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A method for determination of thermodynamics and solubility parameters of polymers in dilute solutions from critical volume fractions

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Abstract

An equation using the critical volume fraction and segment number of polymer was proposed for the partial molar entropy change of a polymer for mixing in dilute solution. The partial molar enthalpy change of polymer for mixing was determined from the thermodynamic equilibrium property of two polymer phases at the critical temperature. The solubility or cohesion parameter of a polymer fraction at the critical temperature was calculated by using the partial molar enthalpy change and repeat unit volume of the polymer. The solubility parameter of high molar mass polymer at the theta temperature was determined by extrapolating solubility parameter values of the polymer fractions to high molar mass by using the solubility parameter-segment number relation of polymer fraction. This relation gives good straight line. The solubility parameter of the polymer at the theta temperature and the exchange energy parameter for polymer–solvent pair were obtained directly from the intercept and the slope of this line, respectively. These equations were applied to the critical point data of polystyrene (PS) in methylcyclohexane (MCH) and in cyclohexane (CH) solutions. The results obtained in this study coincide with the literature values for the solubility parameter of PS and exchange energy parameter for PS in CH solution. It was also found that the partial molar entropy change of a polymer for mixing at theta temperatures has about a constant value.

Keywords: Thermodynamics and solubility parameters of polymers; Solubility parameter-segment number relation; Exchange energy parameter of a polymer–solvent pair

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1. Introduction

The theories [1–5] developed for analysing the thermodynamic equilibrium properties of polymer solutions generally consider only the solvent which for reasons of simplicity, and the entropy and enthalpy changes of polymer for mixing determined by these theories are not satisfactory. Therefore, the solubility parameter of a polymer cannot be determined directly from the experiment [6]. Several indirect methods have been employed, most of which use a series of potential solvents with known solubility parameters. Most commonly the solubility parameter of a polymer is taken as being that of the solvent which gives the maximum degree of swelling for network polymers and the maximum intrinsic viscosity for soluble polymers.

In this study, an equation using the critical volume fraction and segment number of polymer will be proposed for the partial molar entropy change of a polymer for mixing in diliute solution. The partial molar enthalpy change of polymer is determined from the thermodynamic equilibrium property of two polymer phases at the critical temperature. The solubility parameter of each polymer fraction at the critical temperature is calculated by using the partial molar enthalpy change and repeat unit volume of the polymer. The solubility parameter of the polymer is determined by extrapolating solubility parameter values of the polymer fractions to high molar mass by using the solubility parameter-segment number relation. Good straight line is obtained, and the solubility parameter of the polymer at the theta temperature is obtained directly from the intercept of this line. In addition, the slope of this line gives an estimate of the exchange energy parameter for polymer–solvent pair introduced in the equation of state theory [2].

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2. Theory

For dilute polymer solutions, typically $<20\ \mathrm{g/dm^3}$, for which $n_1 \gg n_2$, the volume fraction ϕ_2 and mole fraction X_2 of the polymer are given by the following equations [7]

$$\phi_2 = [xn_2/(n_1 + xn_2)] \approx xn_2/n_1 \tag{1}$$

$$X_2 = [n_2/(n_1 + n_2)] \approx n_2/n_1 \tag{2}$$

where n_1 and n_2 are the number of moles of solvent and polymer, respectively, and x is the number of segments of polymer. From Eqs. (1) and (2), the following equation is obtained

$$X_2 = \phi_2/x \tag{3}$$

The partial molar entropy change of polymer for mixing is given by [5]

$$\overline{\Delta S}_2 = -R \ln X_2 \tag{4}$$

Substituting Eq. (3) into Eq. (4) gives

$$\overline{\Delta S}_2 = -R \ln(\phi_2/x) \tag{5}$$

For the critical condition, Eq. (5) can be written as follow

$$\overline{\Delta S}_{2\mathrm{c}} = -R \ln(\phi_{2\mathrm{c}}/x_\mathrm{c}) \tag{6}$$

Flory [7] suggested that the dilute polymer solution behaves as an ideal solution under theta conditions $T = \theta$. This ideal state of a polymer solution can also be applied to critical conditions. Eq. (4) is correct for an ideal solution. Then, all equations that follow Eq. (4) can be used for determination of entropy change of polymer.

