A Method for Determining the Flory Theta Temperature and Entropy Parameter of Single- or Multicomponent-Polymer–Single Solvent Systems from the Critical Solution Point Data

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ABSTRACT: An attempt was made to determine the concentration dependence coefficients, p_1 and p_2 , of the polymer–solvent interaction parameter χ [$\chi = \chi_0(1 + p_1v_p + p_2v_p^2)$; χ_0 : concentration independent coefficient, v_p : polymer–volume fraction] from the critical solution concentration v_p^c and the weight- and z -average relative molar volume ratios of the polymer to the solvent, X_w and X_z , of polymer samples in multicomponent polymer–single solvent systems and evaluate the Flory's theta solution temperature θ and entropy parameter ψ for a system using the critical solution temperature T_c and critical χ_0 parameter χ_0^c . For this purpose, a theory is proposed to calculate χ_0^c from p_1 , p_2 , X_w , and X_z . The method was applied to the literature data of upper and lower critical solution point (UCSP and LCSP) regions for polystyrene (PS)–cyclohexane (CH) and PS–methylcyclohexane systems. The values of p_1 and p_2 , thus obtained for UCSP of PS–CH system, were in good agreement with those estimated by Kamide *et al.* from the cloud point curve. The θ and ψ values obtained are compared with those by the Koningsveld *et al.* method using the same critical point data and with those by the second virial coefficient method.

KEY WORDS Concentration Dependence Parameter / Polymer–Solvent Interaction Parameter / Critical Solution Temperature / Entropy Parameter / Multicomponent Polymer–Solvent System / Polystyrene /

The Flory temperature θ and entropy parameter ψ were experimentally determined from the temperature dependence of the second virial coefficient A_2 (θ as the temperature at which A_2 becomes zero and ψ from the temperature dependence of A_2 (see eq 25) at θ , respectively) and the critical point (the temperature T_c and the volume fraction v_p^c), extrapolating by the Shultz–Flory² method for a polymer of infinite molecular weight (see eq 21'). Although being only approximate, the Shultz–Flory method has found rather widely use. For all polymer–solvent systems investigated, it was confirmed that θ temperatures evaluated by the above two procedures agree fairly well with each other, but ψ values estimated by the second virial coefficient method

are significantly smaller than those obtained by the critical point method.³ Stockmayer⁴ pointed out the inadequacy of the basic equation (eq 21') of the Shultz–Flory theory and proposed an alternative equation (eq 18), rigorously derived for polydisperse polymer solutions. Another factor is the concentration dependence of the χ -parameter, which was completely neglected in the Shultz–Flory and Stockmayer methods. To solve this problem, Koningsveld *et al.*¹² estimated a method for estimating θ and ψ from data on critical concentration v_p^c and critical temperature T_c for a series of solutions differing in average molecular weight. They employed a pair interaction parameters g , expanding as a series function of the polymer volume fraction v_p in

the form,

$$g = \sum_{i=0}^n g_i v_p^i \quad (1)$$

Here they assumed that g_0 could be divided into temperature-independent and -dependent components given by

$$g_0 = g_{00} + g_{01}/T \quad (2)$$

The ψ and θ can be calculated from

$$\psi = \frac{1}{2} - g_{00} - g_1 \quad (3)$$

$$\theta = g_{01}/\psi \quad (4)$$

Note that the concentration- and temperature-dependence of the g parameter, in other words, the parameters g_{00} , g_{01} , g_1 , and g_2 were evaluated so that the deviation of the experimental v_p^c and T_c data for all samples from the theory would be minimum. Koningsveld *et al.*'s procedure was applied to polystyrene (PS)-cyclohexane (CH) and PS-methylcyclohexane (MCH) and the ψ values were calculated. In their method, the curve fitting method was repeatedly used to determine g_i (for example, see Figures 1 and 2). The concentration dependence of the g parameter (accordingly, χ -parameter) can also be determined not only from the critical point, but by various other methods such as osmotic pressure, light scattering, ultracentrifuge, vapor pressure, and phase separation, by which the χ -parameter is directly obtained.

In this article, we have attempted to clarify whether and to what extent ψ and θ are influenced by the concentration dependence of the χ -parameter and polymolecularity of the samples and propose a method for estimating ψ and θ from T_c alone, taking into account the above two factors determined independently by other methods, without assuming a specific temperature dependence of the χ -parameter, as in the case of using experimental data from the literature, we applied our method to polystyrene solutions for a comparison with the

results obtained by other method, such as those of Shultz-Flory,² Stockmayer,⁴ Koningsveld *et al.*,^{8,12} and the second virial coefficient method.

THEORETICAL BACKGROUND

The χ -parameter can be completely phenomenologically expressed in a power series of the concentration,⁵

$$\chi = \sum_{j=0}^n \chi_i v_p^j \\ = \chi_0 \left(1 + \sum_{j=1}^n p_j v_p^j \right) \quad (5)$$

for multicomponent polymer-single solvent systems. Here, χ_0 is a parameter independent of concentration, and p_j , the concentration-dependence parameter. Kamide *et al.*^{6,7} showed from the phase separation experiment for polystyrene in cyclohexane and methylcyclohexane that χ_0 is empirically given by

