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COMPARISON OF TWO DIRECT METHODS FOR ESTIMATING THE CLOUD POINT CURVE OF QUASI-BINARY SYSTEMS CONSISTING OF MULTICOMPONENT POLYMERS DISSOLVED IN A SINGLE SOLVENT

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Abstract—An attempt was made to compare two direct methods, proposed by Kamide *et al.* and Šolc, for determining the cloud point curve (CPC) of a quasi-binary system consisting of a multicomponent polymer with the same chemical composition dissolved in a single solvent. Although both methods are based on the same modified Flory–Huggins theory combined with the principle of Gibbs' two phase equilibrium, the Kamide method is more general than the Šolc method because in the former the molecular weight-dependence of the χ-parameter is fully considered. The procedure of direct integration employed in the Kamide method was concluded to be more general than the polynomial expansion procedure in the Šolc method. Systematic computer experiments on the CPC were carried out under the same operating conditions according to the above two methods and Šolc's method compared with our direct integration procedure. The Kamide method gave the CPC almost identical with that estimated by the Šolc method, but the former method has an advantage in accurate calculation of the CPC in the low polymer concentration region.

INTRODUCTION

Kamide, Matsuda and coworkers [1–4] established a phase equilibrium theory for a quasi-binary system consisting of a multicomponent polymer and a single solvent, taking into account the polymer concentration- and polymer molecular weight-dependences of the thermodynamic polymer–solvent interaction parameter χ and proposed a direct method for calculating the cloud point curve (CPC) from their fundamental equations [see equations (23) and (24)] derived on their theory, in place of an indirect method, proposed in 1965 by Rehage *et al.* [5], where the CPC was determined as the intercept of the initial concentration axis and the coexisting curve. Note that Rehage *et al.* [5] carried out some experiments only for the determination of the CPC for the polystyrene/cyclohexane system and thereafter Koningsveld and Staverman [6] calculated the CPC, according to the Rehage method [5], for the same polymer–solvent system. In addition, Kamide *et al.* [1–3] carried out, using their method, extensive and systematic computer experiments in order to clarify the effects of the molecular weight distribution (MWD) of the original polymer, its weight-average degree of polymerization, X_w, and the concentration-dependence of χ on the CPC and "cloud particle", and indicated that the CPC is extremely sensitive to the first and second order concentration-dependence parameter p_1 and p_2 of χ (see, Fig. 12 of Ref. [3]). They also calculated the CPC, for comparison with the actual experiment on a polystyrene/cyclohexane system [3], under the same conditions as those in an actual experiment and concluded that an experimental CPC can be reasonably interpreted by their phase equilibrium theory when the combinations of the first and second order concentration dependence parameters are adequately chosen and the molecular weight dependence of χ is also considered, in particular, in the low concentration range. On the other hand, Šolc [7] proposed another direct method for determining the CPC for a quasi-binary system when χ is independent of the concentration [see, equation (42)], after expressing statistical moments of MWD of the polymers partitioned in a cloud particle in terms of the summation of the products of the partition coefficient σ [see, equations (11)–(13)] and statistical moments of MWD of the original polymer [8]. He studied energetically, using his direct method, three- and four-phase equilibria [9–16]. Šolc extended his original method to the quasi-binary system where χ depends on the concentration [15] [see equation (55)]. In this article we intend (i) to compare carefully the detailed derivation of two direct methods, i.e. the Kamide fundamental equation [equations (23) and (24)] and Šolc's "CPC equation" [equation (42) or (55)], for calculation of the CPC and (ii) to examine which method gives the more accurate CPC and shadow curve.

THEORETICAL BACKGROUND

The χ parameter is empirically expressed as functions of the polymer volume fraction v_p and the number—average degree of polymerization X_n in the form [1–4],

$$\chi = \chi_0\left(1 + \sum_{j=1}^{n} p_j v_p^j\right) \tag{1}$$

where χ_0 is given by

$$\begin{aligned} \chi_0 &= \chi_{00}(1 + k'/X_n) && (2) \\ &= (a + b/T)\left[1 + \frac{k_0}{X_n}\left(1 - \frac{\theta}{T}\right)\right] && (3) \end{aligned}$$

p_j is the jth concentration-dependent parameter, n is the maximum order of the concentration dependence of χ, θ is the Flory temperature, T, the Kelvin temperature, k' (or k_0) is the molecular weight-dependent parameter, χ_{00} is a parameter independent of v_p and the degree of polymerization X_i and dependent on T only, a and b are parameters independent of X_n, v_p and T and characteristic of the system [2]. In deriving equation (3), we employed the following empirical relations [1, 2]:

$$k' = k_0(1 - \theta/T) \tag{4}$$

$$\chi_{00} = a + b/T. \tag{5}$$

The chemical potentials of solvent and the X_i-mer in quasi-binary system, $\Delta\mu_0$ and $\Delta\mu_{xi}$ are, according to the modified Flory–Huggins solution theory, given by equations (6) and (7).

$$\begin{aligned} \Delta\mu_0 = \tilde{\mathrm{R}}T\Bigg[&\ln(1 - v_p) + \left(1 - \frac{1}{X_n}\right)v_p \\ &+ \chi_{00}\left(1 + \frac{k'}{X_n}\right)\left(1 + \sum_{j=1}^{n} p_j v_p^j\right)v_p^2\Bigg] \end{aligned} \tag{6}$$

$$\begin{aligned} \Delta\mu_{x_i} = \mathrm{R}T[&\ln v_{x_i} - (X_i - 1) + X_i\left(1 - \frac{1}{X_n}\right)v_p \\ &+ X_i(1 - v_p)^2\chi_{00}\Bigg[\!\!\Bigg[\left(1 + \frac{k'}{X_n}\right) \\ &\times\left\{1 + \sum_{j=1}^{n}\frac{p_j}{j+1}\left[\sum_{q=0}^{j}(q+1)v_p^q\right]\right\} \\ &+ k'\left(\frac{1}{X_i} - \frac{1}{X_n}\right) \\ &\times\left[\frac{1}{1 - v_p} + \sum_{j=1}^{n}\frac{p_j}{j+1}\left(\sum_{q=0}^{j}\frac{v_p^q}{1 - v_p}\right)\right]\Bigg]\!\!\Bigg] \end{aligned} \tag{7}$$

where $\tilde{R}$ is the gas constant. Of course, $\Delta\mu_0$ and $\Delta\mu_{x_i}$ satisfy the Gibbs–Duhem relation [4].

When the quasi-binary system is, at constant temperature and constant pressure, in two-phase equilibrium, $\Delta\mu_0$ and $\Delta\mu_{x_i}$ should be subjected to the Gibbs' conditions given by

$$\Delta\mu_{0(1)} = \Delta\mu_{0(2)} \tag{8}$$

$$\Delta\mu_{x_{i(1)}} = \Delta\mu_{x_{i(2)}} \quad (i = 1 \ldots m). \tag{9}$$

Here, the suffixes (1) and (2) mean the polymer-lean phase and the polymer-rich phase, respectively, and m is the total number of components in the polymer.

Substitution of equation (6) into equation (8) leads to equation (10).

$$\begin{aligned} \chi_{00} = \Bigg[&\ln\frac{1 - v_{p(1)}}{1 - v_{p(2)}} + (v_{p(1)} - v_{p(2)}) \\ &- \left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}}\right)\Bigg]\Bigg/\Bigg\{(v_{p(2)}^2 - v_{p(1)}^2) \\ &+ k'\left(\frac{v_{p(2)}^2}{X_{n(2)}} - \frac{v_{p(1)}^2}{X_{n(1)}}\right) + \sum_{j=1}^{n} p_j\Bigg[(v_{p(2)}^{j+2} - v_{p(1)}^{j+2}) \\ &+ k'\left(\frac{v_{p(2)}^{j+2}}{X_{n(2)}} - \frac{v_{p(1)}^{j+2}}{X_{n(1)}}\right)\Bigg]\Bigg\}. \end{aligned} \tag{10}$$

Substituting equation (7) into equation (9) gives the partition coefficient σ_i [,1 2],

$$\sigma_i \equiv \frac{1}{X_i}\ln\frac{v_{x_{i(2)}}}{v_{x_{i(1)}}} = \sigma_0 + \sigma_{01}/X_i \tag{11}$$

where $v_{x_{i(1)}}$ and $v_{x_{i(2)}}$ are the polymer volume fractions of X_i-mer in the polymer-lean phase and the polymer-rich phase, respectively and σ_0 and σ_{01} in equation (11) are given by [3, 4]

$$\begin{aligned} \sigma_0 = (v_{p(1)} - v_{p(2)}) &- \left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}}\right) \\ &- \chi_{00}\Bigg\{2(v_{p(1)} - v_{p(2)}) - (v_{p(1)}^2 - v_{p(2)}^2) \\ &+ \sum_{j=1}^{n} p_j\Bigg[\frac{j+2}{j+1}(v_{p(1)}^{j+1} - v_{p(2)}^{j+1}) \\ &- (v_{p(1)}^{j+2} - v_{p(2)}^{j+2})\Bigg]\Bigg\} \\ &- \chi_{00}k'\Bigg\{\left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}}\right) - \left(\frac{v_{p(1)}^2}{X_{n(1)}} - \frac{v_{p(2)}^2}{X_{n(2)}}\right) \\ &+ \sum_{j=1}^{n} p_j\Bigg[\left(\frac{v_{p(1)}^{j+1}}{X_{n(1)}} - \frac{v_{p(2)}^{j+1}}{X_{n(2)}}\right) \\ &- \left(\frac{v_{p(1)}^{j+2}}{X_{n(1)}} - \frac{v_{p(2)}^{j+2}}{X_{n(2)}}\right)\Bigg]\Bigg\} \end{aligned} \tag{12}$$

and

$$\begin{aligned} \sigma_{01} = -k'\chi_{00}\Bigg[&(v_{p(1)} - v_{p(2)}) \\ &+ \sum_{j=1}^{n}\frac{p_j}{j+1}(v_{p(1)}^{j+1} - v_{p(2)}^{j+1})\Bigg]. \end{aligned} \tag{13}$$