Applying the thermodynamic criteria for the critical composition to the Flory–Huggins model yields [5]

$$\phi_{2\mathrm{c}} = 1/(1 + x_\mathrm{c}^{1/2}) \tag{7}$$

Substituting Eq. (7) into Eq. (6) gives the following equation

$$\overline{\Delta S}_{2\mathrm{c}} = -R \ln[1/(x_\mathrm{c} + x_\mathrm{c}^{3/2})] \tag{8}$$

This equation gives the relation between the partial molar entropy change and the segment number of the polymer. The segment number of the polymer at the critical point x_c was determined from Eq. (7)

$$x_\mathrm{c} = [(1 - \phi_{2\mathrm{c}})/\phi_{2\mathrm{c}}]^2 \tag{9}$$

The temperature composition phase diagrams for polymer solutions show that single-phase and two-phase regions are at equilibrium at the critical solution temperature T_c corresponding to the critical volume fraction $\phi_{2\mathrm{c}}$. Then, the following equation can be written at the critical condition

$$\overline{\Delta G}_{2\mathrm{c}} = \overline{\Delta H}_{2\mathrm{c}} - T_\mathrm{c}\overline{\Delta S}_{2\mathrm{c}} = 0 \tag{10}$$

where $\overline{\Delta G}_{2\mathrm{c}}$ and $\overline{\Delta H}_{2\mathrm{c}}$ are the partial molar Gibbs free energy change and the partial molar enthalpy change of polymer for mixing at the critical point, respectively.

It has been found in this study that $\overline{\Delta H}_{2\mathrm{c}}$ is approximately equal to the cohesive enthalpy per molar structural unit of the polymer. Then, the cohesion parameter or solubility parameter δ of a polymer fraction at the critical condition can be calculated from the following equation

$$\delta = (\overline{\Delta H}_{2\mathrm{c}}/V^\mathrm{u})^{1/2} \tag{11}$$

where V^u is the volume per molar structural or repeat unit.

According to the equation of state theory [2], χ/X_{12} is a linear function of $1/T$, where χ is the Flory–Huggins polymer–solvent interaction parameter and X_{12} is the exchange energy parameter. At $T = T_\mathrm{c}$, χ can be substituted by χ_c. According to the Flory–Huggins model [5], $\chi_\mathrm{c} = 1/x_\mathrm{c}^{1/2} + 1/2x_\mathrm{c} + 1/2$. Then, $1/T_\mathrm{c}$ should be linear with $(1/X_{12})(1/x_\mathrm{c}^{1/2} + 1/2x_\mathrm{c})$. It is seen from Eqs. (10) and (11) that δ^2 is proportional to T_c. Therefore, $1/\delta^2$ should be a linear function of $(1/X_{12})(1/x_\mathrm{c}^{1/2} + 1/2x_\mathrm{c})$. Ratzsch and Kranh [8] have extrapolated the solubility parameter values δ of homologous series to high molar mass δ_∞ at constant temperature by means of relationships such as

$$\log \delta = \log \delta_\infty + Bn^{-1} \tag{12}$$

where n is the number of carbon atoms. Similarly, it is possible to extrapolate δ values of polymer fractions to high molar mass of polymer δ_θ by means of the following equation

$$1/\delta^2 = 1/\delta_\theta^2 + (1/\hat{X}_{12})(1/x_\mathrm{c}^{1/2} + 1/2x_\mathrm{c}) \tag{13}$$

where $\hat{X}_{12}$ is proportional to X_{12} and can be taken as the estimate of this parameter. A plot of $1/\delta^2$ versus $1/x_\mathrm{c}^{1/2} + 1/2x_\mathrm{c}$ will give straight line with a slope of $1/\hat{X}_{12}$ and an intercept of $1/\delta_\theta^2$. However, in some studies [9], it has been given that $1/T_\mathrm{c}$ is a linear function of $1/M_\mathrm{w}^{1/2}$. Then, Eq. (13) can be written as

$$1/\delta^2 = 1/\delta_\theta^2 + (1/\hat{X}_{12})(1/x_\mathrm{c}^{1/2}) \tag{14}$$

In the same way, a plot of $1/\delta^2$ versus $1/x_\mathrm{c}^{1/2}$ will give a straight line with a slope of $1/\hat{X}_{12}$ and an intercept of $1/\delta_\theta^2$.