$$\chi_0 = \chi_{00}(1 + k_0(1 - \theta/T)/X_n) \quad (6)$$

where χ_{00} is a parameter independent of the ratio of the molar volume of the polymer (*i.e.*, X -mer) to that of the solvent X_i , X_n ; number average of X_i , k_0 ; parameter independent of temperature and X_i , and T ; the temperature. The applicability of eq 6 has not yet been widely confirmed by actual experiments,^{6,7} and the molecular weight dependence of χ , expressed by eq 6 is not considered. χ , χ_0 , p_i , and P_n are directly related to g , g_i , and g_n through the relations,

$$\chi = g - (1 - v_p) \left(\frac{\partial g}{\partial v_p} \right) \quad (7)$$

$$\chi_0 = g_0 - g_1 \quad (8)$$

$$p_i = (i+1) \frac{g_i - g_{i+1}}{g_0 - g_1} \quad (9)$$

$$p_n = (n+1) \frac{g_n}{g_0 - g_1} \quad (10)$$

According to the Koningsveld theory, p_i is a

function of temperature through g_0 . An alternative expression of the concentration-dependence of g was proposed by Koningsveld *et al.*⁸ as

$$g = \alpha + \frac{\beta}{1 - \gamma v_p} \quad (11)$$

with

$$\beta = \beta_{00} + \beta_{01}/T \quad (12)$$

Here, α , β_{00} , β_{01} , and γ are constants for a given polymer/solvent system. If $0 < \gamma < 1$ holds, $0 < \gamma v_p < 1$ can be obtained and the second term in the right-hand side of eq 11 expanded as a series function

$$g = \alpha + \beta + \sum_{i=1}^{\infty} \beta(\gamma v_p)^i \quad (13)$$

$$\simeq \alpha + \beta + \sum_{i=1}^n \beta(\gamma v_p)^i$$

Equation 13 reduces to eq 1 by putting $\alpha + \beta = g_0$ and $\beta\gamma^i = g_i$ ($i=1, \dots, n$). In this case, χ_0 and p_i can be expressed in terms of α , β , and γ by

$$\chi_0 = \alpha + \beta(1 - \gamma) \quad (8)'$$

$$p_i = (i+1) \frac{\beta\gamma^i(1-\gamma)}{\alpha + \beta(1-\gamma)} \quad (i=1, \dots, n-1) \quad (9)'$$

$$p_n = (n+1) \frac{\beta\gamma^n}{\alpha + \beta(1-\gamma)} \quad (10)''$$

Note that P_i is sometimes temperature dependent due to the temperature dependence of α , β , and γ . At the critical point, the following equations can be derived,⁹

$$\frac{1}{X_w v_p^c} + \frac{1}{1 - v_p^c} - \chi_0^c \left(2 + \sum_{j=1}^n p_j(j+2)v_p^{c,j} \right) = 0 \quad (14)$$

and

$$\frac{1}{(1 - v_p^c)^2} - \frac{X_z}{(X_w v_p^c)^2} - \chi_0^c \sum_{j=1}^n p_j j(j+2)v_p^{c,j-1} = 0 \quad (15)$$

where χ_0^c is the critical χ_0 , X_w , the weight-

average X , and X_z , the z -average X .

Both χ_0^c and v_p^c can be obtained concurrently through application of eq 14 and 15, using a numerical method, to the data of X_w , X_z , and p_j ($j=1, 2$). χ_0^c is related to T_c , ψ , θ through the relation^{1,5}

$$\frac{1}{T_c} = \frac{\chi_0^c}{\theta\psi} + \frac{1}{\theta} \left(1 - \frac{1}{2\psi} \right) \quad (16)$$

with

$$\psi \equiv 1/2 - \chi_{0,s}, \quad \theta \equiv \chi_{0,h}/(1/2 - \chi_{0,s}) \quad (17)$$

$\chi_{0,s}$ and $\chi_{0,h}$ are the entropy and enthalpy components of χ_0 , respectively (*i.e.*, $\chi_0 = \chi_{0,s} + \chi_{0,h}$). Using χ_0^c , calculated from eq 14 and 15, and experimental T_c , we can determine θ and ψ from the plot of $1/T_c$ against χ_0^c . This method is hereafter simply referred to as the Kamide-Matsuda method.

Putting $p_j=0$ (for $j=1, \dots, n$) in eq 14, we obtain

$$\chi_0^c = \frac{1}{2} \left(\frac{1}{X_w v_p^c} + \frac{1}{1 - v_p^c} \right) \quad (18)$$

Substitution of the Stockmayer equation which was derived rigorously for a multicomponent polymers-single solvent system, assuming $p_j=0$ ($j=1, \dots, n$),

$$v_p^c = \frac{1}{1 + X_w/X_z^{1/2}} \quad (19)$$

into eq 18 yields

$$\chi_0^c = \frac{1}{2} \left(\frac{X_z^{1/2}}{X_w} + \frac{1}{X_w} \right) \left(\frac{X_w}{X_z^{1/2}} + 1 \right) \quad (20)$$

Combining eq 16 with eq 20, we obtain

$$\frac{1}{T_c} = \frac{1}{\theta\psi} \left\{ \frac{1}{2} \left(\frac{1}{X_w^{1/2}} + \left(\frac{X_z}{X_w} \right)^{1/2} \right) \times \left(\frac{1}{X_w^{1/2}} + \left(\frac{X_w}{X_z} \right)^{1/2} \right) \right\} + \frac{1}{\theta} \left(1 - \frac{1}{2\psi} \right) \quad (21)$$