In the case where the initial polymer volume fraction v_p^0 is less than the critical polymer concentration v_p^c ($v_p^0 < v_p^c$), which is given as a solution of the following simultaneous equations (3):

$$\begin{aligned} \frac{1}{X_w^0 v_p} + \frac{1}{1 - v_p} - \chi_{00}&\left[1 + k'\left(1 + \frac{1}{X_n^0} - \frac{X_w^0}{X_n^0}\right)\right] \\ &\times\left[2 + \sum_{j=1}^{n} p_j(j+2)v_p^j\right] = 0 \end{aligned} \tag{14}$$

$$\begin{aligned} \frac{1}{(1 - v_p)^2} - \frac{X_z^0}{(X_w^0 v_p)^2} - \chi_{00}&\left\{1 + k'\left(1 + \frac{1}{X_n^0} - \frac{X_w^0}{X_n^0}\right)\right\} \\ &\times\left\{\sum_{j=1}^{n} p_j j(j+2)v_p^{j-1} = 0\right\} \end{aligned} \tag{15}$$

where X_w^0 and X_z^0 and the weight- and z-average X_i of the original polymer, respectively, the volume fractions of X_i-mer in the two phases at cloud point, $v_{x_{i(1)}}$ and $v_{x_{i(2)}}$, are given by [3, 4]:

$$v_{x_{i(1)}} = v_{x_i}^0 \tag{16a}$$

$$v_{x_{i(2)}} = v_{x_i}^0 \exp(\sigma_i X_i) \tag{16b}$$

where $v_{x_i}^0$ is the X_i-mer volume fraction in the starting solution, and the ratio of the volume of polymer lean phase, $V_{(1)}$, to that of polymer rich phase, $V_{(2)}$, $R(=V_{(1)}/V_{(2)})$ attains infinity, and the polymer-rich phase becomes "cloud particle" (i.e. $V_{(1)} = V$ and $V_{(2)} = 0$; V is the total volume of the system) [3, 4].

In the case of $v_p^0 > v_p^c$, $R = 0$ (i.e. $V_{(1)} = 0$ and $V_{(2)} = V$) is realized at the cloud point and $v_{x_{i(1)}}$ and $v_{x_{i(2)}}$ are given by equations (17a) and (17b) [3, 4]:

$$v_{x_{i(1)}} = v_{x_i}^0 \exp(-\sigma_i X_i) \tag{17a}$$

$$v_{x_{i(2)}} = v_{x_i}^0. \tag{17b}$$

In this case, the polymer-lean phase becomes "cloud particle". $v_{x_i}^0$ [$\equiv v_0(X_i)$] is given as $g_0(X_i)/V$ (here, $g_0(X_i)$ is normalized MWD of the original polymer) and then $v_{x_{i(1)}}$ [equation (16b)] (or $v_{x_{i(2)}}$ [equation (17a)]) is a function of a single variable of σ_i at the cloud point. $v_{p(1)}$, $v_{p(2)}$, $X_{n(1)}$ and $X_{n(2)}$ are calculated by using the following equations:

$$v_{p(1)} = \sum_{i=1}^{m} v_{x_{i(1)}} \tag{18a}$$

$$v_{p(2)} = \sum_{i=1}^{m} v_{x_{i(2)}} \tag{18b}$$

$$X_{n(1)} = \sum_{i=1}^{m} v_{x_{i(1)}} \Bigg/ \left[\sum_{i=1}^{m} (v_{x_{i(1)}}/X_i)\right] \tag{19a}$$

$$X_{n(2)} = \sum_{i=1}^{m} v_{x_{i(2)}} \Bigg/ \left[\sum_{i=1}^{m} (v_{x_{i(2)}}/X_i)\right]. \tag{19b}$$

Hence, at the cloud point, $v_{p(1)}$ and $X_{n(1)}$ (or $v_{p(2)}$ and $X_{n(2)}$) are functions of σ_0 and σ_{01} and moreover, χ_{00}:

$$\chi_{00} = \chi_{00}(\sigma_0, \sigma_{01}). \tag{20}$$

True σ_0 and σ_{01} at the cloud point (hereafter referred to as σ_0^{cp} and σ_{01}^{cp}) can be evaluated self-consistently by resolving the simultaneous equations as follows:

$$\sigma_0(\sigma_0^a, \sigma_{01}^a) - \sigma_0^a = 0 \tag{21}$$

$$\sigma_{01}(\sigma_0^a, \sigma_{01}^a) - \sigma_{01}^a = 0. \tag{22}$$

Equations (21) and (22) are "fundamental equations" for calculation of the CPC. Here, σ_0^a and σ_{01}^a are the assumed σ_0 and σ_{01}, respectively. Substituting σ_0^{cp} and σ_{01}^{cp}, obtained from equations (21) and (22), into equation (20), we obtain the true χ_{00} at cloud point, χ_{00}^{cp}, which can be converted, using equation (5), to T at the cloud point, T^{cp}, and finally the CPC (T^{cp} vs v_p^0 curve) can be calculated.

In the case of $v_p^c < v_p^c$, true $v_{x_{i(1)}}$, $v_{x_{i(2)}}$, $v_{p(1)}$, $v_{p(2)}$, $X_{n(1)}$ and $X_{n(2)}$ at the cloud point, $v_{x_{i(1)}}^{cp}$, $v_{x_{i(2)}}^{cp}$, $v_{p(1)}^{cp}$, $v_{p(2)}^{cp}$, $X_{n(1)}^{cp}$ and $X_{n(2)}^{cp}$ can be obtained:

$$v_{x_{i(1)}}^{cp} = v_{x_i}^0 \tag{16a$'$}$$

$$v_{x_{i(2)}}^{cp} = v_{x_i}^0 \exp(\sigma_i^{cp} X_i) \; (= v_{x_i}^{cp}) \tag{16b$'$}$$

$$v_{p(1)}^{cp} = v_p^0 \tag{18a$'$}$$

$$v_{p(2)}^{cp} = \sum_{i=1}^{m} v_{x_{i(2)}}^{cp} (= v_p^{cp}) \tag{18b$'$}$$

$$X_{n(1)}^{cp} = X_n^0 \tag{19a$'$}$$

$$X_{n(2)}^{cp} = \sum_{i=1}^{m} v_{x_{i(2)}}^{cp} \Bigg/ \left[\sum_{i=1}^{m} (v_{x_{i(2)}}^{cp}/X_i)\right] (= X_n^{cp}) \tag{19b$'$}$$

where $v_{x_i}^{cp}$ [$v_p^{cp}(X_i)$], v_p^{cp} and X_n^{cp} are v_{x_i}, v_p and X_n of polymer partitioned into "cloud particle" respectively.

In the case of $v_p^0 > v_p^c$, $v_{x_{i(1)}}^{cp}$, $v_{x_{i(2)}}^{cp}$, $v_{p(1)}^{cp}$, $v_{p(2)}^{cp}$, $X_{n(1)}^{cp}$ and $X_{n(2)}^{cp}$ can be obtained:

$$v_{x_{i(1)}}^{cp} = v_{x_i}^0 \exp(-\sigma_i^{cp} X_i) \; (= v_{x_i}^{cp}) \tag{17a$'$}$$

$$v_{x_{i(2)}}^{cp} = v_{x_i}^0 \tag{17b$'$}$$

$$v_{p(1)}^{cp} = \sum_{i=1}^{m} v_{x_{i(1)}}^{cp} (= v_p^{cp}) \tag{18a$''$}$$

$$v_{p(2)}^{cp} = v_p^0 \tag{18b$''$}$$

$$X_{n(1)}^{cp} = \sum_{i=1}^{m} v_{x_{i(1)}}^{cp} \Bigg/ \left[\sum_{i=1}^{m} (v_{x_{i(1)}}^{cp}/X_i)\right] (= X_n^{cp}) \tag{19a$''$}$$

$$X_{n(2)}^{cp} = X_n^0. \tag{19b$''$}$$

Substitution of equation (12) into equation (21) yields equation (23) and substitution of equation (13) into equation (22) gives equation (24).

$$\begin{aligned}
&\sigma_0(\sigma_0^a, \sigma_{01}^a) - \sigma_0^a \\
&\quad = (v_{p(1)} - v_{p(2)}) - \left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}}\right) \\
&\qquad - \chi_{00}\Bigg\{2(v_{p(1)} - v_{p(2)}) - (v_{p(1)}^2 - v_{p(2)}^2) \\
&\qquad + \sum_{j=1}^{n} p_j\left[\frac{j+2}{j+1}(v_{p(1)}^{j+1} - v_{p(2)}^{j+1}) - (v_{p(1)}^{j+2} - v_{p(2)}^{j+2})\right]\Bigg\} \\
&\qquad - \chi_{00}k'\Bigg\{\left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}}\right) - \left(\frac{v_{p(1)}^2}{X_{n(1)}} - \frac{v_{p(2)}^2}{X_{n(2)}}\right) \\
&\qquad + \sum_{j=1}^{n} p_j\Bigg[\left(\frac{v_{p(1)}^{j+1}}{X_{n(1)}} - \frac{v_{p(2)}^{j+1}}{X_{n(2)}}\right) \\
&\qquad - \left(\frac{v_{p(1)}^{j+2}}{X_{n(1)}} - \frac{v_{p(2)}^{j+2}}{X_{n(2)}}\right)\Bigg]\Bigg\} - \sigma_0^a = 0
\end{aligned} \tag{23}$$

$$\begin{aligned}
&\sigma_{01}(\sigma_0^a, \sigma_{01}^a) - \sigma_{01}^a \\
&\quad = -k'\chi_{00}\left\{(v_{p(1)} - v_{p(2)}) + \sum_{j=1}^{n} \frac{p_j}{j+1}(v_{p(1)}^{j+1} - v_{p(2)}^{j+1})\right\} \\
&\qquad - \sigma_{01}^a = 0.
\end{aligned} \tag{24}$$

Here, χ_{00} is given by equation (10).

