

## Phase Equilibria of Quasi-Ternary Systems Consisting of Multicomponent Polymers in a Binary Solvent Mixture IV. Spinodal Curve and Critical Solution Point

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**ABSTRACT:** An attempt was made to construct a quasi-ternary system consisting of multicomponent polymers dissolved in binary solvent mixture (solvents 1 and 2) to derive the equations of spinodal and neutral equilibrium conditions and to clarify the effects of three thermodynamic interaction  $\chi$ -parameters between solvent 1 and solvent 2, solvent 1 and polymer, and solvent 2 and polymer ( $\chi_{12}$ ,  $\chi_{13}$ , and  $\chi_{23}$ ) and the weight-average degree of polymerization  $X_w^0$  and the ratio of  $X_w^0$  to the number-average degree of polymerization  $X_n^0$  of the original polymer on the spinodal curve and the critical points (the critical concentration  $v_p^c$ ) calculated from the above mentioned equations. The cloud point curve was also calculated indirectly from coexisting curve evaluated according to a method in our previous papers and constant  $v_p^s$  (starting polymer volume fraction) line. The cross point of a constant  $v_p^s$  line and a coexisting curve is a cloud point. The cloud point curve thus calculated was confirmed to coincide, as theory predicted with the spinodal curve, at the critical point.  $v_p^c$  decreases with an increase in  $\chi_{12}$ ,  $\chi_{23}$ , and  $X_w^0$ , and increases with an increase in  $\chi_{13}$  and  $X_w^0/X_n^0$ .

**KEY WORDS** Quasi-Ternary Polymer Solution / Spinodal Curve / Critical Solution Point /  $\chi$ -Parameter / Cloud Point Curve / Average Degree of Polymerization /

Recently, Kamide, Matsuda and their collaborators proposed a theoretical method for calculating a cloud point curve (CPC) and critical solution point (CSP) of a quasi-binary solution consisting of multicomponent polymers in a single solvent on the basis of the polydispersity of the original polymer and the concentration- and molecular weight-dependences of the polymer-solvent thermodynamic interaction parameter  $\chi$ .<sup>1</sup> They disclosed the effects of the concentration dependence of  $\chi$  and the molecular characteristics (*i.e.*, the weight-average and the breadth of the molecular weight distribution (MWD)) on CPC and CSP in a systematic manner. Koningsveld and Staverman<sup>2</sup> also derived for

a quasi-binary system a rigorous expression of the critical point, where the concentration dependence of  $\chi$ -parameter was considered along with the polydispersity of polymer and proposed a method for estimating the concentration dependent parameter of  $\chi$  using the experimental CSP data. But they did not investigated systematically CSP for the system. Kamide and Matsuda<sup>3-5</sup> established a theory and a computer simulation technique, based on the theory, of the phase equilibrium of a quasi-ternary system consisting of multicomponent polymers dissolved in binary solvent mixture. They studied (i) a suitable choice of solvent 1 and solvent 2 (three thermodynamic interaction parameters between solvent 1-2

( $\chi_{12}$ ), polymer-solvent 1 ( $\chi_{13}$ ) and polymer-solvent 2 ( $\chi_{23}$ ),<sup>3</sup> (ii) role of initial concentration and relative amounts of polymers dissolved in two phases,<sup>4</sup> (iii) effects of average molecular weight and MWD of the original polymer,<sup>5</sup> and (iv) effects of concentration dependence of three thermodynamic interaction parameters<sup>6</sup> for two-phase equilibrium of quasi-ternary systems. As early as 1949, Scott<sup>7</sup> derived equations giving CSP of a ternary system consisting monodisperse polymer, solvent and non-solvent. Two equations derived by Scott for spinodal and so-called neutral equilibrium conditions (*i.e.*, eq 25 and 26 in ref 7) are, as will be discussed in more detail, not thermodynamically consistent and in particular the latter equation is incorrect. Kurata<sup>8</sup> proposed general and strict equations of CSP of the mixed solvent system including a ternary system, consisting of the monodisperse polymer dissolved in a binary solvent mixture. All the studies made by Tompa,<sup>9</sup> Bamford and Tompa,<sup>10</sup> Okamoto,<sup>11</sup> and Nakagaki and Sunada,<sup>12</sup> who put their theoretical starting point on the Scott equations, are obviously not theoretically rigorous. Of course, no theoretical study has ever been published on CPC and CSP of quasi-ternary system.

In this article, an attempt is made to establish a theory of CSP of quasi-ternary system, studying the effects of  $\chi_{12}$ ,  $\chi_{13}$ , and  $\chi_{23}$  and that of  $X_w^0$  and  $X_w^0/X_n^0$  of the original polymer on CSP and to propose a method for calculating indirectly CPC for the system, as intercepts of line of constant starting concentration  $v_p^0 (= V_3^0/(V_1^0 + V_3^0))$ ;  $V_1^0$ , volume of solvent 1,  $V_3^0$ , volume of polymer) with a coexisting curve theoretically obtained.

## THEORETICAL BACKGROUND

The spinodal for quasi-ternary system is given by

$$|\Delta G'| \equiv \begin{vmatrix} \Delta \bar{G}'_{NN} & \Delta \bar{G}'_{N1} & \cdots & \Delta \bar{G}'_{Nm} \\ \Delta \bar{G}'_{1N} & \Delta \bar{G}'_{11} & \cdots & \Delta \bar{G}'_{1m} \\ \Delta \bar{G}'_{2N} & \Delta \bar{G}'_{21} & \cdots & \Delta \bar{G}'_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ \Delta \bar{G}'_{mN} & \Delta \bar{G}'_{m1} & \cdots & \Delta \bar{G}'_{mm} \end{vmatrix} = 0 \quad (1)$$

and the Gibbs free energy change of mixing per unit volume,  $\Delta G'$  is given by

$$\Delta G' = v_1 \left( \frac{\Delta \mu_1}{V_0} \right) + v_2 \left( \frac{\Delta \mu_2}{V_0} \right) + \sum_{i=1}^m v_{x_i} \left( \frac{\Delta \mu_{x_i}}{X_i V_0} \right) \quad (2)$$

and  $\Delta \bar{G}'_{ij}$  is defined by eq 3

$$\Delta \bar{G}'_{ij} = \left( \frac{\partial^2 \Delta G'}{\partial v_{x_i} \partial v_{x_j}} \right)_{T, P, v_{x_k}} \quad (i, j = N, 1, 2, \dots, m; k \neq i, j) \quad (3)$$