When $X_w = X_z$ is assumed, eq 19 and 21 reduce to the well-known equations derived by Shultz and Flory.²

$$v_p^c = \frac{1}{1 + X_w^{1/2}} \quad (19')$$

and

$$\begin{aligned} \frac{1}{T_c} &= \frac{1}{\theta\psi} \left(\frac{1}{2} \left(\frac{1}{X_w^{1/2}} + 1 \right)^2 \right) + \frac{1}{\theta} \left(1 - \frac{1}{2\psi} \right) \\ &= \frac{1}{\theta\psi} \left(\frac{1}{X_w^{1/2}} + \frac{1}{2X_w} \right) + \frac{1}{\theta} \quad (21') \end{aligned}$$

Note that eq 21', is strictly valid only for a monodisperse polymer-solvent system, in which the χ -parameter is assumed to be independent of the molecular weight of the polymer and concentration. When eq 6 is applicable, eq 14 and 15 can be modified as,

$$\begin{aligned} \frac{1}{X_w v_p^c} + \frac{1}{1 - v_p^c} - \chi_{00}^c \left(1 + k \left(1 - \frac{\theta}{T_c} \right) \right. \\ \left. \times \left(1 + \frac{1}{X_n} - \frac{X_w}{X_n} \right) \right) \\ \times \left(2 + \sum_{j=1}^n p_j(j+2)v_p^{c^j} \right) = 0 \quad (14') \end{aligned}$$

$$\begin{aligned} \frac{1}{(1 - v_p^c)^2} - \frac{X_z}{(X_w v_p^c)^2} - \chi_{00}^c \left(1 + k_0 \left(1 - \frac{\theta}{T_c} \right) \right. \\ \left. \times \left(1 + \frac{1}{X_n} - \frac{X_w}{X_n} \right) \right) \\ \times \left(\sum_{j=1}^n p_j j(j+2)v_p^{c^{j-1}} \right) = 0 \quad (15') \end{aligned}$$

In the Koningsveld *et al.* method, g_1 and g_2 in eq 1 are calculated from v_p^c , X_w and X_z by applying the curve fitting method to the equation

$$\begin{aligned} Y &\equiv g_1 - g_2 + 4g_2 v_p^c \\ &= \frac{1}{6} \left(\frac{1}{(1 - v_p^c)^2} - \frac{X_z}{(X_w v_p^c)^2} \right) \quad (22) \end{aligned}$$

of neutral equilibrium conditions. g_0 is evaluated from g_1 and g_2 , thus determined and v_p^c and X_w , using the spinodal equation,

$$\begin{aligned} 2g_0 &= \frac{1}{1 - v_p^c} + \frac{1}{v_p^c X_w} \\ &+ 2g_1(1 - 3v_p^c) + 6g_2(1 - 2v_p^c)v_p^c \quad (23) \end{aligned}$$

Equation 22 is basically equivalent to eq 15 and eq 23 is the same as eq 14. g_{00} and g_{01} can be estimated from the plot of $\dot{g}_0$ vs. $1/T_c$ according to eq 2. Replacing χ_0^c with $g_0 - g_1$ in eq 16, eq 3 and 4 can be derived.

Whether the concentration dependence of the χ -parameter and polymolecularity of the polymer should be taken into account to explain the critical point and, in the former case what would be the most reasonable values of $p_1, p_2, \dots, p_n$, can be decided by comparing the experimental v_p^c ($v_p^c(\text{exp})$) and theoretical v_p^c ($v_p^c(\text{theo})$) data calculated using eq 14, 15 (Kamide-Matsuda), eq 19 (Stockmayer), and eq 19' (Shultz-Flory). An analysis of the data on $v_p^c(\text{exp})$, X_z , and X_w would provide the most ideal values of $p_1, p_2, \dots$, and p_n as a combination yielding minimum δ , defined by

$$\delta = \sum_{i=1}^{N_0} (v_p^c(\text{exp}) - v_p^c(\text{theo}))^2 / N_0 \quad (24)$$

(N_0 , total number of samples).

That is, an appropriate choice of $p_1, \dots, p_n, v_p^c(\text{theo})$ will fit $v_p^c(\text{exp})$ for an entire set of data. If $v_p^c(\text{exp})$ and experimental T_c ($T_c(\text{exp})$) data are available for a polymer-solvent system, we can determine $p_1, \dots, p_n$ from the plot of $v_p^c(\text{exp})$ vs. $v_p^c(\text{theo})$ and θ and ψ from the $1/T_c - \chi_0^c$ plot concurrently.

Table I presents the features of the various methods proposed so far for estimating θ and ψ from critical point data.

APPLICATION TO EXPERIMENTAL DATA

a) Atactic Polystyrene(PS)-Cyclohexane (CH)

For PS-CH solutions, Kamide *et al.* determined $p_1 = 0.6$ and $p_2 = 0$ from a phase equilibrium experiment¹⁰ and $p_1 = 0.643$ and

Table I. Various methods for estimating θ and ψ from critical point data

Method	Parameter prerequisite for applying method			Parameters deduced from the method
	Molecular characteristics	Critical point data	Concentration dependence of χ	
Schulz-Flory (eq 20')	X_w	T_c	—	θ, ψ, v_p^c
Stockmayer (eq 20)	X_w, X_z	T_c	—	θ, ψ, v_p^c
Koningsveld <i>et al.</i> (eq 3, 4)	X_w, X_z	T_c, v_p^c	—	$\theta, \psi, g_{00}, g_{01}, g_1, g_2$
Kamide-Matsuda (eq 14–16)	X_w, X_z	T_c	p_1, p_2	$\theta, \psi, v_p^c, \chi_{00}$

$p_2=0.200$ from a cloud point experiment.⁹ The p_1 and p_2 values of this system have been evaluated by other workers by osmotic pressure,¹¹ isothermal distillation,¹¹ vapor pressure,¹¹ critical solution point,^{12,13} and ultra-centrifuge.¹⁴ For example, Koningsveld and his coworkers¹² analyzed critical solution data using their procedure to obtain $\alpha=-0.1597$, $\beta_{00}=0.4987$, $\beta_{01}=111.74$, and $\gamma=0.2365$ (accordingly, $p_1=0.623$ and $p_2=0.290$ at 307K). Kuwahara *et al.*¹³ obtained $p_1=0.607$ and $p_2=0.512$ at 299K from critical points by the Koningsveld *et al.* method.