In the case of $k' = 0$ ($k_0 = 0$) and $p_j \neq 0$, we obtain $\sigma_{01} = 0$ [then equation (13) diminishes] and σ_i is independent of X_i and is equal to $\sigma(=\sigma_0)$. Accordingly, variables in equation (23) reduce to the single variable (σ_0) and equation (23) can be transformed into equation (25), which is a fundamental equation of the CPC at $k' = 0$.

$$\begin{aligned}\sigma_0(\sigma_0^a) - \sigma_0^a &= (v_{p(1)} - v_{p(2)}) - \left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}}\right) \\ &- \chi_{00}\left\{2(v_{p(1)} - v_{p(2)}) - (v^2_{p(1)} - v^2_{p(2)}) \right. \\ &+ \sum_{j=1}^{n} p_j \left[\frac{j+2}{j+1}(v^{j+1}_{p(1)} - v^{j+1}_{p(2)}) \right. \\ &\left.\left. - (v^{j+2}_{p(1)} - v^{j+2}_{p(2)})\right]\right\} - \sigma_0^a = 0. \end{aligned} \tag{25}$$

$\chi_{00}(=\chi_0$ at $k' = 0)$ in equation (25) can be estimated by putting $k' = 0$ in equation (10), i.e.

$$\chi_0 = \chi_0(\sigma_a) = \frac{\ln\dfrac{1 - v_{p(1)}}{1 - v_{p(2)}} + [v_{p(1)} - v_{p(2)}] - \left[\dfrac{v_{p(1)}}{X_{n(1)}} - \dfrac{v_{p(2)}}{X_{n(2)}}\right]}{[v^2_{p(2)} - v^2_{p(1)}] + \sum_{j=1}^{n} p_j[v^{j+2}_{p(2)} - v^{j+2}_{p(1)}]}. \tag{26}$$

In the case of $k' = 0$ $(k_0 = 0)$ and $p_j = 0$ $(j = 1 \ldots n)$, equation (25) can be simplified further to

$$\begin{aligned}\sigma_0(\sigma_0^a) - \sigma_0^a &= (v_{p(1)} - v_{p(2)}) - \left[\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(1)}}{X_{n(2)}}\right] \\ &- \chi_{00}\{2[v_{p(1)} - v_{p(2)}] - [v^2_{p(1)} - v^2_{p(2)}]\} - \sigma_0^a = 0 \end{aligned} \tag{27}$$

with

$$\begin{aligned}\chi_0(\sigma_a)(=\chi_{00}) &= \left\{\ln\frac{1 - v_{p(1)}}{1 - v_{p(2)}} + [v_{p(1)} - v_{p(2)}] \right. \\ &\left. - \left[\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}}\right]\right\} \Big/ [v^2_{p(2)} - v^2_{p(1)}]. \end{aligned} \tag{28}$$

Simultaneous, self-consistent equations [equations (21) and (22)], derived by Kamide *et al.* [3, 4], can be easily generalized for determination of the CPC of the system consisting of two multicomponent polymers with different chemical compositions (polymer blend) [17].

Šolc [7] derived an equation which allows direct calculation of the CPC [see equation (42)] for the case of $k' = k_0 = 0$ and $p_j = 0$: When $k' = k_0 = 0$ and $p_j = 0$, equations (6) and (7) become

$$\Delta\mu_0 = \tilde{R}T\left[\ln(1 - v_p) + \left(1 - \frac{1}{X_n}\right)v_p + \chi_{00}v_p^2\right] \tag{6'}$$

$$\begin{aligned}\Delta\mu_{x_i} &= \tilde{R}T\left[\ln v_{x_i} - (X_i - 1) \right. \\ &\left. + X_i\left(1 - \frac{1}{X_n}\right)v_p + X_i\chi_{00}(1 - v_p)^2\right]. \end{aligned} \tag{7'}$$

Substitution of equation (6′) into equation (8) gives equation (29):

$$\begin{aligned}0 &= \ln\frac{1 - v_{p(2)}}{1 - v_{p(1)}} + (v_{p(2)} - v_{p(1)}) \\ &- \left(\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}}\right) + \chi_{00}(v^2_{p(2)} - v^2_{p(1)}). \end{aligned} \tag{29}$$

Substitution of equation (7′) into equation (9) yields equation (30):

$$\begin{aligned}\sigma_0 = -[v_{p(2)} - v_{p(1)}] &+ \left[\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}}\right] \\ &- \chi_{00}\{[1 - v_{p(2)}]^2 - [1 - v_{p(1)}]^2\}. \end{aligned} \tag{30}$$

By eliminating $[v_{p(2)} - v_{p(1)}] - [v_{p(2)}/X_{n(2)} - v_{p(1)}/X_{n(1)}]$ from both equations (29) and (30), equation (31) is obtained:

$$\sigma_0 = \ln\frac{1 - v_{p(2)}}{1 - v_{p(1)}} + 2\chi_{00}[v_{p(2)} - v_{p(1)}]. \tag{31}$$

[Equation (31)] × $[v_{p(1)} + v_{p(2)}]/2$ – [equation (29)] gives a modified two phase-equilibrium condition, given by

$$\begin{aligned}\sigma_0^a\left[\frac{v_{p(1)} + v_{p(2)}}{2}\right] &+ [v_{p(2)} - v_{p(1)}] + \left[\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}}\right] \\ &+ \left[1 - \frac{v_{p(1)} + v_{p(2)}}{2}\right]\ln\frac{1 - v_{p(2)}}{1 - v_{p(1)}} = 0. \end{aligned} \tag{32}$$

In the process of calculation of the CPC equation, Šolc [7] represented the MWD of the polymer partitioning in "cloud particle" $g^{cp}(X_i)$ as

$$g^{cp}(X_i) \equiv \lim_{Q\to 0}\frac{v^{cp}(X_i)}{v_p^0} = g_0(X_i)\exp(K\sigma X_i). \tag{33}$$

Here, in the range of $v_p^0 < v_p^c$

$$Q = 1/R \tag{34a}$$

$$K = +1 \tag{34b}$$

$$v^{cp}(X_i) = v^{cp}_{x_i(2)}[= v^{cp}_{(2)}(X_i)] \tag{34c}$$

and in the range $v_p^0 > v_p^c$,

$$Q = R \tag{35a}$$

$$K = -1 \tag{35b}$$

$$v^{cp}(X_i) = v^{cp}_{x_i(1)}[= v^{cp}_{(1)}(X_i)]. \tag{35c}$$

Thus equation (33) is the same as the expression of equations (16b′) and (17a′).

He defined the kth moment of $g_0(X_i)$ and $g^{cp}(X_i)$, as denoted by μ_k and ν_k, by equations (36) and (37), respectively.

$$\mu_k = \int_0^\infty X_i^k g_0(X_i)\,dX_i \tag{36}$$

$$\nu_k = \int_0^\infty X_i^k g^{cp}(X_i)\,dX_i. \tag{37}$$

Substituting equation (33) into equation (37) and after carrying out a series expansion of the term $\exp(K\sigma X_i)$, we have

$$\nu_k = \int_0^\infty X_i^k g_0(X_i)\sum_{h=0}^{\infty}\frac{(K\sigma X_i)^h}{h!}\,dX_i. \tag{37'}$$

Using equation (36), equation (37′) can be rewritten in the form,

$$\nu_k = \sum_{h=0}^{\infty}\left[\frac{(K\sigma)^h}{h!}\mu_{k+h}\right] \tag{38}$$

$$= \sum_{h=0}^{h_m}\left[\frac{(K\sigma)^h}{h!}\mu_{k+h}\right] \tag{38'}$$

where h_m is the minimum h with which we can judge equation (38′) to be correct. Note that Šolc did not discuss the concrete value of h_m and so we cannot judge to what order we should calculate.

Statistical moments of MWD of the original polymer, μ_k, are expressed by the average degree of polymerization as

$$\mu_{-1} = 1/X_n^0 \tag{39a}$$

$$\mu_0 = 1 \tag{39b}$$

$$\mu_1 = X_w^0 \tag{39c}$$

$$\mu_k = X_w^0 \prod_{q-0}^{k-2} X_{z+q}^0 \quad (k \geqslant 2). \tag{39d}$$

$v_{p(1)}$, $v_{p(2)}$, $X_{n(1)}$ and $X_{n(2)}$ can be expressed in terms of v_p^0, ν_0, ν_{-1}, and μ_{-1}.

For $v_p^0 < v_p^c$

$$v_{p(1)} = v_p^0 \,(= \mu_0/V) \tag{40a}$$

$$v_{p(2)} = v_p^0 \nu_0 \tag{40b}$$

$$X_{n(1)} = 1/\mu_{-1} \tag{40c}$$

$$X_{n(2)} = \nu_0/\nu_{-1}. \tag{40d}$$

For $v_p^0 > v_p^c$

$$v_{p(1)} = v_p^0 \nu_0 \tag{41a}$$

$$v_{p(2)} = v_p^0 (= \mu_0/V) \tag{41b}$$

$$X_{n(1)} = \nu_0/\nu_{-1} \tag{41c}$$

$$X_{n(2)} = 1/\mu_{-1}. \tag{41d}$$

Substituting equations (40a)–(40d) or equations (41a)–(40d) into equation (32), we obtain

$$F(\sigma_0^a) \equiv \frac{K\sigma_0^a(1+\nu_0)}{2} + (\nu_0 - 1) - (\nu_{-1} - \mu_{-1}) + \left(\frac{1}{v_p^0} - \frac{1+\nu_0}{2}\right) \ln \frac{1 - v_p^0 \nu_0}{1 - v_p^0} = 0. \tag{42}$$

Here, as described before, in the range $v_p^0 < v_p^c$, $K = +1$ and in the range $v_p^0 > v_p^c$, $K = -1$. Since μ_{-1} is known, ν_{-1} and ν_0 are functions of σ_0^a only and equation (42) can be expressed by σ_0^a alone. The value of σ_0^a, which satisfies $F(\sigma_0^a) = 0$ for a given initial polymer volume fraction, is σ_0 at the CPC, i.e. σ_0^{cp}.