$V_0$  is the molar volume of solvents 1 and 2,  $v_1$  and  $v_2$ , the volume fraction of solvents 1 and 2,  $v_{x_i}$  ( $i = 1, 2, \dots, m$ ), the volume fraction of  $X_i$ -mer,  $\Delta \mu_1$ ,  $\Delta \mu_2$ , and  $\Delta \mu_{x_i}$ , the chemical potential of solvent 1, solvent 2, and  $X_i$ -mer,  $m$ , the total number of the components making up the polymer. In eq 1 and 3, the suffix  $N$  denotes non-solvent (in this case, solvent 2) in order to distinguish the component of the polymer ( $i = 2$ ) and the suffixes  $T$  and  $P$  are temperature and pressure respectively.

The neutral equilibrium condition is expressed by eq 4.

$$|\Delta G''| \equiv \begin{vmatrix} \frac{\partial |\Delta G'|}{\partial v_2} & \frac{\partial |\Delta G'|}{\partial v_{x_1}} & \frac{\partial |\Delta G'|}{\partial v_{x_2}} & \cdots & \frac{\partial |\Delta G'|}{\partial v_{x_m}} \\ \Delta \bar{G}'_{1N} & \Delta \bar{G}'_{11} & \Delta \bar{G}'_{12} & \cdots & \Delta \bar{G}'_{1m} \\ \Delta \bar{G}'_{2N} & \Delta \bar{G}'_{21} & \Delta \bar{G}'_{22} & \cdots & \Delta \bar{G}'_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Delta \bar{G}'_{mN} & \Delta \bar{G}'_{m1} & \Delta \bar{G}'_{m2} & \cdots & \Delta \bar{G}'_{mm} \end{vmatrix} = 0 \quad (4)$$

We assume that (a) three thermodynamic interaction parameters  $\chi_{ij}$  ( $i < j$ , and  $i, j = 1, 2, 3$ ) are independent of polymer molecular weight and concentration, (b) the molar volume of solvent 1 is the same as that of solvent 2, (c) polymer, solvents 1 and 2 are volumetrically additive, and (d) the densities of polymer, solvents 1 and 2 are the same (= unity).

Then  $\Delta\mu_1$ ,  $\Delta\mu_2$ , and  $\Delta\mu_{x_i}$  in eq 2 are given by<sup>3</sup>

$$\Delta\mu_1 = \tilde{R}T \left[ \ln v_1 + \left(1 - \frac{1}{X_n}\right)v_p + \chi_{12}v_2(1-v_1) + \chi_{13}v_p(1-v_1) - \chi_{23}v_2v_p \right] \quad (5)$$

$$\Delta\mu_2 = \tilde{R}T \left[ \ln v_2 + \left(1 - \frac{1}{X_n}\right)v_p + \chi_{12}v_1(1-v_2) + \chi_{23}v_p(1-v_2) - \chi_{13}v_1v_p \right] \quad (6)$$

$$\Delta\mu_{x_i} = \tilde{R}T \left[ \ln v_{x_i} - (X_i - 1) + X_i \left(1 - \frac{1}{X_n}\right)v_p + X_i \left\{ \chi_{13}v_1(1-v_p) + \chi_{23}v_2(1-v_p) - \chi_{12}v_1v_2 \right\} \right] \quad (7)$$

where  $\tilde{R}$  is the gas constant,  $v_p$ , the polymer volume fraction ( $= \sum_{i=1}^m v_{x_i}$ ). Substitution of eq 5, 6, and 7 into eq 2 yields

$$\Delta\bar{G}' = \left(\frac{\tilde{R}T}{V_0}\right) \left[ v_1 \ln v_1 + v_2 \ln v_2 + \sum_{i=1}^m \frac{v_{x_i}}{V_0} \ln v_{x_i} + \chi_{12}v_1v_2 + \chi_{13}v_1v_p + \chi_{23}v_2v_p \right] \quad (8)$$

From eq 3 and 8, we obtain

$$\left(\frac{V_0}{\tilde{R}T}\right) \Delta\bar{G}'_{ij} = \frac{1}{v_1} - 2\chi_{13} \equiv M \quad (\text{for } i \neq j, i \text{ and } j \neq N) \quad (9a)$$

$$\left(\frac{V_0}{\tilde{R}T}\right) \Delta\bar{G}'_{ij} = M + \chi_{13} + \chi_{23} - \chi_{12} \equiv M + K \quad (\text{for } i \neq j, i \text{ or } j = N) \quad (9b)$$

$$\left(\frac{V_0}{\tilde{R}T}\right) \Delta G_{ij} = M + \frac{1}{v_2} + 2(\chi_{13} - \chi_{12}) \equiv M + U \quad (\text{for } i = j = N) \quad (9c)$$

$$\left(\frac{V_0}{\tilde{R}T}\right) G_{ij} = M + \frac{1}{X_i v_{x_i}} \equiv M + M_i \quad (\text{for } i = j \neq N) \quad (9d)$$

Combining eq 9a–9d with eq 1 and 4, we finally obtain eq 10 and 11, respectively (see Appendix A) to give the composition of CSP.