Literature data on the upper critical solution points (UCSP) (v_p^c and T_c) of Koningsveld *et al.*¹² and of Kuwahara and his collaborators^{13,15} and on lower critical solution points (LCSP) of Saeki *et al.*¹⁵ are available for determining p_1 , and p_2 , using Koningsveld's and our methods. Here, since Kuwahara *et al.* and Saeki *et al.* evaluated only X_w and X_n for these samples, we estimated X_z assuming the Schulz-Zimm type molecular weight distribution for all PS samples.

Figure 1 shows a plot of Y in eq 22 versus v_p^c for the literature data on the UCSP and LCSP of a PS/CH system. From this figure, we estimated, using the least-square regression method, g_1 to be 0.214 and g_2 , 0.057 for UCSP and $g_1=0.1345$ and $g_2=0.0079$ for LCSP. The plot for LCSP is very far from linearity because experimental techniques become much more difficult, thus limiting the accuracy of the g_1 and g_2 values for LCSP. g_0 was calculated by putting the g_1 and g_2 values thus obtained

Figure 1. Plot of Y in eq 21 against v_p^c for the UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. $\circ$, Koningsveld *et al.*¹²; $\bullet$, Kuwahara *et al.*¹³; $\circ$, Saeki *et al.*¹⁵ **Figure 2.** Plot of g_0 in eq 22 versus $1/T_c$ for the UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. $\circ$, Koningsveld *et al.*¹²; $\bullet$, Kuwahara *et al.*¹³; $\circ$, Saeki *et al.*¹⁵

Table II. Flory θ temperature and entropy parameter ψ of the upper solution critical point for the polystyrene-cyclohexane system

Method		Concentration dependence of χ		θ/K	ψ
		p_1	p_2		
Critical point	Shultz-Flory (eq 20')	0	0	306.2 (306.2, ^a 307.0, ^b 307.2, ^c 306.4 ^d)	0.75 (0.78, ^a 0.79, ^b 1.056 ^c)
	Stockmayer (eq 20)	0	0	306.5	0.80
	Koningsveld <i>et al.</i> (eq 3, 4)	0.623	0.308	305.2	0.29
		0.623 ^e	0.290 ^e	305.6	0.30
	Kamide-Matsuda: Phase separation (eq 14-16)	0.6 ⁿ	0 ⁿ	306.4	0.35
	Cloud point	0.643 ^f	0.200 ^f	306.6	0.27
	Critical point	0.623 ^e	0.290 ^e	305.6	0.27
	Critical point	0.642	0.190	305.1	0.27
	Membrane osmometry	—	—	307.6 ^g	0.36 ^g
		—	—	307.6 ^h	0.23 ^h
Second virial coefficient	Light scattering	—	—	308.4 ⁱ	0.19 $\pm$ 0.05 ⁱ
		—	—	307.0 ^j	0.36 ^k
		—	—	307.4 ^l	0.18 ^m

^a ref 11; ^b ref 15; ^c ref 2; ^d ref 11; ^e ref 8; ^f ref 9; ^g ref 3; ^h ref 11; ⁱ ref 16; ^j ref 17; ^k calculated using $\theta(\partial A_2/\partial T)_\theta$ data in ref 17; ^l ref 20; ^m calculated using $\theta(\partial A_2/\partial T)_\theta$ data in ref 20; ⁿ ref 10.

Table III. Flory temperature θ and entropy parameter ψ of the lower solution critical point for the polystyrene-cyclohexane system

Method	p_1	p_2	θ/K	ψ
(i) Critical point				
Shultz-Flory (eq 20')	0	0	486.6 (486.0 ^a)	-1.20 (-1.19 ^a)
Stockmayer (eq 20)	0	0	486.8	-1.20
Koningsveld <i>et al.</i> (eq 3, 4)	0.571	-0.047	487.5	-0.61
Kamide-Matsuda: Phase separation	0.60 ^b	0 ^b	487.6	-0.52
Critical point	0.602	-0.347	487.2	-0.42

^a ref 15; ^b ref 10.

and v_p^c into eq 23 and plotting them as a function of T_c^{-1} in Figure 2. g_{00} was determined as 0.213 and g_{01} as 151.7 for UCSP and $g_{00}=1.2447$ and $g_{01}=-297.0$ were obtained for LCSP. Using these g functions, p_1 , p_2 (both at θ), θ , and ψ were evaluated as summarized in Tables II and III.

Figure 3 shows the plot of $v_p^c(\text{exp})$ vs. $v_p^c(\text{theo})$ calculated for some typical combinations of p_1 and p_2 for the UCSP and LCSP of a PS/CH system. In this figure the same data as those in Figures 1 and 2 were utilized. Figure 4 shows the relations among p_1 , p_2 and δ for

the PS/CH system. The most reasonable combination of p_1 and p_2 , evaluated from Figure 4, is $p_1=0.642$ and $p_2=0.190$ for UCSP and $p_1=0.602$ and $p_2=-0.347$ for LCSP (Tables II and III).

