A novel method to estimate various equation-of-state parameters

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In the estimation of thermodynamic equation-of-state parameters, the ratio of contact sites of polymer segment and solvent molecule (s_2/s_1) is an important quantity to be determined. In this work we have evaluated this ratio by using a novel method of approximation. For this purpose, we have arbitrarily changed the value of s_2/s_1 and obtained the most suitable value yielding $\chi_2 = 0.303$ by interpolation.

(Keywords: equation-of-state parameters; polymer–solvent interaction; theta temperature)

Introduction

Recently, we have used equation-of-state theory[1] to evaluate exchange energy (X_{12}) and entropy (Q_{12}) parameters of poly(4-chlorostyrene)[2] and poly(ethyl methacrylate)[3] in various solvents around the θ temperatures from intrinsic viscosity measurements, or from experimental data based on inverse gas chromatography[4].

In estimation of the above-mentioned thermodynamic parameters, the ratio of surface areas (or contact sites) for a polymer segment and solvent molecule, s_2/s_1, is always an important quantity to be determined. In earlier work[5], this ratio was calculated considering the solvent molecule as a sphere with volume equal to the characteristic molar volume of the solvent, and the polymeric chain was assumed to be a chain-linked segment, cylindrical in shape and with a length of 2.54 Å. In another approach. the value of s_2/s_1 is obtained from the sum of the surface areas of constituent groups[6]. This method considerably overestimates the available surface area of a polymer owing to the fact that it ignores the shielding of constituent groups by intramolecular contacts between near-neighbours in the chain. The values of X_{12} and Q_{12} were chosen arbitrarily in order to fit the theory and experimental results, as carried out in previous works[7–9].

In this work, the ratio of s_2/s_1 is calculated by using a novel method of approximation, whereas the thermodynamic parameters are evaluated using equation-of-state theory for the polystyrene–cyclohexane system.

Theoretical background

The polymer–solvent interaction parameter χ is a measure of the intermolecular potential energies, and consequently the polymer–solvent interactions in the solution. χ is a function of concentration and temperature. At constant temperature, χ can be expanded in a series of polymer volume fractions (v_2):

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \dots \qquad (1)$$

where χ_1, χ_2 and χ_3 are the thermodynamic interaction parameters which are functions of temperature. For infinitely dilute solutions, i.e. when v_2 goes to zero, χ equals χ_1.

According to the equation-of-state theory, χ_1 is given as[1]:

$$\lim_{v_2 \to 0} \chi = \chi_1 = (p_1^* V_1^* / v_1 RT)[(A^2 \alpha_1 T/2) + Y_{12}] - V_1^* Q_{12} (s_2/s_1)^2 / R \qquad (2)$$

where

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

and

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

The symbols in these equations are defined as follows: R is the universal gas constant; α_1 is the thermal expansion coefficient of the solvent; V_1^*, p_1^* and T_1^* are the characteristic molar volume, pressure and temperature of the solvent; p_2^* and T_2^* are the corresponding quantities for the polymer. v_1 ($= V_1/V_1^*$) is the reduced volume, s_2/s_1 is the ratio of surface areas (or contact sites) for a polymer segment and solvent molecule, and X_{12} and Q_{12} are the exchange energy and entropy parameters of interaction, respectively, for the formation of a contact between a polymer segment and a solvent molecule.

Equation (2) is rearranged to give the following form:

$$\chi_1 = p_1^* V_1^* \alpha_1 A^2 / 2 v_1 R - (s_2/s_1)^2 V_1^* Q_{12}/R + (s_2/s_1)^2 V_1^* X_{12} / v_1 RT \qquad (3)$$

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Table 1 The changes in v_2 and χ_1 values with temperature for two polystyrene samples in cyclohexane[16,17]

$MW = 10 \times 10^6$			$MW = 8.6 \times 10^6$		
T (°C)	$v_2 \times 10^3$	χ_1	T (°C)	$v_2 \times 10^3$	χ_1
29.0	2.757	0.502	28.417	4.294	0.503
30.0	2.338	0.501	28.966	3.940	0.502
31.0	1.871	0.500	29.457	3.551	0.501
32.0	1.571	0.499	29.761	3.302	0.501
34.5	1.224	0.496	30.893	2.405	0.500
38.0	0.986	0.493	31.481	2.078	0.499
42.0	0.832	0.490	32.370	1.859	0.498
44.5	0.778	0.488	33.037	1.736	0.498
50.0	0.684	0.483	33.597	1.558	0.497
55.0	0.604	0.480	35.002	1.320	0.496
60.0	0.552	0.476			

If it is assumed that all equation-of-state parameters are independent of temperature in the studied temperature range, equation (3) shows that the χ_1 *versus* $1/T$ plot must give a straight line with characteristics:

$$\text{slope} = (s_2/s_1)^2 V_1^* X_{12}/v_1 R$$

$$\text{intercept} = p_1^* V_1^* \alpha_1 A^2/2v_1 R - Q_{12}(s_2/s_1)^2 V_1^*/R$$