$$\left(\frac{1}{v_1} + \frac{1}{v_2} - 2\chi_{12}\right) \left(\frac{1}{v_p X_w^0} + \frac{1}{v_1} - 2\chi_{13}\right) - \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12}\right)^2 = 0 \quad (10)$$

$$\left[ \frac{1}{v_p^2 X_w^0} \left(\frac{1}{v_1^2} - \frac{1}{v_2^2}\right) + \frac{1}{v_1^2} \left(\frac{1}{v_2} - 2\chi_{23}\right) - \frac{1}{v_2^2} \left(\frac{1}{v_1} - 2\chi_{13}\right) \right] \left(\frac{1}{v_p X_w^0} + \frac{1}{v_1} - 2\chi_{13}\right) - \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12}\right) \left[ \frac{1}{v_1^2} \left(\frac{1}{v_2} - 2\chi_{23}\right) + \frac{1}{v_1^2 v_p X_w^0} + \frac{X_z^0}{v_p X_w^0} \left\{ \frac{1}{v_1 v_2} - \frac{2\chi_{13}}{v_2} - \frac{2\chi_{23}}{v_1} + 2(\chi_{12}\chi_{13} + \chi_{13}\chi_{23} + \chi_{23}\chi_{12}) - (\chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2) \right\} \right] = 0 \quad (11)$$

Note that the following relation holds

$$v_1 + v_2 + v_p = 1 \quad (12)$$

Equations 10 and 11 are evidently symmetrical with respect to the exchange of solvents 1 and 2 (see Appendix B). By solving simultaneous equations (eq 10–12) with given  $X_w^0$  and  $X_z^0$  of the original polymer and  $\chi_{12}$ ,  $\chi_{13}$ , and  $\chi_{23}$ , we can calculate  $v_1$ ,  $v_2$ , and  $v_p$  at critical point, referred to as  $v_1^c$ ,  $v_2^c$  and  $v_p^c$ .

The conditions of spinodal and neutral equilibrium for monodisperse polymer with  $X$  in binary solvent mixture are given by eq 1' and eq 4', respectively.

$$|\Delta G'| \equiv \begin{vmatrix} \Delta \bar{G}_{NN} & \Delta \bar{G}_{Nx} \\ \Delta \bar{G}_{1N} & \Delta \bar{G}_{xx} \end{vmatrix} = 0 \quad (1')$$

$$|\Delta G''| \equiv \begin{vmatrix} \frac{\partial |\Delta G'|}{\partial v_2} & \frac{\partial |\Delta G'|}{\partial v_x} \\ \Delta \bar{G}'_{xN} & \Delta \bar{G}'_{xx} \end{vmatrix} = 0 \quad (4')$$

where  $v_x$  is the volume fraction of the  $X$ -mer. From eq 1' and 4' we obtain eq 10' and 11', respectively.

$$\left(\frac{1}{v_1} + \frac{1}{v_2} - 2\chi_{12}\right) \left(\frac{1}{v_x X} + \frac{1}{v_1} - 2\chi_{13}\right) - \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12}\right)^2 = 0 \quad (10')$$

$$\left[ \frac{1}{v_x X} \left(\frac{1}{v_1^2} - \frac{1}{v_2^2}\right) + \frac{1}{v_1^2} \left(\frac{1}{v_2} - 2\chi_{23}\right) - \frac{1}{v_2^2} \left(\frac{1}{v_1} - 2\chi_{13}\right) \right] \left[ \frac{1}{v_x X} + \frac{1}{v_1} - 2\chi_{13} \right] - \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12}\right) \left[ \frac{1}{v_1^2} \left(\frac{1}{v_2} - 2\chi_{23}\right) + \frac{1}{v_1^2 v_x X} + \frac{1}{v_x} \left\{ \frac{1}{v_1 v_2} - \frac{2\chi_{13}}{v_2} - \frac{2\chi_{23}}{v_1} + 2(\chi_{12}\chi_{13} + \chi_{13}\chi_{23} + \chi_{23}\chi_{12}) - (\chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2) \right\} \right] = 0 \quad (11')$$

In deriving eq 10' and 11', reduced eq 2 to the case of a monodisperse polymer (*i.e.*,  $m=1$ ) was employed. Equations 10 and 11 reduce to eq 10' and 11' by putting  $X_w = X_z = X$  and  $v_p = v_x$ , and are equivalent to Kurata's eq (2, 3, 15) and (2, 3, 16) in ref 8. In addition, eq 10' coincides completely with eq 26 in ref 7 (Scott's equation). An alternative equation of neutral equilibrium conditions, consistent with eq 1', is given in the form,

$$\begin{vmatrix} \frac{\partial |\Delta G'|}{\partial v_2} & \frac{\partial |\Delta G'|}{\partial v_x} \\ \Delta \bar{G}'_{NN} & \Delta \bar{G}'_{Nx} \end{vmatrix} = 0 \quad (4'')$$

Though eq 4'' is consistent with 4', eq 4'' cannot be generalized to one similar to eq 4 for multicomponent polymers. Replacing one of the polymer component rows eq 1 by a row vector ( $\partial |\Delta G'| / \partial v_i$ ) ( $i = N, 1, 2, \dots, m$ ;  $v_{xN} = v_2$ ), we cannot obtain the equation equivalent to eq 11 (eq A-6). Curiously, at least for us, Scott's equation (eq 27)<sup>7</sup> can be derived from neither eq 4' nor eq 4''.