The plots of $1/T_c$ against X_0^c for the PS/CH system are shown in Figure 5. The results are summarized in Tables II and III, in which θ and ψ values estimated originally in literature are shown in parenthesis for comparison. Krigbaum and his coworkers,^{3,11,16} and Schulz and Baumann¹⁷ determined the θ and ψ of UCSP for the PS/CH system from the tem-

Figure 3. The critical concentration, experimentally determined, $v_p^c(\text{exp})$ plotted against the critical concentration, theoretically calculated, $v_p^c(\text{theo})$ for the UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. $\triangle$, Shultz-Flory² [eq 19]; $\blacktriangle$, Stockmayer⁴ [eq 19]; $\circ$, Kamide-Matsuda [eq 14, 15, $p_1=0.6$, $p_2=0$]; $\bullet$, Kamide-Matsuda [eq 14, 15, $p_1=0.623$, $p_2=0.290^8$]; $\square$, Kamide-Matsuda [eq 14, 15, $p_1=0.642$, $p_2=0.190$ for UCSP and $p_1=0.602$, $p_2=-0.347$ for LCSP].

Figure 4. Relations among p_1 , p_2 and δ for the UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. Number on curve denotes $\delta \times 10^4$. Filled mark corresponds to the most ideal combination of p_1 and p_2 to describe the critical solution point.

perature dependence of the second virial coefficient near θ temperature. The literature data show variation in ψ from 0.18 to 0.36 and in θ from 307.0 to 308.4K, as listed in Table II.

b) Atactic Polystyrene(PS)–Methylcyclohexane (MCH)

Kamide *et al.* determined $p_1=0.7$ and $p_2 \approx 0$ by phase separation in the UCSP region¹⁰ and $p_1=0.78$ and $p_2=0.33$ by osmotic pressure.¹⁸ Dobashi and his coworkers¹⁹ estimated UCSP

as the intercept of the co-existence curve and its diameter for PS samples with $X_w/X_n < 1.06$ and obtained $p_1=0.604$ and $p_2=0.299$ at 344K using Koningsveld *et al.*'s method.⁸

Here, we analyzed the literature data of the UCSP of Dobashi *et al.* (9 samples)¹⁹ and the UCSP and LCSP of Saeki and his coworkers (6 samples)¹⁵. X_z was calculated assuming the SZ distribution for all samples.

Figure 6 shows a plot of Y vs. v_p^c for PS/MCH system. A comparison of the re-

Figure 5. $1/T_c$ plotted against χ_0^0 for the UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. Triangle, Schultz-Flory plot [eq 21]; circle, Kamide-Matsuda plot [eq 14, 15, $p_1=0.6$, $p_2=0$]; rectangle, Kamide-Matsuda plot [eq 14, 15, $p_1=0.623$, $p_2=0.290^8$]; diamond Kamide-Matsuda plot [eq 14, 15, $p_1=0.642$, $p_2=0.190$ for UCSP and $p_1=0.602$, $p_2=-0.347$ for LCSP]; unfilled mark, data of Koningsveld *et al.*¹²; filled mark, data of Kuwahara *et al.*¹³; half-filled mark, data of Saeki *et al.*¹⁵

lations between Y and v_p^c with eq 22 yields $g_1 = 0.219_2$ and $g_2 = 0.060_1$ for UCSP and $g_1 = -0.007$ and $g_2 = -0.167$ for LCSP.

Figure 7 shows g_0 plotted against $1/T_c$ for the same system, we obtain $g_{00} = 1.053$ and $g_{01} = -273.4$ for LCSP. The p_1 , p_2 , (both at θ), θ and ψ values calculated from g function are listed in Tables IV and V.

Figure 8 shows plots of $v_p^c(\text{exp})$ against $v_p^c(\text{theo})$, calculated, assuming various values of p_1 and p_2 , for PS/MCH system.

Figure 9 shows the relations among p_1 , p_2 , and δ for the UCSP and LCSP of the PS/MCH system. From this figure, we obtain the most reasonable combination $p_1 = 0.602$ and $p_2 = 0.234$ for UCSP and $p_1 = 0.649$ and $p_2 = -1.183$ for LCSP.

Figure 10 shows $1/T_c$ plotted as a function of χ_0^0 for the PS/MCH system. From the intercept and slope of the plot θ and ψ were evaluated and summarized in Tables IV and V.

Schulz and Baumann¹⁷ determined θ to be 68°C and $\theta(\partial A_2/\partial T)_\theta$ to be $2.16 \times 10^{-3} \text{ cm}^3$

Figure 6. Plot of Y in eq 21 against v_p^c for the UCSP (a) and LCSP (b) of the polystyrene/methylcyclohexane system. $\circ$, Saeki *et al.*¹⁵; $\bullet$, Dobashi *et al.*¹⁹