Equation (42) is Šolc's CPC equation, which is expressed by ν_{-1} and ν_0, in place of $v_{p(1)}$, $v_{p(2)}$, $X_{n(1)}$ and $X_{n(2)}$, used by the method of Kamide *et al.* Substitution of equations (40a)–(40d) or (41a)–(41d) into equation (31) leads to

$$2\chi_{00} v_p^0(\nu_0 - 1) = K\sigma_0 + \ln \frac{1 - v_p^0}{1 - v_p^0 \nu_0}. \tag{43}$$

By putting σ_0^{cp}, obtained from equation (42), into equation (43), we obtain the true χ_{00} at the CPC for given v_p^0.

It can be shown that equation (32) is derived by substituting χ_{00} given by equation (28) into equation (31) and that equation (30) is derived from combination of equations (27) and (28). Equations (42) and (43) can be derived from equations (30)–(32) under the condition of infinitely small volume of the cloud particle. Accordingly, Šolc's CPC equation [equation (42)] and equation (43) are equivalent with Kamide–Matsuda's fundamental equation of the CPC [equation (27)] and equation (28) which are in the case of $k' = k_0 = 0$ and $p_j = 0$.

Recently, Šolc *et al.* [15] derived a generalized "CPC equation" for the quasi-binary system by using the expression of g-parameter, $g(T, v_p)$, which is the polymer–solvent interaction parameter defined by Koningsveld and Staverman [18] in the expression of the Gibbs' free energy change of mixing ΔG:

$$\Delta G = \mathrm{RTL}\left(v_0 \ln v_0 + \sum_{i=1}^{m} \frac{v_{X_i}}{X_i} \ln v_{X_i} + g v_0 v_p\right) \tag{44}$$

where v_0 is the volume fraction of solvent ($= 1 - v_p$) and L, the total number of the lattice points. Parameter g can be expressed by the series expansion of v_p in the form [18]–[20],

$$g = \sum_{j=0}^{n} g_j v_p^j \tag{45}$$

where $g_0 = g_0(T)$ and $g_1, g_2, \ldots g_n$ are the 1st, 2nd, …, nth concentration-dependence parameters. An alternative expression of g is given in the closed form [21, 22]

$$g = \alpha + \frac{\beta}{1 - \gamma v_p} \tag{46}$$

where α and γ are constants and $\beta = \beta(T)$. Between χ and g, the following relation holds [23].

$$\chi = g - (1 - v_p)\frac{\partial g}{\partial v_p} \tag{47}$$

and equations (6) and (7) can be written as [18]

$$\Delta\mu_0 = \tilde{\mathrm{R}}T\left\{\ln(1 - v_p) + \left(1 - \frac{1}{X_n}\right)v_p + \left[g - (1 - v_p)\frac{\partial g}{\partial v_p}\right]v_p^2\right\} \tag{48}$$

$$\Delta\mu_{X_i} = \tilde{\mathrm{R}}T\left[\ln v_{X_i} - (X_i - 1) + X_i\left(1 - \frac{1}{X_n}\right)v_p + X_i\left(g + v_p\frac{\partial g}{\partial v_p}\right)(1 - v_p)^2\right]. \tag{49}$$

Substituting equation (48) into equation (8) leads to

$$0 = \ln\frac{1 - v_{p(2)}}{1 - v_{p(1)}} + [v_{p(2)} - v_{p(1)}] - \left[\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}}\right] + \left\{g_{(2)} - [1 - v_{p(2)}]\frac{\partial g_{(2)}}{\partial v_p}\right\}v_{p(2)}^2 - \left\{g_{(1)} - [1 - v_{p(1)}]\frac{\partial g_{(1)}}{\partial v_p}\right\}v_{p(1)}^2 \equiv G \tag{50}$$

where

$$g_{(1)} \equiv g[T, v_{p(1)}] \tag{51a}$$

$$g_{(2)} \equiv g[T, v_{p(2)}] \tag{51b}$$

$$\frac{\partial g_{(1)}}{\partial v_p} = \left.\frac{\partial g(T, v_p)}{\partial v_p}\right|_{v_p = v_{p(1)}} \tag{51c}$$

$$\frac{\partial g_{(2)}}{\partial v_p} = \left.\frac{\partial g(T, v_p)}{\partial v_p}\right|_{v_p = v_{p(2)}}. \tag{51d}$$

Substituting equation (49) into equation (9), one obtains

$$\sigma_0 = -[v_{\mathrm{p}(2)} - v_{\mathrm{p}(1)}] + \left[\frac{v_{\mathrm{p}(2)}}{X_{n(2)}} - \frac{v_{\mathrm{p}(1)}}{X_{n(1)}}\right] - \left[g_{(2)} + v_{\mathrm{p}(2)}\frac{\partial g_{(2)}}{\partial v_{\mathrm{p}}}\right][1 - v_{\mathrm{p}(2)}]^2 + \left[g_{(1)} + v_{\mathrm{p}(1)}\frac{\partial g_{(1)}}{\partial v_{\mathrm{p}}}\right][1 - v_{\mathrm{p}(1)}]^2. \qquad (52)$$

Combination of equation (50) and equation (52) yields

$$\sigma_0 = \ln\frac{1 - v_{\mathrm{p}(2)}}{1 - v_{\mathrm{p}(1)}} - [g_{(2)} - g_{(1)}] + v_{\mathrm{p}(2)}\left\{2g_{(2)} - [1 - v_{\mathrm{p}(2)}]\frac{\partial g_{(2)}}{\partial v_{\mathrm{p}}}\right\} - v_{\mathrm{p}(1)}\left\{2g_{(1)} - [1 - v_{\mathrm{p}(1)}]\frac{\partial g_{(1)}}{\partial v_{\mathrm{p}}}\right\} \qquad (53)$$

[equation (53)] × $[v_{\mathrm{p}(1)} + v_{\mathrm{p}(2)}]/2$ − [equation (50)] gives

$$\frac{\sigma_0^{\mathrm{a}}[v_{\mathrm{p}(1)} + v_{\mathrm{p}(2)}]}{2} + [v_{\mathrm{p}(2)} - v_{\mathrm{p}(1)}] + \left[\frac{v_{\mathrm{p}(1)}}{X_{n(1)}} - \frac{v_{\mathrm{p}(2)}}{X_{n(2)}}\right] + \left[1 - \frac{v_{\mathrm{p}(1)} + v_{\mathrm{p}(2)}}{2}\right]\ln\frac{1 - v_{\mathrm{p}(2)}}{1 - v_{\mathrm{p}(1)}} - [g_{(2)} - g_{(1)}]\left[v_{\mathrm{p}(1)}v_{\mathrm{p}(2)} - \frac{v_{\mathrm{p}(1)} + v_{\mathrm{p}(2)}}{2}\right] + \frac{v_{\mathrm{p}(1)} - v_{\mathrm{p}(2)}}{2}\left\{\frac{\partial g_{(2)}}{\partial v_{\mathrm{p}}}v_{\mathrm{p}(2)}[1 - v_{\mathrm{p}(2)}] + \frac{\partial g_{(1)}}{\partial v_{\mathrm{p}}}v_{\mathrm{p}(1)}[1 - v_{\mathrm{p}(1)}]\right\} = 0. \qquad (54)$$

Equation (54) represents the two-phase equilibrium conditions.

If we substitute equations (40a)–(40d) or equations (41a)–(41d) into equations (54) and (50), we obtain equations (55) and (56) respectively:

$$F_1(\sigma_0^{\mathrm{a}}) \equiv K\frac{\sigma_0^{\mathrm{a}}(v_0 + 1)}{2} + v_0 - 1 + (\mu_{-1} - v_{-1}) + \left(\frac{1}{v_{\mathrm{p}}^0} - \frac{1 + v_0}{2}\right)\ln\frac{1 - v_{\mathrm{p}}^0 v_0}{1 - v_{\mathrm{p}}^0} - (g^* - g)\left[v_{\mathrm{p}}^0 - \frac{1 + v_0}{2}\right] + \frac{1 - v_0}{2}v_{\mathrm{p}}^0\left[\frac{\partial g^*}{\partial v_{\mathrm{p}}}v_0(1 - v_{\mathrm{p}}^0 v_0) + \frac{\partial g}{\partial v_{\mathrm{p}}}(1 - v_{\mathrm{p}}^0)\right] = 0 \qquad (55)$$

and

$$2gv_{\mathrm{p}}^0(v_0 - 1) + \ln\frac{1 - v_{\mathrm{p}}^0 v_0}{1 - v_{\mathrm{p}}^0} - K\sigma_0^{\mathrm{a}} - (g^* - g)(1 - 2v_{\mathrm{p}}^0 v_0) - v_{\mathrm{p}}^0\left[\frac{\partial g^*}{\partial v_{\mathrm{p}}}v_0(1 - v_{\mathrm{p}}^0 v_0) - \frac{\partial g}{\partial v_{\mathrm{p}}}(1 - v_{\mathrm{p}}^0)\right] = 0 \quad (56)$$

where

$$g = g_{(1)} \qquad (57a)$$

$$g^* = g_{(2)} \qquad (57b)$$

$$\frac{\partial g}{\partial v_{\mathrm{p}}} = \frac{\partial g_{(1)}}{\partial v_{\mathrm{p}}} \qquad (57c)$$

$$\frac{\partial g^*}{\partial v_{\mathrm{p}}} = \frac{\partial g_{(2)}}{\partial v_{\mathrm{p}}} \qquad (57d)$$

for

$$v_{\mathrm{p}}^0 < v_{\mathrm{p}}^{\mathrm{c}}$$

and

$$g = g_{(2)} \qquad (58a)$$

$$g^* = g_{(1)} \qquad (58b)$$

$$\frac{\partial g}{\partial v_{\mathrm{p}}} = \frac{\partial g_{(2)}}{\partial v_{\mathrm{p}}} \qquad (58c)$$

$$\frac{\partial g^*}{\partial v_{\mathrm{p}}} = \frac{\partial g_{(1)}}{\partial v_{\mathrm{p}}} \qquad (58d)$$

for $v_{\mathrm{p}}^0 > v_{\mathrm{p}}^{\mathrm{c}}$. Equation (55) is Šolc's CPC equation when the concentration dependence of g is taken into consideration. If g is independent of polymer concentration, the last two terms disappear, and equation (55) reduces to equation (42) and equation (56) to equation (43). Equation (55) can be solved definitely if v_0 and v_{-1} are evaluated.