Scott considered the line tangent of the phase boundary (in our vocabulary, coexisting curve for multicomponent polymer-solvent 1-solvent 2 system) at a critical point as a limiting tie line (this approximation is unconditionally acceptable for monodisperse polymer solutions) and introduced a variable  $q$  in the line and determined the critical point (plait point by his expression) by solving the following equations:

$$\frac{d^2 \Delta F}{dq^2} = 0 \quad (13)$$

$$\frac{d^3 \Delta F}{dq^3} = 0 \quad (14)$$

with

$$\Delta F = x_1 \Delta \mu_1 + x_2 \Delta \mu_2 + x_x \Delta \mu_x \quad (15)$$

$\Delta F$  is the partial molar Gibbs free energy (in this case,  $\Delta F = V_0 \Delta \bar{G}'$  because the molar volumes of solvents 1 and 2 and the segment of polymer are the same),  $x_1$ ,  $x_2$ , and  $x_x$  are the mole fractions of solvent 1, 2, and  $X$ -mer. Using Gibbs-Duhem relations, Scott converted eq 13 and 14 to eq 16 and 17, respectively.<sup>7</sup>

$$\frac{d\Delta\mu_1}{dq} = 0, \quad \frac{d\Delta\mu_2}{dq} = 0, \quad \frac{d\Delta\mu_x}{dq} = 0 \quad (16)$$

$$\left(\frac{dx_1}{dq}\right) \left(\frac{d^2\Delta\mu_1}{dq}\right) + \left(\frac{dx_2}{dq}\right) \left(\frac{d^2\Delta\mu_2}{dq}\right) + \left(\frac{dx_x}{dq}\right) \left(\frac{d^2\Delta\mu_x}{dq}\right) = 0 \quad (17)$$

In addition, eq 26 and 27 of ref 7 are said to be derived from eq 16 and 17, but unfortunately we could not follow. As mentioned before, eq 26 and 27 of ref 7 are thermodynamically inconsistent; in other words, eq 27 cannot be theoretically given although eq 26 is correct. The critical points calculated erroneously using Scott's equations (eq 26 and 27 of ref 7) locate precisely on the spinodal curve because eq 26 giving a spinodal curve is correct, but its  $v_p^c$  is some 20–40% higher than the correct  $v_p^c$ , evaluated by our rigorous method (for example, see Figure 5).

### COMPUTER EXPERIMENT

First, put the left-hand side terms in eq 10 and 11 with  $A$  and  $B$ , respectively and express  $v_2$  in terms of  $v_1$  and  $v_p$  using eq 12, we obtain

$$A \equiv \left( \frac{1}{v_1} + \frac{1}{1-v_1-v_p} - 2\chi_{12} \right) \times \left( \frac{1}{v_p X_w^0} + \frac{1}{v_1} - 2\chi_{13} \right) - \left( \frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12} \right)^2 = 0 \quad (18)$$

$$B \equiv \left[ \frac{1}{v_p X_w^0} \left( \frac{1}{v_1^2} - \frac{1}{(1-v_1-v_p)^2} \right) + \frac{1}{v_1^2} \left( \frac{1}{v_2} - 2\chi_{23} \right) - \frac{1}{(1-v_1-v_p)^2} \left( \frac{1}{v_1} - 2\chi_{13} \right) \right] \times \left[ \frac{1}{v_p X_w^0} + \frac{1}{v_1} - 2\chi_{13} \right] - \left( \frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12} \right) \times \left[ \frac{1}{v_1^2} \left( \frac{1}{1-v_1-v_p} - 2\chi_{23} \right) + \frac{1}{v_2^2 v_p X_w^0} + \frac{X_z^0}{v_p X_w^0} \left\{ \frac{1}{v_1(1-v_1-v_p)} - \frac{2\chi_{13}}{1-v_1-v_p} - \frac{2\chi_{23}}{v_1} + 2(\chi_{12}\chi_{13} + \chi_{13}\chi_{23} + \chi_{23}\chi_{12}) - (\chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2) \right\} \right] = 0 \quad (19)$$

If  $\chi_{12}$ ,  $\chi_{13}$ ,  $\chi_{23}$ ,  $X_w^0$  and  $X_z^0$  are known in advance, both  $A$  and  $B$  are functions of  $v_1$  and  $v_p$ :

$$A = A(v_1, v_p) = 0 \quad (20)$$

$$B = B(v_1, v_p) = 0 \quad (21)$$

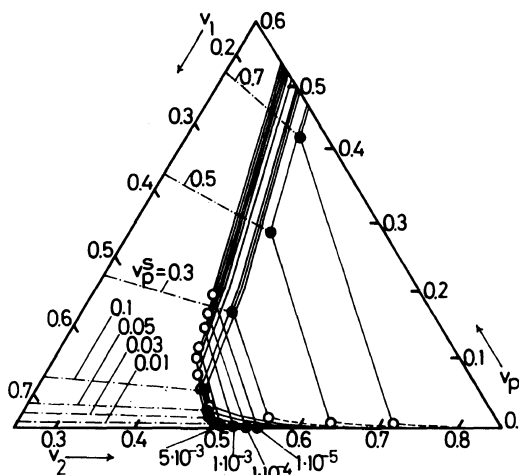
For a given  $v_p$ ,  $A = A(v_1) = 0$  is obtained and  $v_1$  can be evaluated using the single-variable Newton method and gives a spinodal curve. By solving simultaneous equations eq 20 and 21, using the two-variables Newton method, the compositions  $v_1^c$  and  $v_p^c$  (and  $v_2^c$ ) at CSP can be evaluated.

The computer experiments on the critical and coexisting curve were carried out under the following conditions:  $\chi_{12} = 0 \sim 1.0$ ,  $\chi_{13} = 0 \sim 0.5$ ,  $\chi_{23} = 0.8 \sim 1.4$ ,  $X_w^0 = 10^2 \sim 10^5$  and  $X_w^0/X_n^0 = 1 \sim 5$  (original polymer; Shultz-Zimm type molecular weight distribution). The coexisting curves were calculated according to our method<sup>2</sup> under conditions as follows: original polymer, Shultz-Zimm type distribution,  $X_w^0 = 300$ ,  $X_w^0/X_n^0 = 2.0$ ;  $\chi_{12} = 0.5$ ,  $\chi_{13} = 0.2$ ,  $\chi_{23} = 1.0$ ; the starting polymer volume fraction  $v_p^s = 1 \times 10^{-5} \sim 0.7$ .