Table 1
Critical point data for polystyrene in methylcyclohexane

M_w (g/mol)	$\phi_{2\mathrm{c}}$	T_c (K)
1.02×10^4	0.1954	285.71
1.61×10^4	0.1691	295.98
1.72×10^4	0.1658	296.75
2.02×10^4	0.1564	298.95
3.49×10^4	0.1266	309.00
4.64×10^4	0.1148	312.61
1.09×10^5	0.0816	322.71
1.81×10^5	0.0685	327.00
7.19×10^5	0.0393	334.82

Table 2
Calculated values for polystyrene in methylcyclohexane

x_c	$-\ln(\phi_{2c}/x_c)$	$1/\delta^2$ (J/cm^3)$^{-1}$	$1/x_c^{1/2} + 1/2x_c$	$1/x_c^{1/2}$
16.9	4.460	0.9243×10^{-2}	0.272	0.243
24.1	4.969	0.8021×10^{-2}	0.223	0.203
25.3	5.028	0.7899×10^{-2}	0.218	0.198
29.1	5.226	0.7545×10^{-2}	0.202	0.185
47.6	5.929	0.6433×10^{-2}	0.155	0.145
59.4	6.248	0.6033×10^{-2}	0.137	0.129
126.7	7.348	0.4971×10^{-2}	0.092	0.088
184.9	7.901	0.4562×10^{-2}	0.076	0.073
597.6	9.630	0.3655×10^{-2}	0.042	0.041

3. Results and discussion

3.1. Critical volume fractions of PS in MCH solution

The experimentally measured values of M_w, T_c and ϕ_{2c} data for PS in MCH solution taken from the literature [9] were given in Table 1, where M_w is the weight-average molecular weight of polymer fraction in grams per mole. The values calculated by using these data were given in Table 2. In these calculations, the repeat unit volume was taken as 98 cm^3/mol.

Fig. 1 shows a plot of $1/\delta^2$ versus $1/x_c^{1/2} + 1/2x_c$ for data given in Table 2. A least-squares fitting of these data gives $\delta_\theta = 19.6 \pm 0.5$ (J/cm^3)$^{1/2}$ and $\hat{X}_{12} = 42.0 \pm 1.4$ J/(cm^3 × segment number$^{1/2}$) ($r = 0.9998$). Similarly, Fig. 2 shows a plot of $1/\delta^2$ versus $1/x_c^{1/2}$ data and least-squares fitting of these data also gives $\delta_\theta = 19.9 \pm 0.8$ (J/cm^3)$^{1/2}$ and $\hat{X}_{12} = 36.7 \pm 0.9$ J/(cm^3 segment number$^{1/2}$) ($r = 0.9996$). The confidence limits for all values of δ_θ and $\hat{X}_{12}$ were estimated at the 95% confidence level.

3.2. Critical volume fractions of PS in CH solution

The experimentally measured values of M_w, T_c and ϕ_{2c} data for PS in CH solution taken from the literature [9] were given in Table 3, and the values calculated by using these data were given in Table 4. In these calculations, repeat unit volume was also taken as 98 cm^3/mol. Figs. 1 and 2 also show the plots of $1/\delta^2$ versus $1/x_c^{1/2} + 1/2x_c$ and $1/x_c^{1/2}$ data for PS in CH solution, respectively. These data are related to two high molecular weights of polystyrene fractions (0.2×10^6 g/mol and 1.56×10^6 g/mol). The least-squares fittings of these data give the values of 18.8 (J/cm^3)$^{1/2}$ and 18.9 (J/cm^3)$^{1/2}$ for δ_θ, and 34.4 J/(cm^3 segment number$^{1/2}$) and 32.6 J/(cm^3 segment number$^{1/2}$) for $\hat{X}_{12}$ parameters ($r = 1.0000$), respectively.