When χ is used instead of g, equations (54) and (53) become equations (59) and (60), respectively:

$$\frac{\sigma_0^{\mathrm{a}}[v_{\mathrm{p}(1)} + v_{\mathrm{p}(2)}]}{2} + [v_{\mathrm{p}(2)} - v_{\mathrm{p}(1)}] + \left[\frac{v_{\mathrm{p}(1)}}{X_{\mathrm{n}(1)}} - \frac{v_{\mathrm{p}(2)}}{X_{n(2)}}\right] + \left[1 - \frac{v_{\mathrm{p}(1)} + v_{\mathrm{p}(2)}}{2}\right]\ln\frac{1 - v_{\mathrm{p}(2)}}{1 - v_{\mathrm{p}(1)}} + \frac{\chi_0}{2}[v_{\mathrm{p}(2)} - v_{\mathrm{p}(1)}]^2 \times \left[\sum_{j=1}^{n}\frac{1}{j+1}p_j(v_{\mathrm{p}(2)}^j - v_{\mathrm{p}(1)}^j)\right] = 0 \qquad (59)$$

and

$$\sigma_0^{\mathrm{a}} = \ln\frac{1 - v_{\mathrm{p}(2)}}{1 - v_{\mathrm{p}(1)}} + 2\chi_0\left\{[v_{\mathrm{p}(2)} - v_{\mathrm{p}(1)}] + \frac{1}{2}\sum_{j=1}^{n}p_j\frac{j+2}{j+1}[v_{\mathrm{p}(2)}^{j+1} - v_{\mathrm{p}(1)}^{j+1}]\right\}. \qquad (60)$$

The above derivations of equations (23) and (24) (in the method of Kamide *et al.*) seem rather laborious and complicated and it is not easy to compare the equations in these two methods. This reflects that the calculation of the CPC is, in spite of industrial importance, very tedious, unlike the critical solution point (CSP), binodal and spinodal curves. Figure 1 demonstrates a schematic route for the derivations of the equations. Although both methods are based, as described, on the same theory (i.e. modified Flory–Huggins) combined with Gibbs' two phase equilibrium conditions [equations (8) and (9)], the method of Kamide *et al.* has a more general character than Šolc's from the viewpoint of the consideration of the molecular weight-dependence of the χ-parameter [3].

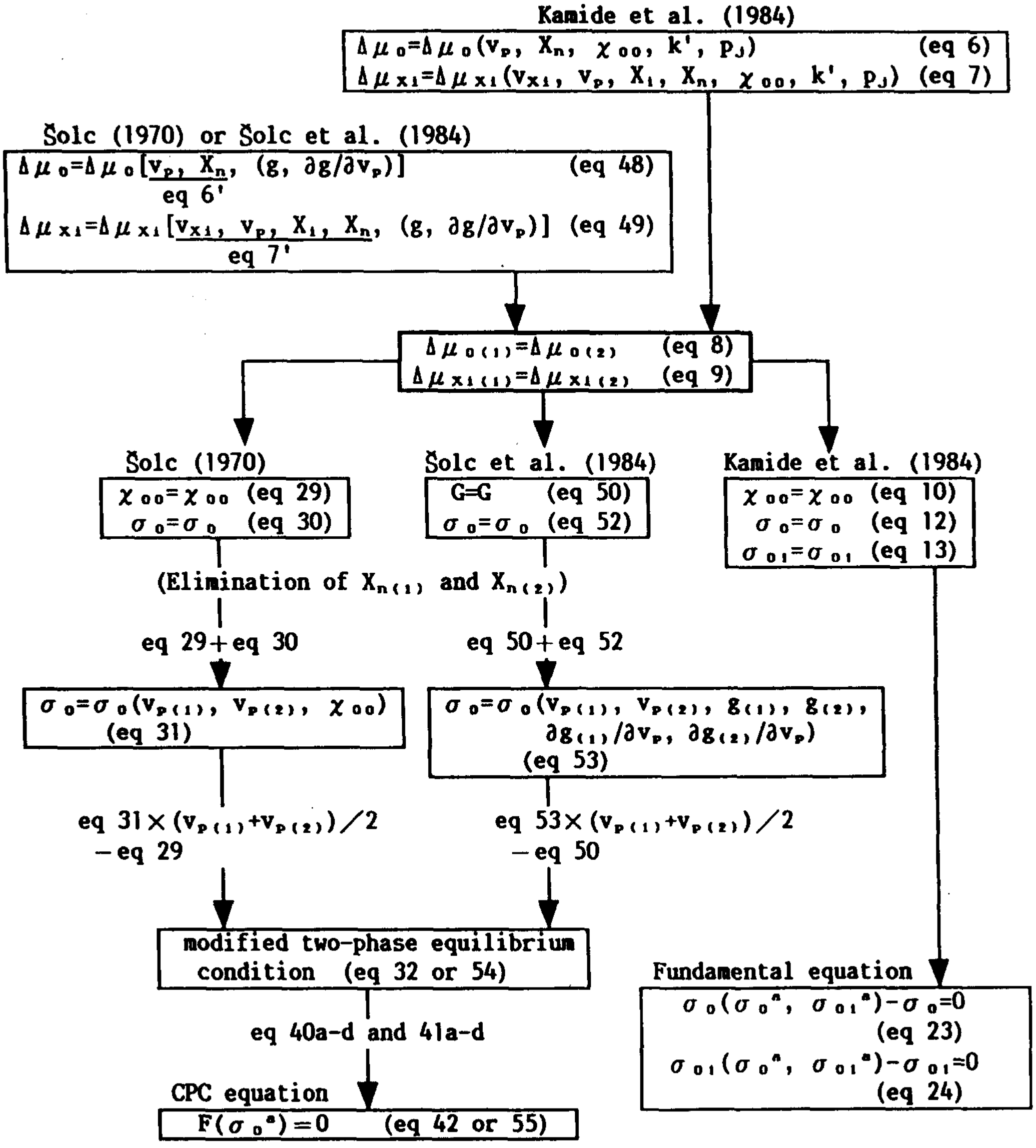

Fig. 1. Schematic route of derivation of fundamental equations [equations (23) and (24)] and CPC equation [equation (42) or equation (55)].

Figure 2 shows an outline of the two methods for calculation of χ_{00}^{cp} in the case of $k' = 0$ and $p_j = 0$. In the Kamide method, we can obtain σ_0^{cp} by putting $v_{\mathrm{p}(1)}$ and $X_{n(1)}$ (or $v_{\mathrm{p}(2)}$ and $X_{n(2)}$) and χ_{00}, all expressed as a function of σ_0^{a} into a fundamental equation. On the other hand, in Šolc's method, ν_{-1} and ν_0 are given as functions of σ_0^{a}. In addition, in the former method $v_{\mathrm{p}(1)}$, $v_{\mathrm{p}(2)}$, $X_{n(1)}$ and $X_{n(2)}$ are estimated from the summation of $v_{x_{i(1)}}$ and $v_{x_{i(2)}}$, which are calculated from equation (16) or (17) with the polymer volume fraction of X_i-mer in the original solution, $v_{x_i}^0$. Šolc's method has a characteristic feature in calculating ν_{-1} and ν_0 from expanding the expression of the statistical moment μ_k of the original MWD [see equation (38)]. Here, μ_k can be calculated from the average X_i of the original polymer only. Additionally, the higher-order average X_i for the polymer with a Schulz–Zimm (SZ) type and Wesslau type MWD can be determined from the number- and weight- average X_i, X_n^0 and X_{w}^0:

SZ type

$$X_{z+q}^0 = (q+2)X_{\mathrm{w}}^0 - (q+1)X_n^0. \tag{61}$$

Wesslau type

$$X_{z+q}^0 = (X_{\mathrm{w}}^0)^{q+2}/(X_n^0)^{q+1}. \tag{62}$$

Therefore, the calculation of ν_k by equation (38) can be readily performed for such polymers. However, for MWD other than the above distributions, the higher-order average X_i cannot be calculated simply from X_n^0 and X_{w}^0, and in these cases, ν_{-1} and ν_0 should be evaluated using equation (37′) and this kind of calculation is of course extremely tedious. In contrast, the method of Kamide *et al.* can apply to any polymer with known MWD.

In the Kamide method, the factors governing the calculation accuracy are the maximum X_i, $X_{\max}$ and the total number of components $N\{N = X_{\max}/DX$; DX, the distance of the adjacent two X_i utilized in the

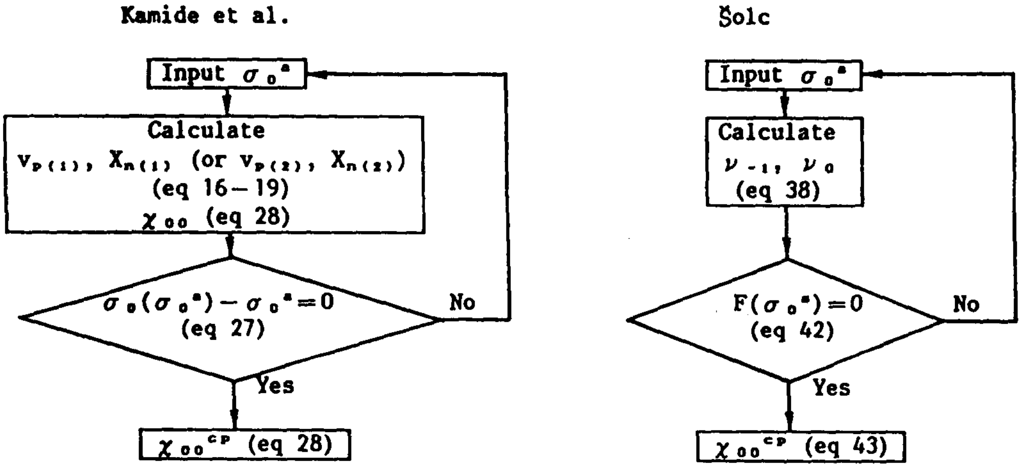

Fig. 2. Outline of two methods for calculation of χ_{00}, for $k' = 0$ and $p_j = 0$.

calculation [see, equations (63) and (64)]}. and in Šolc's method, h_m in equation (38′).