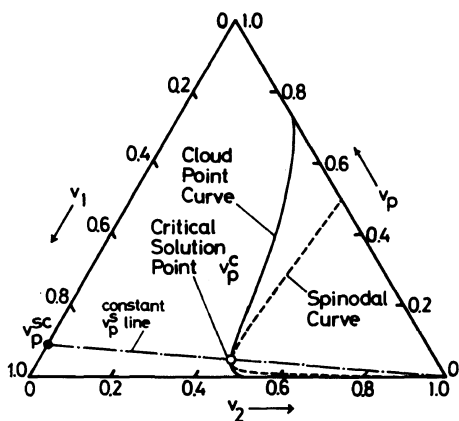
The calculations were performed with FACOM M360.

### RESULTS AND DISCUSSION

Figure 1 shows a coexisting curve by full line for some quasi-ternary solutions having the starting polymer volume fraction  $v_p^s$  ranging from  $10^{-5} \sim 0.7$ . Here, a chain line is a constant  $v_p^s$  line and the cross point of constant  $v_p^s$  line and a coexisting curve correspond to a given  $v_p^s$ , a cloud point demonstrated as a filled mark in the figure. An unfilled circle is the composition of the polymer-lean ( $v_p^0 > v_p^c$ ,  $v_p^0$  (initial concentration) =  $V_3^0/(V_1^0 + V_2 + V_3^0)$ ,  $V_2$ , volume of solvent 2) or -rich ( $v_p^0 < v_p^c$ ) phase which is separated from the mother solution at the cloud point. The polymer lean branch of the coexisting curve at  $v_p^0 > v_p^c$ , which could not be calculated for some unresolved

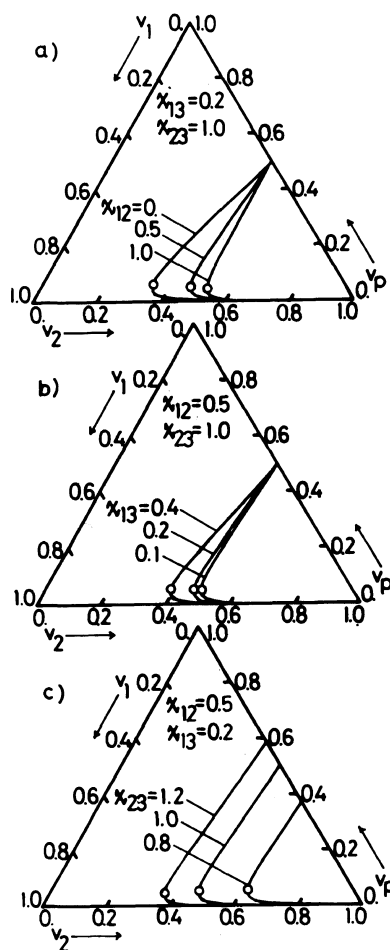


**Figure 1.** Binodal curve (solid line) and cloud point (filled circle) separated from the original solution of the quasi-ternary system with the starting polymer volume fraction  $v_p^s = 1 \times 10^{-5} \sim 0.7$ . Original polymer, Schulz-Zimm type distribution ( $X_w^0 = 300$ ,  $X_w^0/X_n^0 = 2$ );  $\chi_{12} = 0.5$ ,  $\chi_{13} = 0.2$ , and  $\chi_{23} = 1.0$ ; chain line, constant  $v_p^s$  line; filled and unfilled circle are the coexisting phases.



**Figure 2.** Cloud point curve (full line), constructed from Figure 1, spinodal curve (broken line) and critical solution point (unfilled circle) of quasi-ternary system. Original polymer, Schulz-Zimm type distribution ( $X_w^0 = 300$ ,  $X_w^0/X_n^0 = 2$ );  $\chi_{12} = 0.5$ ,  $\chi_{13} = 0.2$ , and  $\chi_{23} = 1.0$ .

problems in our simulation technique, is a hypothetical curve and denoted as broken line in the figure. A cloud point curve for the system can be obtained by connecting the filled marks and so-called shadow curve by connecting unfilled marks and a line linking filled and

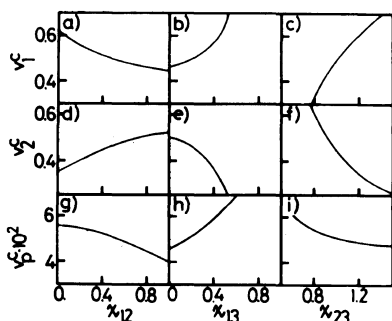


**Figure 3.** Effects of  $\chi_{12}$ ,  $\chi_{13}$ , and  $\chi_{23}$  on the spinodal curve and CSP of quasi-ternary systems consisting of multicomponent polymers with Schulz-Zimm type distribution ( $X_w^0 = 300$ ,  $X_w^0/X_n^0 = 2$ ) in a binary solvent mixture. a)  $\chi_{13} = 0.2$ ,  $\chi_{23} = 1.0$ ; b)  $\chi_{12} = 0.5$ ,  $\chi_{23} = 1.0$ ; c)  $\chi_{12} = 0.5$ ,  $\chi_{13} = 0.2$ .

unfilled marks is a “limiting tie line”.

Figure 2 exemplifies CPC, constructed in the same manner as shown in Figure 1, the spinodal curve and CSP for quasi-ternary solutions. As theory requires, the cloud point and spinodal curves intercept beautifully on CSP. This strongly implies that both the present theory and the simulation technique proposed here are reasonable and unconditionally acceptable.