Figure 7. Plot of g_0 in eq 22 versus $1/T_c$ for the UCSP (a) and LCSP (b) of the polystyrene/methylcyclohexane system. $\circ$, Saeki *et al.*¹⁵; $\bullet$, Dobashi *et al.*¹⁹

g^{-2} for UCSP by light scattering method. ψ was thus calculated by the following equation

$$\psi = (V_1/\bar{v}^2)\theta(\partial A_2/\partial T)_\theta \quad (25)$$

as 0.30 . Here, $(\partial A_2/\partial T)_\theta$ is the temperature dependence of A_2 , V_1 , the molar volume of solvent ($136.4 \text{ cm}^3 \text{ mol}^{-1}$) and $\bar{v}$, the specific volume of the polymer ($0.99 \text{ cm}^3 \text{ g}^{-1}$). Kotera *et al.*²¹ also evaluate-independently θ and ψ for

Figure 8. The critical concentration, experimentally determined, $v_p^c(\text{exp})$ plotted against the critical concentration, theoretically calculated $v_p^c(\text{theo})$ for the UCSP (a) and LCSP (b) of the polystyrene/methylcyclohexane system. $\triangle$, Shultz-Flory [eq 19]; $\blacktriangle$, Stockmayer [eq 19]; $\circ$, Kamide-Matsuda [eq 14, 15, $p_1 = 0.6$, $p_2 = 0$]; $\bullet$, Kamide-Matsuda [eq 14, 15, $p_1 = 0.7$, $p_2 = 0$]; $\square$, Kamide-Matsuda [eq 14, 15, $p_1 = 0.604$, $p_2 = 0.299$]; $\blacksquare$, Kamide-Matsuda [eq 14, 15, $p_1 = 0.602$, $p_2 = 0.234$ for UCSP and $p_1 = 0.649$, $p_2 = -1.183$ for LCSP].

Figure 9. Relations among p_1 , p_2 , and δ for the UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. Number on curve denotes $\delta \times 10^4$. Filled mark corresponds to the most ideal combination of p_1 and p_2 to describe the critical solution point.

UCSP using the same method. The results are in Table IV.

DISCUSSION

It is evident from Figures 3 and 8 that the Shultz-Flory and Stockmayer theories significantly underestimate v_p^c : $v_p^c(\text{exp}) > v_p^c(\text{theo})$

Figure 10. $1/T_c$ plotted against χ_0^c for the UCSP (a) and LCSP (b) of the polystyrene/methylcyclohexane system. Triangle, Shultz-Flory plot [eq 21]; circle, Kamide-Matsuda plot [eq 14, 15, $p_1 = 0.7$, $p_2 = 0$]; rectangle, Kamide-Matsuda plot [eq 14, 15, $p_1 = 0.604$, $p_2 = 0.299$]; diamond Kamide-Matsuda plot [eq 14, 15, $p_1 = 0.602$, $p_2 = 0.234$ for UCSP and $p_1 = 0.649$, $p_2 = -1.183$ for LCSP]; unfilled mark, data of Saeaki *et al.*¹⁵; filled mark, data of Dobashi *et al.*¹⁹

and that consideration of the simple parameter p_1 in Kamide-Matsuda's method greatly re-

Table IV. Flory temperature θ and entropy parameter ψ of the upper solution critical point for the polystyrene-methylcyclohexane system

Method		p_1	p_2	θ/K	ψ	
Critical point	Shultz–Flory (eq 20')	0	0	342.3 (344 ^a)	0.61 (0.56 ^a)	
	Stockmayer (eq 20)	0	0	342.3	0.61	
	Koningsveld <i>et al.</i> (eq 3, 4)	0.602	0.363	339.6	0.27	
			0.604 ^b	0.299 ^b	343.4	—
		Kamide–Matsuda: Phase separation (eq 14—16)	0.70 ^c	0 ^c	335.7	0.24
	Coexistence curve	0.604 ^b	0.299 ^b	340.4	0.23	
Second virial coefficient	Light scattering	Critical point	0.602	0.234	340.2	0.25
			—	—	341 ^d	0.30 ^e
			—	—	340.4 ^f	0.16 ^g

^a ref 15; ^b ref 19; ^c ref 10; ^d ref 17; ^e calculated using the $\theta(\partial A_2/\partial T)_\theta$ data in ref 17; ^f ref 20; ^g calculated using the $\theta(\partial A_2/\partial T)_\theta$ data in ref 20.

Table V. Flory temperature θ and entropy parameter ψ of the lower solution critical point for polystyrene-methylcyclohexane

Method		p_1	p_2	θ/K	ψ
(i) Critical point					
	Shultz-Flory (eq 20')	0	0	485.1 (484 ^a)	-0.96 (-0.94 ^a)
	Stockmayer (eq 20)	0	0	485.1	-0.96
	Koningsveld <i>et al.</i> (eq 3, 4)	0.643	-1.00 ^g	487.8	-0.56
	Kamide-Matsuda: Phase separation (eq 14–16)	0.7 ^b	0 ^b	489.5	-0.31
	Critical point	0.649	-1.183	487.9	-0.54

^a ref 15; ^b ref 10.

duces the disagreement between $v_p^c(\text{exp})$ and $v_p^c(\text{theo})$. However, usage of the single parameter p_1 is not sufficient to cover a wide range of v_p^c . For example, $v_p^c(\text{theo})$, calculated using $p_1=0.6$ for the UCSP of the PS/MCH system, agrees well with $v_p^c(\text{exp})$, only at the lowest X_w fraction and its difference with $v_p^c(\text{theo})$ increases linearly and that between $v_p^c(\text{theo})$, calculated with $p_1=0.7$, and $v_p^c(\text{exp})$ increases with decreasing $v_p^c(\text{theo})$.