The coefficient χ_2 in the series expansion in equation (1) of χ is given as[10]:

$$\begin{aligned}\chi_2 = \{&2(1 - s_2/s_1)(Y_{12} + Z_{12}T) \\ &+ [2Y_{12} + (1 - p_2^* T_1^*/p_1^* T_2^*)A]A\alpha_1 T \\ &- (3 + 2\alpha_1 T + 2\alpha_1^2 T^2)(2\alpha_1 TA^3/9)\}(p_1^* V_1^*/v_1 RT)\end{aligned} \quad (4)$$

where Y_{12} and A were defined earlier, and

$$Z_{12} = -Q_{12}(s_2/s_1)^2 v_1/p_1^*$$

For a polystyrene chain the values of expansion factor α were calculated by the following equation[11,12]:

$$\frac{14}{4N} v_2(1 - \alpha^2) = \sigma\left(\frac{\theta}{T} - 1\right) v_2^2 - \tfrac{2}{3} v_2^3 \quad (5)$$

where v_2 is the volume fraction of a chain of N segments with radius of gyration S, and $\alpha = \langle S^2 \rangle^{1/2}/\langle S_0^2 \rangle^{1/2}$ represents the expansion factor. In addition, the following relations are necessary if viscosity measurements are used to evaluate the dimensions of the chains:

$$v_2 = v_2^0/\alpha^3 \quad (6)$$

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta = \alpha^{2.43} \quad (7)$$

where v_2^0 is the volume fraction of segments in the unperturbed state[10]; α is the expansion factor, and $[\eta]$ and $[\eta]_\theta$ represent the intrinsic viscosities in ordinary and θ solvent, respectively[13,14].

The volume fraction of polymer at the θ temperature, v_2^0, depending on molecular weight is calculated as 1.22×10^{-3} and 1.32×10^{-3} for molecular weights 10×10^6 and 8.6×10^6, respectively, as noted in a previous paper[10].

Results and discussion

The following empirical relation is obtained for polymer–solvent interaction parameter χ for a binary system of polystyrene–cyclohexane:

$$\begin{aligned}\chi_1 = 0.2305 + 81.67T^{-1} + (-0.018 + 98.01T^{-1})v_2 \\ + (-0.168 + 135.50T^{-1})v_2^2\end{aligned} \quad (8)$$

where v_2 is the volume fraction of the polymer[15].

Values of χ_1 were calculated from experimental data reported for two polystyrene samples[16,17] of molecular weights 8.6×10^6 and 10×10^6. The results are given in *Table 1*. The calculated values of χ_1 as a function of reciprocal values of absolute temperature for two polystyrene samples are plotted in *Figure 1*. This figure also includes the results based on ref. 12, where the expansion factor of a polystyrene sample of molecular weight 8.6×10^6 was evaluated by using equation (5). Subsequently v_2 and χ_1 were calculated using equations (6) and (8), respectively.

The equation-of-state energy (X_{12}) and entropy (Q_{12}) parameters and the ratio of s_2/s_1 for the polystyrene–cyclohexane system below and above the θ temperature were calculated using equations (3) and (4) and from the evaluated values of slopes and intercepts of the straight lines shown in *Figure 1*. The following parameters were used for this calculation: $V_1^* = 84.4\ \text{cm}^3\ \text{mol}^{-1}$, $T_1^* = 4742$ K, $T_2^* = 7489$ K, $p_1^* = 528\ \text{J cm}^{-3}$, $p_2^* = 541\ \text{J cm}^{-3}$, $\alpha_1 = 1.248 \times 10^{-3}$ K, $v_1 = 1.304$ ($\theta = 35$°C)[9,10].

It was shown that the equation-of-state contribution of χ_1 is insensitive to the ratio of s_2/s_1, whereas χ_2 is sensitive[3,5]. In this work the θ temperature was taken as a reference point. It is known that the theoretical[10] and experimental[18] values of χ_2 are found to be 0.303. The temperature dependence of Q_{12} and X_{12} parameters is negligible.

We have arbitrarily changed the value of s_2/s_1 from 0.30 to 0.90 and, using the data given in *Table 1*, we have calculated Q_{12} and X_{12} values below and above the θ temperature for two polystyrene samples. The results are given in *Tables 2* and *3*. The values of χ_2 calculated from equation (4), are also included in the last column of these tables. The values of s_2/s_1 yielding $\chi_2 = 0.303$ are denoted by an asterisk in *Tables 2* and *3*. These values are 0.521 and 0.539 for $T < \theta$. A smaller value of s_2/s_1, 0.501, was