Figure 3a)–c) shows the effects of  $\chi_{12}$ ,  $\chi_{13}$ ,



**Figure 4.** Plots of  $v_1^c$ ,  $v_2^c$ , and  $v_3^c$  against  $\chi_{12}$ ,  $\chi_{13}$ , and  $\chi_{23}$  of quasi-ternary solutions. Original polymer, Schulz-Zimm type distribution ( $X_w^0 = 300$ ,  $X_w^0/X_n^0 = 2$ ); a), d), and g)  $\chi_{13} = 0.2$ ,  $\chi_{23} = 1.0$ ; b), e), and h)  $\chi_{12} = 0.5$ ,  $\chi_{23} = 1.0$ ; c), f), and i)  $\chi_{12} = 0.5$ ,  $\chi_{13} = 0.2$ .

and  $\chi_{23}$  on the spinodal curve and critical point. With a decrease in  $\chi_{12}$  and with an increase in  $\chi_{13}$  and  $\chi_{23}$ , the spinodal curve and accordingly CSP shifts in a direction of decreasing content of solvent 2 (non-solvent).  $\chi_{23}$  has the strongest effect on the spinodal curve and  $\chi_{12}$  is second. At a point of  $v_1 = 0$  (i.e., the case of polymer-solvent 2 mixture) the spinodal curve is almost independent of  $\chi_{12}$  and  $\chi_{13}$  and is governed by  $\chi_{23}$  alone, because the composition of this point can be given by solving the equation;

$$v_p + \frac{v_2}{X_w^0} - 2\chi_{23}v_2v_p = 0 \quad (22)$$

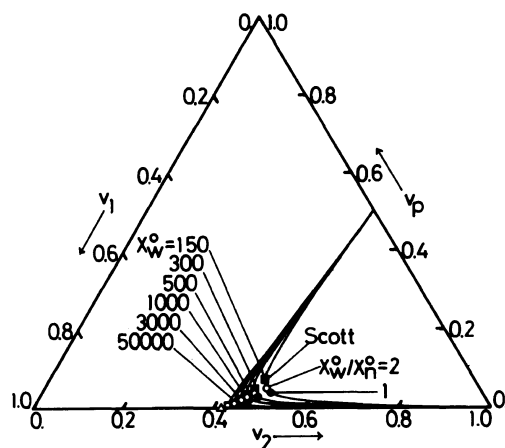
and at the limit of  $X_w^0 \rightarrow \infty$  eq 22 reduces to

$$v_p = 1 - \frac{1}{2\chi_{23}} \quad (23a)$$

$$v_2 = \frac{1}{2\chi_{23}} \quad (23b)$$

Equation 22 can be readily derived from eq B-3.

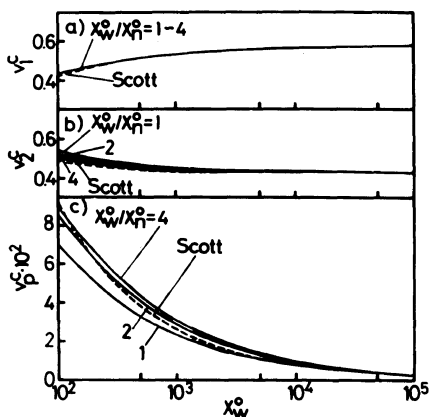
Figure 4 shows the effects of  $\chi_{12}$ ,  $\chi_{13}$ , and  $\chi_{23}$  on  $v_1^c$ ,  $v_2^c$ , and  $v_3^c$  for quasi-ternary solutions of a polymer with Schulz-Zimm type distribution ( $X_w^0 = 300$ ,  $X_w^0/X_n^0 = 2$ ). For smaller  $\chi_{12}$  and larger  $\chi_{13}$ , both  $v_1^c$  and  $v_3^c$  are larger and  $v_2^c$  is smaller. For larger  $\chi_{23}$ ,  $v_1^c$  is larger and both  $v_2^c$



**Figure 5.** Effects of the average molecular weight of the original polymer on spinodal curve and CSP of quasi-ternary solutions. Original polymer, Schulz-Zimm type distribution ( $X_w^0/X_n^0 = 2$ , unfilled circle), monodisperse (filled circle);  $\chi_{12} = 0.5$ ,  $\chi_{13} = 0.2$ ,  $\chi_{23} = 1.0$ . Filled rectangle, CSP of ternary solutions (Scott).

and  $v_3^c$  are smaller. The effects of  $\chi_{12}$  on change in  $v_1^c$ ,  $v_2^c$ , and  $v_3^c$  are smaller than those of  $\chi_{13}$  and  $\chi_{23}$ .

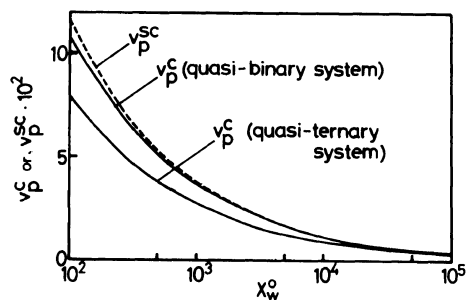
Figure 5 shows the effects of  $X_w^0$  on the spinodal curve and CSP for quasi-ternary solutions of polymers with Schulz-Zimm distribution ( $X_w^0/X_n^0 = 2$ , unfilled circle) and monodisperse polymer (filled circle). For comparison, CSP for monodisperse polymer in a binary solvent mixture was calculated using Scott's equations (eq 26 and 27 of ref 7) and is shown as the filled rectangles. CSP calculated by Scott's method is located on the spinodal curve, but it is significantly different from the true critical point obtained using the method proposed here, and shifted to a higher polymer volume fraction range. In other words, Scott's critical point for monodisperse polymer-solvent 1-solvent 2 system corresponds to the true critical point for multicomponent polymers with relatively large heterogeneity-solvent 1-solvent 2 system. With an increase in  $X_w^0$ , CSP changes roughly linearly in the phase diagram, approaching a point on the  $v_2$ -axis at limit of  $X_w^0 \rightarrow \infty$ . This point is denoted as the unfilled



**Figure 6.** Plots of the composition of critical solution points  $v_1^c$ ,  $v_2^c$ , and  $v_p^c$  versus  $X_w^0$  of quasi-ternary solutions. Original polymer, Schulz-Zimm type distribution ( $X_w^0/X_n^0=1, 2$ , and  $4$ );  $\chi_{12}=0.5$ ,  $\chi_{13}=0.2$ ,  $\chi_{23}=1.0$ : Broken line,  $v_1^c$ ,  $v_2^c$ , and  $v_p^c(v_p^c)$  versus  $X_w^0(X)$  of ternary solutions (Scott).

triangle in the figure, giving the solvent composition of the Flory's theta solvent for given values of  $\chi_{12}$ ,  $\chi_{13}$ , and  $\chi_{23}$  at a given temperature. In other words, we can predict theoretically the solvent composition of the theta solvent mixture from three  $\chi$  values.