Not only p_1 , but also p_2 are necessary and sufficient to describe the v_p^c of polymer solutions as in the case of the cloud point curve.⁹ Note that the phase separation characteristics of the two phase equilibrium can be approximately explained by only considering p_1 and the effect of p_2 on these are insignificant, probably due to the large error involved in the separation experiments.

Three procedures are available to determine p_1 and p_2 concurrently, from the critical solution point (v_p^c and T_c) (Koningsveld *et al.*^{8,12} and Kamide and Matsuda) or cloud point curve (Kamide *et al.*⁹). Previous work by Kamide *et al.*⁹ on the cloud point curve in the UCSP region for the PS/CH system yields results on p_1 and p_2 thoroughly consistent with those of the present study: $p_1=0.64$ and $p_2=0.19$ were estimated for the UCSP of the PS/CH system and Tables II–V show Koningsveld *et al.*'s method and Kamide-Matsuda's method, both based on the critical solution point, to yield almost the same p_1 for the UCSP and LCSP of the the polymer/solvent systems investigated, but the difference in p_2 obtained by two methods is remarkable. The plot of Y against v_p^c scatters considerably (see, Figures 1 and 6) and the relationships

r between them are not satisfactorily high, for example, $r=0.87$ and -0.80 for the UCSP and LCSP of PS/CH system. The slope of the plots give $4g_2$ and relatively larger uncertainty in the estimated value of g_2 may cause this pronounced scattering. The situation is almost the same even in the Kamide–Matsuda method but the p_2 value is also rather less accurate (see, Figures 4 and 9). These low degrees of accuracy in estimating p_2 in both methods can explain the noticeable variation in p_2 values. As will be demonstrated latter, since the contribution of p_2 to θ and ψ is fortunately relatively small, the scattering of p_2 is not a serious problem.

In this paper, we assumed p_1 and p_2 to be temperature-independent over a narrow temperature range. But this assumption may hold for a very limited extent over a wide temperature range for both UCSP and LCSP. However, for the UCSP and LCSP regions of the PS/CH and PS/MCH systems, p_1 was found to be 0.6 ± 0.04 by the Kamide–Matsuda method. This does not mean that p_1 is constant over a wide temperature range since there is the possibility that p_1 not in the theta region deviates from that in the UCSP and LCSP regions. For these systems, p_2 is always positive in the UCSP region, but negative in the LCSP region.

All the Shultz–Flory, Stockmayer and Kamide–Matsuda plots (Figures 5 and 10), though the former two underestimate v_p^c significantly, give very straight lines between T_c and χ_0^c and thus they cannot be evaluated simply on the basis of their linearity. These plots have an approximately common intercept at $\chi_0^c (=0.5)$ so that the θ value obtained by these methods is roughly constant, regardless of the analytical method employed, for a given polymer/solvent system. A detailed investigation showed that for the UCSP of the PS/CH and PS/MCH systems, in which both p_1 and p_2 are positive, the Shultz–Flory and Stockmayer methods overestimate θ by a few degrees, but for the LCSP

of these systems in which $p_1 > 0$ and $p_2 < 0$, these methods underestimate θ slightly. For all the systems, the Koningsveld *et al.* procedure and Kamide–Matsuda method give almost the same values of θ , within ± 0.1 — 0.3 K. The value of θ , estimated by the second virial coefficient method, is about 2.5 K higher than that either by the Koningsveld *et al.* or Kamide–Matsuda method for the PS/CH system and is very near to that estimated by the Shultz–Flory method. On the other hand, for the PS/MCH system, the value of θ obtained by the second virial coefficient method agrees fairly well with those by the Koningsveld *et al.* method and Kamide–Matsuda methods. Up to now, the Shultz–Flory method has been used most for estimating θ as compiled in the Polymer Handbook²¹ from the critical point data and θ temperatures estimated thus may have an experimental uncertainty of $\pm$ a few degree, even if monodisperse polymer samples are used.

As long as the polymolecularity of the polymer samples is small, ($X_w/X_n < 1.1$) as in the case of the vast majority samples used for analysis of PS/CH and PS/MCH systems, and/or the critical solution points are determined directly as points at which the two phase volume ratio is unity as is the case of Koningsveld *et al.*'s data¹² for the UCSP of the PS/CH system, there is no significant difference in θ value, as the theory predicts, between Shultz–Flory and Stockmayer method.

For polystyrene solutions, the absolute magnitude of ψ values estimated by the methods of Koningsveld *et al.* and Kamide and Matsuda are only half or 1/3 those by the Shultz–Flory and Stockmayer methods. The latter two methods give the same ψ , which is usually very large compared with that by the second virial coefficient method. The Kamide–Matsuda method yields a slightly smaller ψ (by -0.02) than that of Koningsveld *et al.* ψ estimated for the UCSP of PS/CH by the second virial coefficient method varies from 0.18 — 0.36 and averages 0.264 , which agrees

fairly well with $\psi=0.27$ obtained by the Kamide–Matsuda method. For the UCSP of PS/MCH, ψ was independently determined as 0.30 and 0.16 from the temperature dependence of the second virial coefficient. Their average value (0.23) was near to 0.25 as estimated by the Kamide–Matsuda method. Hence, as far as a non-polar polymer solution is concerned, ψ values estimated so far by the Shultz–Flory method, are erroneously over-estimated owing to the neglect of the concentration dependence of the χ -parameter.

