2*. If one applies our procedure, it is apparent from *Figure 2a* that the most suitable value of s_2/s_1 should be between 0.6 and 0.7 for $\chi_2 \approx 1/3$. The values of segment surface areas for polymer segment and solvent molecule have been calculated in a previous paper[8] as 0.598 and 0.877 for the PDMS–benzene system. As mentioned in the Introduction, these values are found from the approximation that the solvent may be represented by a sphere and the solute by a cylinder and also from the sum of the surface areas of constituent groups given by Bondi[9]. As can be seen from *Figure 2a*, the values obtained for χ_2 are 0.387 and 0.136 for the s_2/s_1 values of 0.598 and 0.877, respectively, while the theory predicts that $\chi_2 \approx 1/3$ at the theta point. For $s_2/s_1 = 0.757$ (the value used in ref. 8), which is between the values chosen arbitrarily by Flory's group, χ_2 is 0.260. In our procedure, we obtained $s_2/s_1 = 0.67$ from the theoretical value of $\chi_2 = 1/3$ for the PDMS–benzene pair. So, this procedure gives reasonable values of s_2/s_1, being close to the former value in the above-mentioned calculation procedures.

The equation of state exchange energy and entropy parameter values for $s_2/s_1 = 0.67$ are found to be 16.64 J cm^{-3} and -0.0394 J cm^{-3} K^{-1}, respectively, for the PDMS–benzene system in this study. These values are comparable with the X_{12} and Q_{12} values given as 22 J cm^{-3} and -0.04 J cm^{-3} K^{-1}, respectively, by Flory and Shih[8]. The lower X_{12} value indicates better solubility. On the other hand, the positive Q_{12} value shows that the solubility as well as the entropy of the mixture increase with temperature, or vice versa. The solubility of a mixture is determined by the magnitude of the effective exchange energy parameter, $\bar{X}_{12}$ defined as $X_{12} - \tilde{v}TQ_{12}$, where $\tilde{v}$ is the reduced volume of the mixture and T is the absolute temperature. So, if the effective exchange energy parameter, $\bar{X}_{12}$, is low enough, the mixture is miscible.

Finally, by using the obtained values of Q_{12}, X_{12} and s_2/s_1, values of χ_1 and χ_2 were calculated according to the equation of state theory and plotted as functions of temperature in *Figure 3* for the system PDMS–benzene. Both of them decrease with temperature.

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