Figure 6 illustrates the effects of  $X_w^0$  on CSP ( $v_1^c$ ,  $v_2^c$  and  $v_p^c$ ) for quasi-ternary solutions ( $X_w^0/X_n^0=1, 2, 4$ : solid line) and CSP obtained from Scott's equations (broken line). Scott's  $v_p^c$  is 20–40% higher than the correct  $v_p^c$  in the range of  $X_w^0=100\sim 300$ , evaluated by our method. With an increase in  $X_w^0$ ,  $v_1^c$  increases and  $v_2^c$  decreases approaching asymptotic values. This point gives the composition of the Flory solvent.  $v_p^c$  decreases gradually approaching zero at infinite  $X_w^0$ .  $v_p^c$  for ternary solutions is significantly smaller than  $v_p^c$  for binary solutions. When solvent 2 is added to polymer solutions with the starting concentration  $v_p^s$ , CSP can be realized only at a specific  $v_p^s$  (denoted by  $v_p^{sc}$ , see Figure 2).  $v_p^{sc}$  is rather comparable with  $v_p^c$  for binary solutions. In order to determine the composition of the Flory solvent, it is necessary to use polymers with  $X_w^0$  larger than at least  $1 \times 10^3$  and desirably  $1 \times 10^4$ .  $v_1^c$  is practically inde-

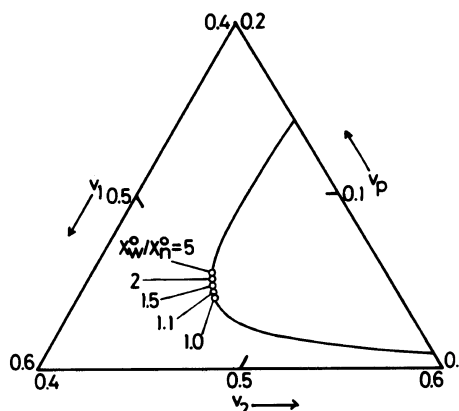


**Figure 7.** Plots of  $v_p^c$  for quasi-binary and ternary systems and  $v_p^{sc}$  for quasi-ternary system as function of  $X_w^0$ . Original polymer, Schulz-Zimm type distribution ( $X_w^0=300$ ,  $X_w^0/X_n^0=2$ ); for quasi-binary system  $p_j=0$  ( $j=1, 2, \dots, n$ ) and  $k'=0$  in eq 2 of ref 1; for quasi-ternary system  $\chi_{12}=0.5$ ,  $\chi_{13}=0.2$ , and  $\chi_{23}=1.4$ :  $v_p^c$ , full line;  $v_p^{sc}$ , broken line.

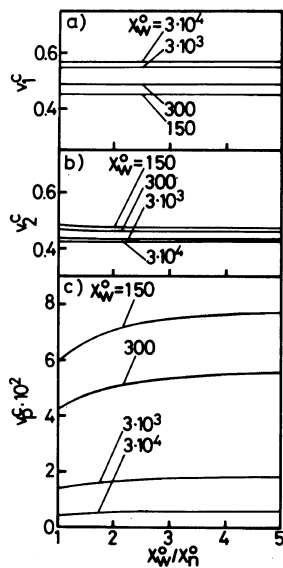
pendent of  $X_w^0/X_n^0$  of the polymer, in  $X_w^0/X_n^0$  range investigated. As  $X_w^0/X_n^0$  increases, both  $v_2^c$  and  $v_p^c$  decrease significantly and the effects of  $X_w^0/X_n^0$  on  $v_2^c$  and  $v_p^c$  become quite remarkable in a lower  $X_w^0$  range. The corresponding values estimated by Scott's equations deviate noticeably from true values for polymers with lower  $X_w^0$  and larger  $X_w^0/X_n^0$ . These deviations are apparently in the same direction of increasing  $X_w^0/X_n^0$ .

Figure 7 shows the  $X_w^0$  dependence of  $v_p^c$  for quasi-binary and ternary system and  $v_p^{sc}$  for quasi-ternary system, where the polymer has the Schulz-Zimm type molecular weight distribution ( $X_w^0=300$ ,  $X_w^0/X_n^0=2$ ), and for the quasi-binary system,  $\chi$  parameter was assumed to be independent of the concentration and the molecular weight ( $p_j$  ( $j=1, 2, \dots, n$ ))=0 and  $k'=0$  in eq 2 of ref 1) and for the quasi-ternary system,  $\chi_{12}=0.5$ ,  $\chi_{13}=0.2$ , and  $\chi_{23}=1.4$  were employed. For a given  $X_w^0$ ,  $v_p^c$  in the quasi-binary system is significantly larger than in the quasi-ternary system, but similar to  $v_p^{sc}$  in magnitude. Note that the total volume of the quasi-binary system  $V$  was maintained constant over the entire range of  $X_w^0$ , but  $V$  of quasi-ternary system was variable, depending on the amount of solvent 2 added and then decreasing with increasing  $X_w^0$ .