Table 1 shows the comparison of characteristic features of the above two direct methods.

In this article, in order to avoid the above mentioned uncertainty of Šolc's method, we also employed our direct integral procedure [equations (63) and (64)] for estimating v_p^{cp} and X_n^{cp} in Šolc's method [equation (59)] in addition to Šolc's original procedure [infinite series expansion procedure, equation (38′)] and compared the two procedures (see Table 3).

COMPUTER EXPERIMENT

The computer experiments were carried out under the following conditions:

The original polymer was assumed to have the SZ type MWD with $X_w^0 = 2117$ and $X_w^0/X_n^0 = 2.8$, which has the same MWD as employed before for computer and actual (atactic polystyrene) experiments of phase-equilibria [3]. The first and second order concentration dependence parameters were taken as $p_1 = 0.643$ and $p_2 = 0.200$ (this is a combination of p_1 and p_2 experimentally determined for the atactic polystyrene/cyclohexane system) [3] and χ was assumed to be independent of the polymer molecular weight [i.e. $k'(= k_0) = 0$]. In the Kamide method, we regarded that the equation (25) was solved when the condition of $|\sigma(\sigma_0^a) - \sigma_0^a| < 0.2 \times 10^{-9}$ was satisfied; in Šolc's method, we regarded that the equation (59) was solved when the condition of $|F(\sigma_0^a)| < 0.2 \times 10^{-9}$ was satisfied. In the method of Kamide *et al.*, we performed the calculation of v_p^{cp} and X_n^{cp}, given by the following equations, respectively,

$$v_p^{cp} = \sum_{i=1}^{N} v^{cp}(X_i) \cdot DX \tag{63}$$

$$X_n^{cp} = v_p^{cp} \bigg/ \sum_{i=1}^{N} \frac{v^{cp}(X_i)}{X_i} \cdot DX \tag{64}$$

under the condition of $X_{max} = 25000$, $DX = 5$ and accordingly, $N = 5000$ which is a reasonable component number for the SZ type distribution [24]. In Šolc's method, when $|v(h') - v(h' - 1)|$ was smaller than 1.0×10^{-12}, v_k was considered to be determined, i.e. $h' = h_m$ [see equation (38′)]. All calculations were performed using FACOM M360.

RESULTS AND DISCUSSION

Figure 3 shows the left-hand side of equation (25) plotted as a function of σ_0^a. At the point where the left-hand side term becomes zero (denoted by open circle in the figure), the assumed $\sigma_0(\sigma_0^a)$ coincides with the true σ_0^{cp} and that is the solution of equation (25). From equations (14) and (15) we obtain the critical polymer volume fraction $v_p^c = 0.0766$ for the polymer–solvent system. In the range of $v_p^0 < v_p^c$

Table 1. Comparison of characteristic features of two direct methods for estimating CPC proposed for system of multicomponent polymers in a single solvent

	Šolc (1970)	Šolc *et al.* (1984)	Kamide *et al.* (1984)
Theory	Modified F–H	Modified F–H	Modified F–H
Polydispersity	+	+	+
χ-parameter (or g-parameter)			
Concentration dependence	—	+	+
Molecular weight dependence	—	—	+
Fundamental equation	Equation (42) (CPC equation)	Equation (55) (CPC equation)	Equations (23) and (24)
Method of integration	Polynomial method using expansion of exponential (accompanied with many integration)		Direct-integration (Newton–Cotes integration method)

F–H; Flory–Huggins, +; considered, —; not considered.

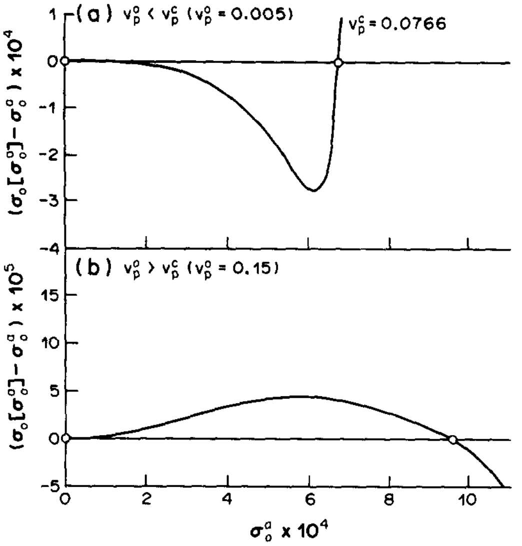

Fig. 3. Plots of main equation $\sigma_0\ (\sigma_0^a) - \sigma_0^a$ vs σ_0^a: original polymer, SZ type distribution ($X_w^0 = 2117$ and $X_w^0/X_n^0 = 2.8$); $p_1 = 0.643$, $p_2 = 0.200$ and $k_0 = 0$. $v_p^c = 0.0766$; (a) $v_p^0 = 0.005$ and (b) $v_p^0 = 0.15$. Open circles correspond to the solution.

(e.g. $v_p^0 = 0.005$), equation (25) is zero at $\sigma_0^a = 0$ and decreases with increase in σ_0^a and attains zero again at $\sigma_0^a = 6.8 \times 10^{-4}$ after passing through a minimum (Fig. 3a). The latter value among the two solutions ($\sigma_0^a = 6.8 \times 10^{-4}$) has evidently physical meaning. In the region $v_p^0 > v_p^c$ (e.g. $v_p^0 = 0.15$), there are two solutions: $\sigma_0^a = 0$ and 9.6×10^{-4} (Fig. 3b) and of course the latter has physical meaning.

Figure 4 shows the left-hand side of equation (25) (i.e. $[\sigma_0(\sigma_0^a) - \sigma_0^a]$), σ_0^a and v_p^0 relations. In the figure the axis of ordinate is the difference $\sigma_0(\sigma_0^a) - \sigma_0^a$ and two abscissa are σ_0^a and v_p^0. Here, v_p^0 was varied from 0 to 0.20 and the open circle is the CSP for this system. $\sigma_0(\sigma_0^a) - \sigma_0^a$ at a given v_p^0 has a minimum without exception in the range $v_p^0 < v_p^c$ and has a maximum in the range $v_p^0 > v_p^c$. Note that in the region near the CPC the $\sigma_0(\sigma_0^a) - \sigma_0^a$ vs σ_0^a curve becomes flat and as a result, unless magnified, the positions of the minimum and maximum of the curve cannot be determined. Although in this case, the error accompanied by the computer simulation becomes sometimes very large, depending on the calculation procedure used, the employment of a double precision method enables us ambiguously to determine the solution, which has physical meaning. The σ_0^{cp} vs v_p^0 curve is continuous, but the polygonal line whose polygonal point agrees well with the CSP, at which the first order differential of σ_0^{cp} with respect to v_p^0, changes sign from negative to positive.

Figure 5 shows the results obtained by solving Šolc's "CPC equation" [in this case equation (59)] with direct integration of v_p^{cp} and X_n^{cp} under the same conditions as those in Fig. 3 (including $n = 2$). In the figure the axis of ordinate $F(\sigma_0^a)$ is defined by the left-hand side of equation (59). As in Fig. 4 the open circle is the CSP and the bold full line is the σ_0^{cp} vs v_p^0 relations, which is, as expected, in excellent coincidence with that estimated by the method of Kamide *et al.*

Table 2 summarizes the σ_0^{cp} and χ_0^{cp} values determined over a wide range of v_p^0 by the method of Kamide *et al.* [equations (25) and (26) with equations (63) and (64)] for the polymer with a SZ type

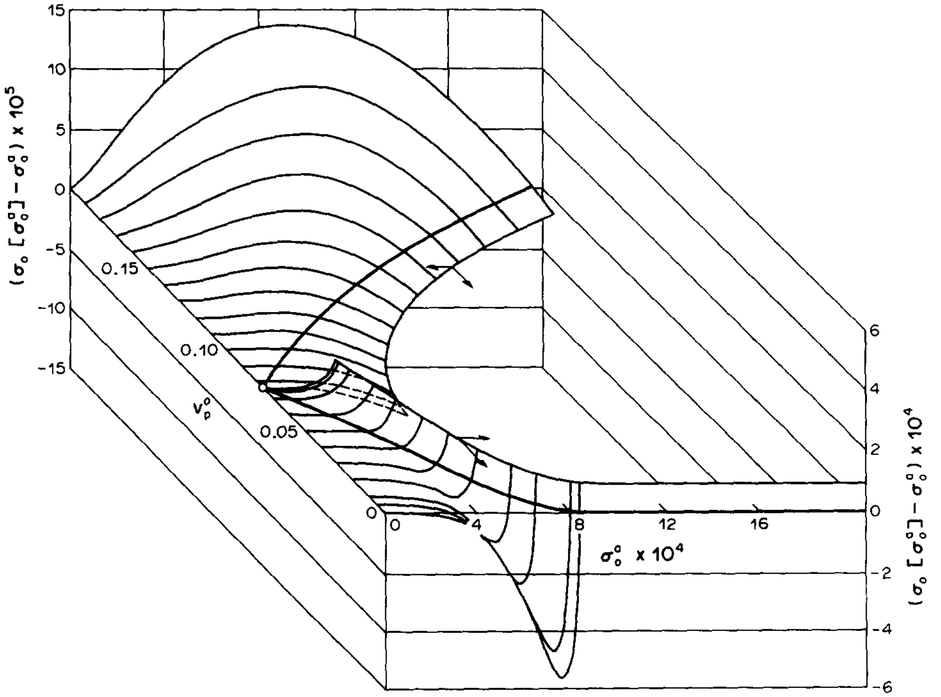

Fig. 4. Three dimensional plots of main equation $\sigma_0\ (\sigma_0^a) - \sigma_0^a$ in $\sigma_0^a - v_p^0$ plane: original polymer, SZ type distribution ($X_x^0 = 2117$ and $X_w^0/X_n^0 = 2.8$); $p_1 = 0.643$, $p_2 = 0.200$ and $k_0 = 0$. Broad solid line, σ_0^{cp} vs v_p^0 curve and open circle, CSP ($v_p^c = 0.0766$).