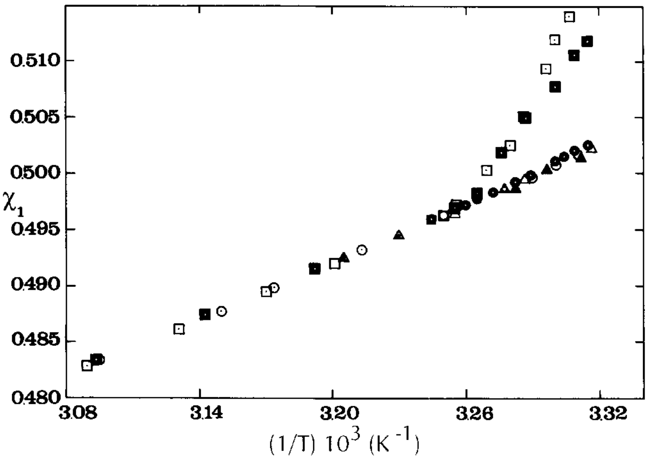

Figure 1 Comparison of the χ_1 values as a function of reciprocal temperature ($1/T$) for the polystyrene–cyclohexane system. The values of χ_1 were calculated from data given in the following references: ○, $MW = 10 \times 10^6$, ref. 17; ●, $MW = 8.6 \times 10^6$, ref. 16; □, $MW = 26 \times 10^6$, ref. 12; △, $MW = 8.42 \times 10^6$, refs 19, 20; ▲, $MW = 20.6 \times 10^6$, refs 19, 20; ■, $MW = 8.6 \times 10^6$, calculated from equation (5), refs 11, 12

Table 2 The variation of X_{12}, Q_{12} and χ_2 with the ratio of s_2/s_1 using data in *Table 1* (PS in cyclohexane, $MW=10\times10^6$)

s_2/s_1[a]	X_{12} (J cm^{-3})	$Q_{12}\times10^2$ (J cm^{-3} °C^{-1})	χ_2 at $T=\theta$
		$T<\theta$	
0.2	287.60	−5.15	0.600
0.3	127.82	3.51	0.467
0.4	71.90	3.70	0.380
0.5	46.01	3.12	0.315
0.518	42.87	3.01	0.305
0.52	42.54	3.00	0.304
*0.521	42.38	2.90	0.303
0.55	38.03	2.81	0.287
0.60	31.95	2.51	0.262
0.70	23.47	2.03	0.215
0.80	17.97	1.66	0.174
0.90	14.20	1.37	0.135
		$T>\theta$	
0.2	264.49	−8.08	0.578
0.3	117.55	1.88	0.450
0.4	66.12	2.73	0.366
0.495	43.17	2.44	0.306
0.5	42.31	2.42	0.304
*0.501	42.15	2.41	0.303
0.51	40.67	2.37	0.298
0.55	34.97	2.20	0.276
0.60	29.38	1.99	0.250
0.70	21.59	1.63	0.206
0.80	16.53	1.35	0.166
0.90	13.06	1.13	0.128

[a] An asterisk represents the most suitable values

obtained for $T>\theta$. This ratio of contact sites is estimated as 0.51 by considering[2,5] the polystyrene molecule as a cylinder of length 2.54 Å and the molar volume of the solvent as $V_1^* = 84.4\ \mathrm{cm^3\ mol^{-1}}$.

For the polystyrene–cyclohexane system, the variation of the values of χ_1 with temperature evaluated from sedimentation measurements[19,20] and photon correlation spectroscopy[12] are also depicted in *Figure 1*. It can be seen that for temperatures above and below the θ point the evaluated χ_1 values are all cumulated on the same straight line. However, χ_1 values calculated from equation (5), based on data from the photon correlation spectroscopy measurements[12] below the θ temperature, define another line with a different slope.

Conclusion

Table 3 The variation of X_{12}, Q_{12} and χ_2 with the ratio of s_2/s_1 using data in *Table 1* (PS in cyclohexane, $MW=8.6\times10^6$, $T<\theta$)

s_2/s_1[a]	X_{12} (J cm^{-3})	$Q_{12}\times10^2$ (J cm^{-3} °C^{-1})	χ_2 at $T=\theta$
0.2	305.81	−3.07	0.618
0.3	135.91	4.68	0.482
0.4	76.45	4.51	0.392
0.5	48.93	3.64	0.325
0.53	43.54	3.40	0.308
0.534	42.89	3.37	0.306
*0.539	42.10	3.33	0.303
0.54	41.95	3.22	0.302
0.60	33.97	2.98	0.270
0.70	24.96	2.32	0.223
0.80	19.11	1.88	0.180
0.90	15.10	1.56	0.141

[a] An asterisk represents the most suitable value

The results given in this work reveal that for meaningful calculation of χ_2 values and other thermodynamic parameters, the use of precise values of s_2/s_2 is important. The values of this ratio are different for the regions above and below the θ temperature for a given polymer–solvent system. The evaluated s_2/s_1 values are larger for the region of $T<\theta$ than for the region of $T>\theta$.

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