From the above, it is clear that the great difference between ψ values obtained from critical points according to the Shultz–Flory procedure and second virial coefficient is evidently not due to the effect of the polydispersity of the polymer on the critical point, but almost entirely to ignorance of the concentration dependence of the χ -parameter (p_1 and p_2) in the Shultz–Flory method. The second virial coefficient corresponds to the term containing v_p^2 when the chemical potential of the solvent in a solution is expanded in a polynomial of v_p and therefore A_2 corresponds to χ_0 , a concentration-independent term of the χ -parameter in eq 5. Therefore, the existence of the concentration dependence of χ has no effect on the results obtained using eq 25, and in this sense, the second virial coefficient method is unconditionally preferable from a theoretical point of view.

The effect of p_1 and p_2 on the ψ parameter were examined for the PS/CH system in Figures 1–5. The results are shown in Figure 11. ψ decreases with an increase in p_1 and p_2 , but the former plays a predominant role and the latter is usually negligible. It is thus confirmed that the relatively low reliability of p_2 causes no significant variation in ψ . The variation in $p_1 \pm 0.1$ brings about a variation in $\psi \pm 0.05$, which is too large to neglect. Therefore, to estimate ψ accurately, p_1 should have a precision at least within ± 0.05 .

The most reasonable values of p_1 and p_2 , evaluated for PS/CH and PS/MCH, are sum-

Figure 11. Effect of p_1 and p_2 on entropy parameter ψ of UCSP for polystyrene/cyclohexane system. The same data in Figures 1–5 were used for calculating ψ .

Table VI. Most ideal combination of p_1 and p_2 for a polymer–solvent system

Polymer	Solvent	UCSP		LCSP	
		p_1	p_2	p_1	p_2
Polystyrene	Cyclohexane	0.64	0.19	0.60	-0.35
Polystyrene	Methyl-cyclohexane	0.60	0.23	0.65	-1.18

marized in Table VI. No possible explanation for the negative p_2 in the LCSP region is offered and this matter is open for further study.

In summary,

1) For a reasonably accurate determination of the critical solution point, two concentration dependence parameters p_1 and p_2 should be carefully taken into account.

2) By comparing the observed critical solution concentration $v_p^c(\text{exp})$ with the theoretical concentration $v_p^c(\text{theo})$, calculating by eq 14 and 15 with assumed values of p_1 and p_2 , we can determine p_1 and p_2 simultaneously.

3) The p_1 value obtained thus for the PS/CH system is in good agreement with that by

the Kamide *et al.* method, using the cloud point curve and that by Koningsveld *et al.* method, using the same critical solution data in each case.

4) Some large disagreement was observed between the p_2 values estimated by our method, and those by Koningsveld *et al.*'s method, using the same critical solution data in either case.

5) ψ as well as θ can be accurately determined by measuring T_c for polymer samples with known X_w and X_z and using p_1 and p_2 determined from the same critical point data or the cloud point curve.

6) If p_1 and p_2 are known in advance, the new procedure is undoubtedly much more straight forward compared to the Koningsveld *et al.* method. The latter method requires v_p^c in addition to T_c .

7) ψ obtained from the critical point for the PS/CH and PS/MCH systems agrees with that calculated by the second virial coefficient, provided, in the former, p_1 and p_2 are reasonably taken into account.

REFERENCES

1. See, for example, P. J. Flory, "Principle of Polymer Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1953.
2. A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 4760 (1952).
3. W. R. Krigbaum, *J. Am. Chem. Soc.*, **76**, 3758 (1954).
4. W. H. Stockmayer, *J. Chem. Phys.*, **17**, 588 (1949).
5. See, for example, M. Kurata, "Thermodynamics of Polymer Solutions," Harwood Academic Pubs., Chur, London, New York, 1982, Chapter 2.
6. K. Kamide and Y. Miyazaki, *Polym. J.*, **13**, 325 (1981).
7. K. Kamide, T. Abe, and Y. Miyazaki, *Polym. J.*, **14**, 355 (1982).
8. R. Koningsveld and L. A. Kleintjens, *Macromolecules*, **5**, 637 (1971).
9. K. Kamide, S. Matsuda, T. Dobashi, and M. Kaneko, *Polym. J.*, **16**, 821 (1984).
10. K. Kamide, Y. Miyazaki, and T. Abe, *Makromol. Chem.*, **177**, 485 (1976).
11. W. R. Krigbaum and D. O. Geymer, *J. Am. Chem. Soc.*, **81**, 1859 (1959).
12. R. Koningsveld, L. A. Kleintjens, and A. R. Shultz, *J. Polym. Sci., A-2*, **8**, 1261 (1970).
13. N. Kuwahara, N. Nakata, and M. Kaneko, *Polymer*, **14**, 415 (1973).
14. Th. G. Scholte, *J. Polym. Sci., A-2*, **8**, 841 (1970).
15. S. Saeki, N. Kuwahara, S. Konno, and M. Kaneko, *Macromolecules*, **6**, 246 (1973).
16. W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1959).
17. G. V. Schulz and H. Baumann, *Makromol. Chem.*, **60**, 120 (1963).
18. K. Kamide, K. Sugamiya, T. Kawai, and Y. Miyazaki, *Polym. J.*, **12**, 67 (1980).
19. T. Dobashi, M. Nakata, and M. Kaneko, *J. Chem. Phys.*, **72**, 15 (1980).
20. A. Kotera, T. Saito, and N. Fukisaki, *Rep. Prog. Polym. Phys. J.*, **VI**, 9 (1963).
21. J. Bandrup and E. H. Immergut, Ed., "Polymer Handbook," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1974, Chapter IV, p 157.