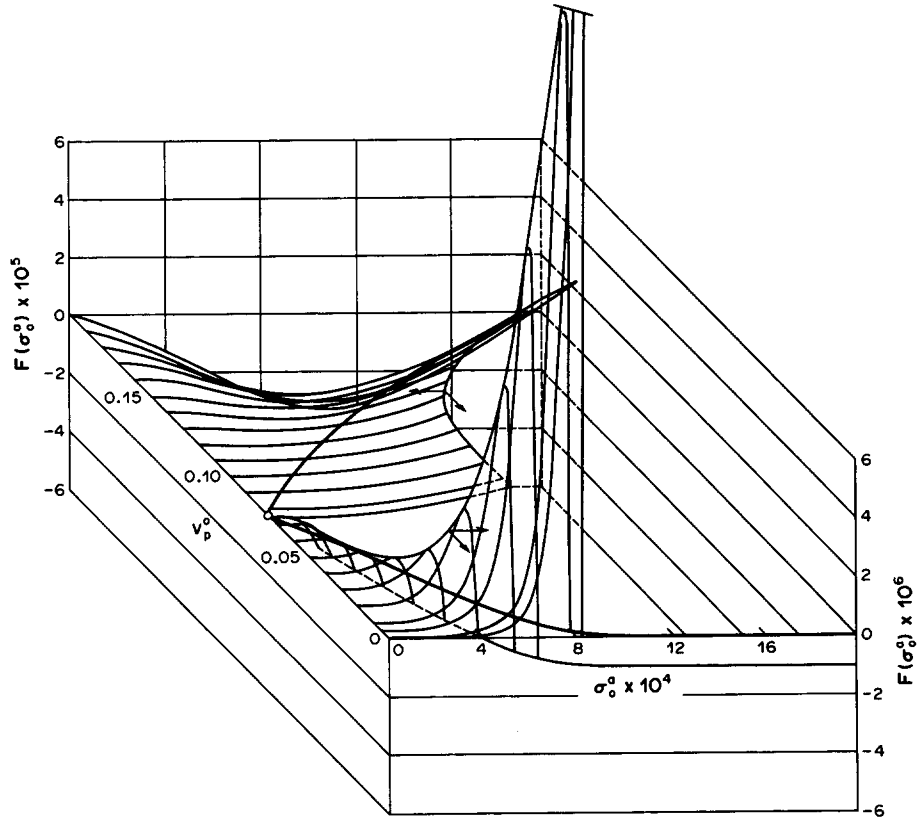

Fig. 5. Three dimensional plots of Šolc's CPC equation in $\sigma_0^a - v_p^0$ plane: original polymer, SZ type distribution ($X_w^0 = 2117$ and $X_w^0/X_n^0 = 2.8$); $p_1 = 0.643$, $p_2 = 0.200$ and $k_0 = 0$. Broad solid line, σ_0^{cp} vs v_p^0 curve and open circle, CSP.

distribution (with $X_w^0 = 2117$ and $X_w^0/X_n^0 = 2.8$) dissolved in a single solvent ($p_1 = 0.643$ and $p_2 = 0.200$) and Table 3 collects σ_0^{cp} and χ_0^{cp} values estimated by both our direct integral procedure [equations (63) and (64)] and polynomial expansion procedure [equation (38′)], which was originally used by Šolc [7], of Šolc's method [equations (55) and (66)] for this polymer–solvent system. $\sigma_0(\sigma_0^{cp}) - \sigma_0^{cp}$ (in Table 2) and $F(\sigma_0^{cp})$ (in Table 3) are also compiled for comparison. In Table 3, h_m values, defined in equation (38′), of ν_{-1} and ν_0 in Šolc's polynomial expansion procedure are also listed. In that procedure, when $v_p^0 \leqslant 0.001$ and $v_p^0 \geqslant 0.14$, ν_{-1} and ν_0 could not be solved because of an overflow error inherent to the computer which was

Table 2. Kamide's σ_0^{cp} and χ_0^{cp} at various initial concentration v_p^0

	Kamide *et al.* [equation (25)]			
v_p^0	$\sigma_0^{cp} \cdot 10^3$	$\sigma_0(\sigma_0^{cp}) \cdot 10^3$	$\sigma_0(\sigma_0^{cp}) - \sigma_0^{cp}$	χ_0^{cp}
0.0005	0.8294649	0.8294649	$-0.4482421 \cdot 10^{-11}$	0.5068843
0.0010	0.7894527	0.7894528	$0.1415837 \cdot 10^{-9}$	0.5066481
0.0050	0.6765704	0.6765704	$0.7176568 \cdot 10^{-10}$	0.5060174
0.0100	0.6083617	0.6083617	$0.5377310 \cdot 10^{-11}$	0.5057250
0.0200	0.5090541	0.5090541	$0.2419572 \cdot 10^{-11}$	0.5054728
0.0300	0.4213474	0.4213474	$0.3975748 \cdot 10^{-11}$	0.5053957
0.0400	0.3351164	0.3351164	$-0.3007202 \cdot 10^{-12}$	0.5054140
0.0500	0.2472484	0.2472484	$-0.5211310 \cdot 10^{-13}$	0.5055011
0.0600	0.1561916	0.1561916	$-0.1052424 \cdot 10^{-13}$	0.5056444
0.0700	0.0608670	0.0608670	$-0.3051619 \cdot 10^{-14}$	0.5058373
0.0750	0.0115759	0.0115759	$0.1039669 \cdot 10^{-15}$	0.5059510
0.0800	0.0396350	0.0396350	$-0.3753067 \cdot 10^{-15}$	0.5060758
0.0900	0.1462143	0.1462143	$-0.2102899 \cdot 10^{-13}$	0.5063576
0.0100	0.2596227	0.2596227	$-0.1265839 \cdot 10^{-13}$	0.5066815
0.0110	0.3807023	0.3807023	$-0.1521097 \cdot 10^{-12}$	0.5070466
0.0120	0.5102899	0.5102899	$-0.2331810 \cdot 10^{-12}$	0.5074529
0.0140	0.7984784	0.7984784	$-0.1421412 \cdot 10^{-12}$	0.5083891
0.0160	1.1315560	1.1315560	$-0.6910338 \cdot 10^{-12}$	0.5094934
0.0180	1.5176370	1.5176370	$0.4824771 \cdot 10^{-12}$	0.5107717
0.0200	1.9657260	1.9657260	$-0.6988389 \cdot 10^{-12}$	0.5122314
0.0220	2.4858450	2.4858450	$-0.1026131 \cdot 10^{-11}$	0.5138814
0.0240	3.0891580	3.0891580	$0.4405498 \cdot 10^{-12}$	0.5157317

Critical volume fraction of polymer, $v_p^c = 0.0766$.

Table 3. Comparison between direct integral procedure's χ_0^{cp} and polynomial expansion procedure's χ_0^{cp} in Šolc's method at various initial concentration v_p^0

	Šolc [equation (59)]							
	Direct integral procedure [equations (63) and (64)]			Polynomial expansion procedure [equation (38′)]				
							h_m [in equation (38′)]	
v_p^0	$\sigma_0^{cp}\cdot 10^3$	$F(\sigma_0^{cp})$	χ_0^{cp}	$\sigma_0^{cp}\cdot 10^3$	$F(\sigma_0^{cp})$	χ_0^{cp}	(v_{-1})	(v_0)
0.0005	0.8294649	$-0.7593535\cdot 10^{-10}$	0.5068843	—	—	—	—	—
0.0010	0.7894527	$-0.1014228\cdot 10^{-9}$	0.5066481	—	—	—	—	—
0.0050	0.6765704	$-0.3773043\cdot 10^{-10}$	0.5060174	0.6518013	$-0.1113997\cdot 10^{-11}$	0.5059439	86	92
0.0100	0.6083617	$-0.1331231\cdot 10^{-10}$	0.5057250	0.5992784	$-0.3376525\cdot 10^{-11}$	0.5057003	86	92
0.0200	0.5090541	$-0.8792652\cdot 10^{-11}$	0.5054728	0.5075786	$0.7825293\cdot 10^{-12}$	0.5054687	51	82
0.0300	0.4213473	$0.1091864\cdot 10^{-11}$	0.5053957	0.4211462	$0.2798365\cdot 10^{-12}$	0.5053949	35	54
0.0400	0.3351163	$0.1809232\cdot 10^{-12}$	0.5054140	0.3351130	$-0.8670955\cdot 10^{-13}$	0.5054139	25	38
0.0500	0.2472481	$0.1244593\cdot 10^{-12}$	0.5055011	0.2472661	$0.2722552\cdot 10^{-13}$	0.5055011	18	28
0.0600	0.1561907	$0.4493058\cdot 10^{-14}$	0.5056444	0.1562089	$-0.4949065\cdot 10^{-15}$	0.5056445	13	19
0.0700	0.0608585	$-0.7216050\cdot 10^{-15}$	0.5058373	0.0608771	$-0.1847419\cdot 10^{-15}$	0.5058374	8	12
0.0750	0.0113003	$0.3773422\cdot 10^{-17}$	0.5059510	0.0113208	$-0.1137062\cdot 10^{-17}$	0.5059511	5	7
0.0800	0.0396627	$-0.4629522\cdot 10^{-17}$	0.5060758	0.0396428	$-0.2542743\cdot 10^{-16}$	0.5060759	7	10
0.0900	0.1462171	$0.1506270\cdot 10^{-14}$	0.5063577	0.1461947	$0.1645313\cdot 10^{-14}$	0.5063578	13	19
0.0100	0.2596240	$0.2325195\cdot 10^{-13}$	0.5066815	0.2595989	$-0.7688479\cdot 10^{-14}$	0.5066516	19	29
0.0110	0.3807031	$-0.6260194\cdot 10^{-13}$	0.5070467	0.3806752	$-0.4512228\cdot 10^{-14}$	0.5070468	29	46
0.0120	0.5102906	$0.1878492\cdot 10^{-13}$	0.5074529	0.5102594	$-0.1049305\cdot 10^{-13}$	0.5074530	52	83
0.0140	0.7984789	$0.1711582\cdot 10^{-12}$	0.5083891	—	—	—	—	—
0.0160	1.1315570	$-0.6531676\cdot 10^{-12}$	0.5094934	—	—	—	—	—
0.0180	1.5176370	$0.2015865\cdot 10^{-12}$	0.5107717	—	—	—	—	—
0.0200	1.9657260	$0.7947712\cdot 10^{-12}$	0.5122314	—	—	—	—	—
0.0220	2.4858460	$-0.1260222\cdot 10^{-11}$	0.5138814	—	—	—	—	—
0.0240	3.0891590	$0.7575863\cdot 10^{-14}$	0.5157317	—	—	—	—	—

—, Calculation is impossible because of overflow.
Critical volume fraction of polymer, $v_p^c = 0.0766$

caused by large σ_0 value, For example, at $v_p^0 = 0.001$ both v_{-1} and v_0 could not converge even at $h = 500$ in equation (38) and finally an overflow error occurred. The same overflow error appeared, e.g. $v_p^0 = 0.14$. On the other hand, in the Kamide method, such an overflow error did not occur under any conditions and accordingly the CPC can be calculated over the whole range of v_p^0. Moreover, the fundamental equation [equation (25)] is expressed in terms of the difference between the true σ_0^{cp} and the assumed σ_0^a and then, at the true cloud point, which was independently determined, σ_0^a coincides completely with σ_0^{cp} as theory requires.