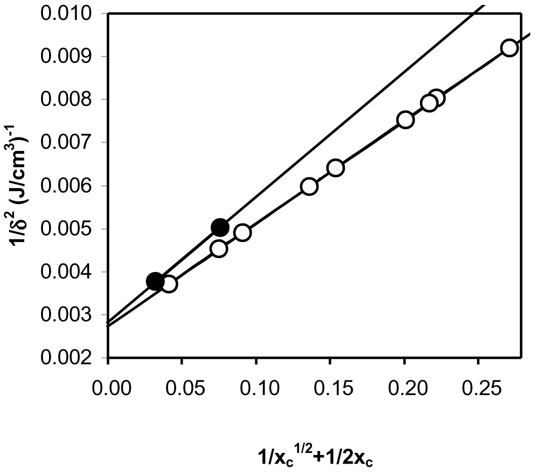

Fig. 1. Plots of $1/\delta^2$ against $1/x_c^{1/2} + 1/2x_c$ for polystyrene: (○) in methylcyclohexane; (●) in cyclohexane.

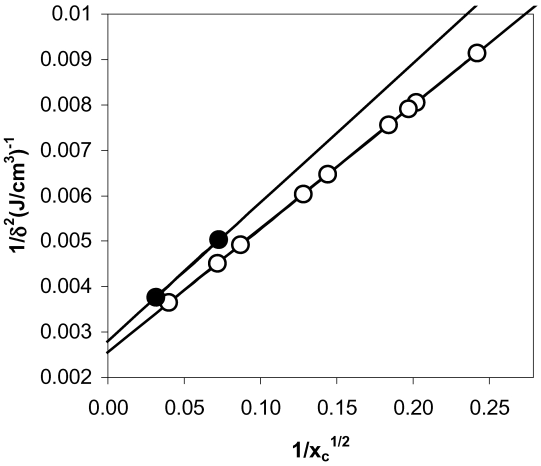

Fig. 2. Plots of $1/\delta^2$ against $1/x_c^{1/2}$ for polystyrene: (○) in methylcyclohexane; (●) in cyclohexane.

It was found that the partial molar entropy change of PS in MCH and CH solutions at their theta temperatures $\overline{\Delta S}_{2\theta}$ has a value of about 112.0 ± 1.8 J/mol K. Then, the following equation can be written for PS

$$\overline{\Delta S}_{2\theta} = (\overline{\Delta H}_{2\theta}/\theta) \approx 112.0 \pm 1.8 \text{ J/mol °K} \qquad (15)$$

The solubility parameter values of PS at 25 °C have been given to be the experimental values of 17.7–20.8 (J/cm^3)$^{1/2}$ and calculated values of 18.2–20.2 (J/cm^3)$^{1/2}$,and preferred value of 18.5 (J/cm^3)$^{1/2}$ in the literature [10]. If the theta temperature is taken to be equal to 25 °C, then, the solubility parameter value of PS is found to be about 18.5 (J/cm^3)$^{1/2}$ from Eqs. (11) and (15). This value is equal to the preferred value.

The exchange energy parameter X_{12} for PS in CH solution has found to be 42.0 J/cm^3 from osmotic pressure data [11]. The value of $\hat{X}_{12}$ parameter obtained for PS in MCH solution is approximately equal to this value. The molecular weights of polymer fractions used for PS in CH solutions are high and close to each other. Therefore, the

Table 3
Critical point data for polystyrene in cyclohexane

M_w (g/mol)	ϕ_{2c}	T_c (K)
0.20×10^6	0.0688	296.99
1.56×10^6	0.0317	303.65

Table 4
Calculated values for polystyrene in cyclohexane

x_c	$-\ln(\phi_{2c}/x_c)$	$1/\delta^2$ (J/cm^3)$^{-1}$	$1/x_c^{1/2} + 1/2x_c$	$1/x_c^{1/2}$
183	7.886	0.5033×10^{-2}	0.0766	0.0739
933	10.289	0.3773×10^{-2}	0.0332	0.0327

value obtained for PS in CH solution is some less than this value. Because, it was found that the value of this parameter depends on the molecular weight range of polymer.

4. Conclusions

As there is not any direct experimental method for determining the solubility parameter of a polymer, it was suggested on the basis of the results obtained in this study that the solubility parameter of a polymer can be determined experimentally by using the critical volume fractions of polymer. The exchange energy parameter of a polymer–solvent pair was estimated from the solubility parameter-segment number relation of polymer fractions. Also, it was found that the partial molar entropy change of a polymer at theta temperatures has about a constant value.

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