In the range of $0.005 \leqslant v_p^0 \leqslant 0.12$, the difference between σ_0^{cp} by the method of Kamide *et al.* and σ_0^{cp} by Šolc's polynomial expansion method increases remarkably as v_p^0 decreases. For example, at $v_p^0 = 0.005$, Šolc's σ_0^{cp} is *ca* 3.7% smaller than Kamide's σ_0^{cp}. In Fig. 6, the CPC values calculated by both Kamide's method and Šolc's polynomial expansion method are shown as solid and broken lines, respectively: Šolc's CPC is apparently underestimated, compared with the CPC by Kamide in the low v_p^0 region. For example, at $v_p^0 = 0.005$, Šolc's $(\chi_0^{cp} - 1/2)$ is 1.22% smaller than Kamide's $(\chi_0^{cp} - 1/2)$. Considering the high accuracy of σ_0^{cp} value by Kamide's method, we can conclude that the method yields more accurate CPC at low v_p^0 region than Šolc's original method does. If we adopt the direct integration procedure [equations (63) and (64)] in place of the polynomial expansion procedure [equation (38′)] in calculating v_{-1} and v_0 in Šolc's method, we can avoid the error which is contained in the polynomial expansion method. Truly, the difference between σ_0^{cp} by Šolc's methcd with a direct integration and σ_0^{cp} by Kamide method is very small, although the difference amounts to at maximum 3% or less near the CSP, and then χ_0^{cp} values by both methods coincide perfectly.

A merit of Šolc's polynomial expansion method is the relatively short calculation time. Especially near the CSP, h_m is < 10 and then, the calculation time is greatly shortened. For example, in the range of $0.005 \leqslant v_p^0 \leqslant 0.12$, the calculation time of Šolc's

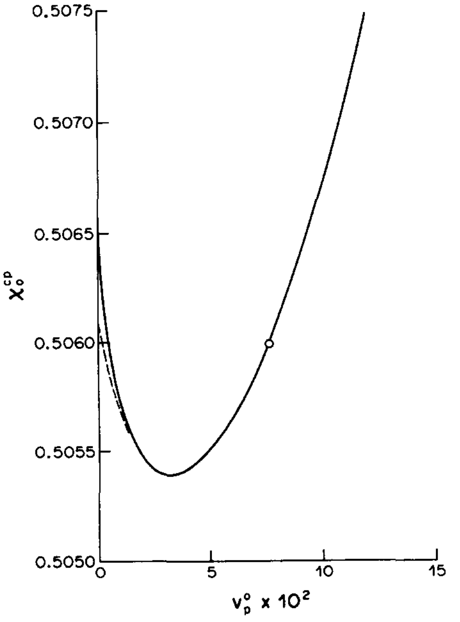

Fig. 6. Comparison of CPC obtained by the method of Kamide *et al.* (solid line) and by Šolc's method (broken line): original polymer, SZ type distribution ($X_w^0 = 2117$, $X_w^0/X_n^0 = 2.8$) and $p_1 = 0.643$, $p_2 = 0.200$, $k' = 0$. Open circle, CSP.

method is < /10 of that of Kamide's method. But the following points should be noted: Kamide's method gives v^{cp} (X_i), accordingly, X_w^{cp} and X_z^{cp} concurrently, as the result of the calculation. In contrast, Šolc's method needs independent calculations of not only v^{cp} (X_i) but also $v_0(X_i)$, if the MWD of the polymer partitioned in "cloud particle" is required. Much less, when X_w^{cp} and X_z^{cp} are needed, we must calculate progression of ν_1 and ν_2. In addition, if we try to solve the overflow problem of ν_{-1} and ν_0 for large σ_0, the computation time becomes very long and accuracy of calculation is unavoidably reduced.

When the accurate CPC calculation is needed over a whole range of v_p^0, the method of Kamide *et al.* is strongly recommended. If CPC calculation only near the CSP is required, Šolc's method is sufficient.

Figure 7 shows the v_p^0 dependence of σ_0^{cp}, the concentration of cloud particle v_p^{cp} and χ_0^{cp}, determined by Kamide and Matsuda's method [3, 4] Here, the open circle is the CSP and the chain line (in Fig. 7b) denotes the $v_p^{cp} = v_p^0$ line. The σ_0^{cp} vs v_p^0 curve is continuous (as shown in Fig. 3) even at the CSP at which σ_0^{cp} becomes zero (Fig. 7a). We cannot expect any preferential partitioning of polymer molecules based on the difference in molecular weight. In contrast v_p^{cp} decreases continuously and monotonously with increasing v_p^0 (Fig. 7b), and coincides at the CSP with v_p^0. The χ_0^{cp} vs v_p^0 relation is also continuous at the CSP (Fig. 7c).

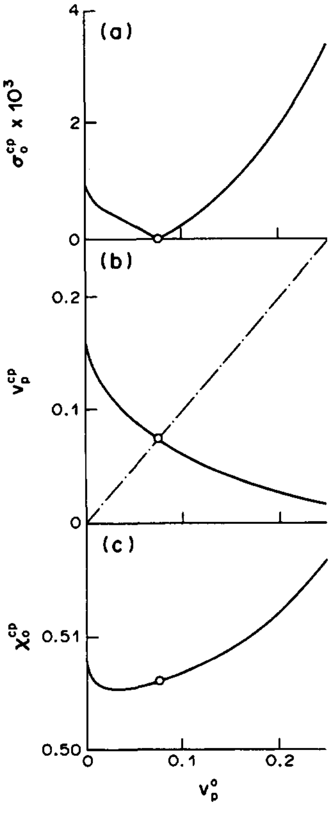

Fig. 7. The partition coefficient, the polymer volume fraction, and χ_0 – parameter at true cloud point, σ_0^{cp}, v_p^{cp} and χ_0^{cp}, plotted as a function of v_p^0: original polymer, SZ type distribution ($X_w^0 = 2117$ and $X_w^0/X_n^0 = 2.8$); $p_1 = 0.643$, $p_2 = 0.200$ and $k_0 = 0$. Open circles correspond to CSP ($v_p^c = 0.0766$).

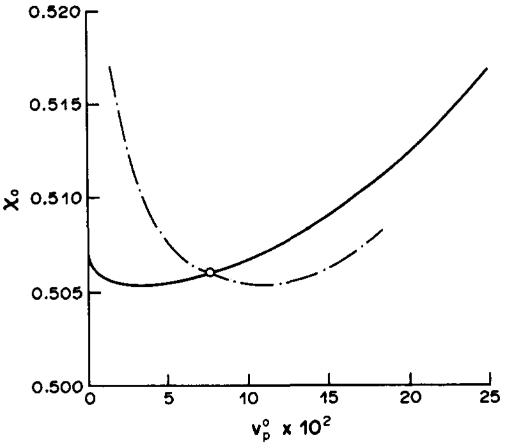

Fig. 8. CPC (solid line) and shadow curve (chain line): original polymer, SZ type distribution ($X_w^0 = 2117$ and $X_w^0/X_n^0 = 2.8$); $p_1 = 0.643$, $p_2 = 0.200$ and $k_0 = 0$. Open circle, CSP.

After estimating the shadow curve from Fig. 7b and overlapping with the CPC (Fig. 7c), Fig. 8 is obtained. In Fig. 8 the chain line is the shadow curve (χ_0^{cp} vs v_p^{cp}), the full line is the CPC (χ_0^{cp} vs v_p^0 curve) and the open circle is the CSP. The shadow curve is also continuous at the CSP. The CPC and shadow curve always have downward curvature (i.e. $d^2\chi_0^{cp}/dv_p^2 > 0$ and $d^2\chi_0^{shadow}/dv_p^2 > 0$) and any depression around the CSP cannot be observed. This is really characteristic of a polymer having a SZ type MWD dissolved in a solvent with molecular weight independent χ. In contrast, the CPC has the depression at the CSP for the same system as shown in Fig. 16 of Ref. [3].

We can easily draw the limiting tie-line (i.e. tie-line for $\chi_0 = \chi_0^{cp}$) in Fig. 8 at any initial concentration v_p^0. The polymer concentration on the shadow curve, in other words the concentration of the polymer partitioned in "cloud particle", must be important information enabling us to predict the polymer solid structure formed by the two phase separation.

Summarizing, the two direct methods of calculating the cloud point curve (i.e. those of Kamide *et al.* and Šolc) were shown to be based on the same theoretical principle and it was made clear that the main difference between the methods is in the procedure of integration of v_p^{cp} and X_n^{cp} and that the direct integration method of Kamide *et al.* has more general character than Šolc's polynomial expansion method from the viewpoint of easy and accurate calculation of any types of MWD without limitation.

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