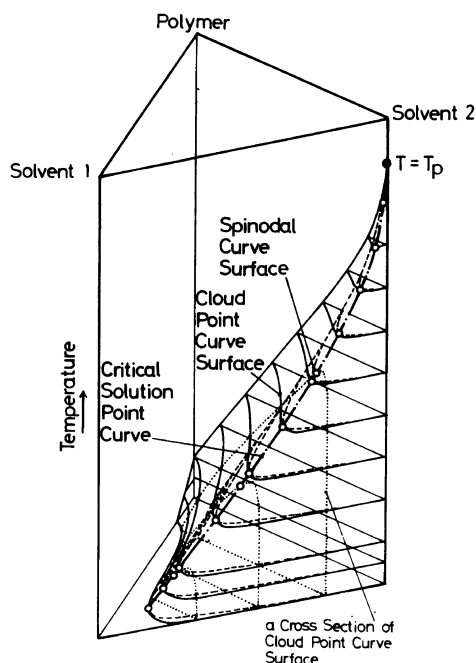


**Figure 8.** Effects of  $X_w^0/X_n^0$  of the original polymer on spinodal curve and critical solution point of quasi-ternary solutions. Original polymer, Schulz-Zimm type distribution ( $X_w^0 = 300$ );  $\chi_{12} = 0.5$ ,  $\chi_{13} = 0.2$ ,  $\chi_{23} = 1.0$ .



**Figure 9.** Dependence of the composition of critical solution point  $v_1^c$ ,  $v_2^c$ , and  $v_p^c$  on  $X_w^0/X_n^0$  of the original polymer of quasi-ternary solutions. Original polymer, Schulz-Zimm type distribution ( $X_w^0 = 150, 300, 3 \times 10^3$ , and  $3 \times 10^4$ );  $\chi_{12} = 0.5$ ,  $\chi_{13} = 0.2$ ,  $\chi_{23} = 1.0$ .

Figure 8 shows the effects of the polydispersity of the polymer on the spinodal curve and CSP for quasi-ternary systems containing a polymer with Schulz-Zimm type distribution ( $X_w^0 = 300$ ). As expected from eq 10, the spinodal curve is absolutely independent of  $X_w^0/X_n^0$ ,



**Figure 10.** Schematic representation of phase diagrams of quasi-ternary system of multicomponent polymers dissolved in binary solvent mixtures: Unfilled circle, upper critical solution point; full line, cloud point curve at constant temperature; broken line, spinodal curve at constant temperature; dotted line, a cross section of the cloud point curve surface with a constant  $v_1$  plane;  $T_p$ , temperature above which the system is a single phase for an entire composition.

depending only on  $X_w^0$  and three  $\chi$  parameters. CSP is only slightly influenced by  $X_w^0/X_n^0$ . It is interesting to note that CSP of a monodisperse polymer does not locate on the peak (maximum  $v_1$  point;  $v_1^p, v_2^p, v_p^p$ ) of spinodal curve, but shifts to the higher  $v_p$  side. In this case,  $(v_1^c, v_2^c, v_p^c) = (0.4920, 0.4661, 0.0419)$  and  $(v_1^p, v_2^p, v_p^p) = (0.4927, 0.4705, 0.0368)$ .

Figure 9 shows the plots of  $v_1^c$ ,  $v_2^c$ , and  $v_p^c$  as functions of  $X_w^0/X_n^0$  of the polymer dissolved in binary solvent mixture (original polymer, Schulz-Zimm type;  $X_w^0 = 150, 300, 3 \times 10^3$  and  $3 \times 10^4$ ). Surprisingly,  $v_1^c$  and  $v_2^c$  are practically constant over a wide range of  $X_w^0/X_n^0$ , but with an increase in  $X_w^0/X_n^0$  from 1 to 5  $v_p^c$  gradually increases from 0.0419 to 0.0559 in the case of  $X_w^0 = 300$ , approaching an asymptotic value.

Change in  $v_p^c$  in the vicinity of  $X_w^0/X_n^0=1$  is rather remarkable for lower  $X_w^0$ . It was confirmed that the solvent composition of the Flory solvent mixture is independent of the polydispersity of the polymer and only a function of three  $\chi$  parameters.

Figure 10 demonstrates the effects of temperature on the phase diagrams, including the cloud point curve, spinodal curve and upper CSP, for a quasi-ternary system consisting of multicomponent polymers in binary solvent mixtures. In the figure, the full and broken lines are the cloud point curve and spinodal curve at constant temperature, respectively. The chain line is the critical solution point curve. The cross section of the cloud point curve surface with a constant  $v_1$  plane is shown as the dotted line, whose shape is very similar to the cloud point curve for a quasi-binary system of multicomponent polymers in a single solvent (for example, see Figure 2 of ref 1). Above a specific temperature  $T_p$ , the quasi-ternary system is a single phase for an entire

composition.

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## APPENDIX A

Derivation of eq 10 and 11

Substituting eq 9a—d into eq 1, we obtain

$$|\Delta G'| = \left(\frac{\bar{R}T}{V_0}\right)^{m+1} \begin{vmatrix} M+U & M+K & M+K & \cdots & M+K \\ M+K & M+M_1 & M & \cdots & M \\ M+K & M & M+M_2 & \cdots & M \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ M+K & M & M & \cdots & M+M_m \end{vmatrix}$$

$$= \left(\frac{\bar{R}T}{V_0}\right)^{m+1} \left[ (-1)^2(M+U) \begin{vmatrix} M+M_1 & M & \cdots & M \\ M & M+M_2 & \cdots & M \\ \vdots & \vdots & \ddots & \vdots \\ M & M & \cdots & M+M_m \end{vmatrix} \right]$$

$$\begin{aligned}
 & + \sum_{j=1}^m (-1)^{2j+3}(M+K)\{(-1)^2(M+K) \\
 & \times \begin{vmatrix} M+M_1 & M & \cdots & M & M & \cdots & M \\ M & M+M_2 & \cdots & M & M & \cdots & M \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_{j-1} & M & \cdots & M \\ M & M & \cdots & M & M+M_{j+1} & \cdots & M \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ M & M & \cdots & M & M & \cdots & M+M_m \end{vmatrix} \\
 & + \sum_{i \neq j}^m (-1)^{2i+3}(M+K) \begin{vmatrix} M & & & & & & \\ M & M_1 & & & & & \\ \vdots & \vdots & & & & & \\ M & & M_{i-1} & & & & \\ M & & & M_{i+1} & & & \\ \vdots & & & \vdots & & & \\ M & 0 & & & M_{j-1} & & \\ M & & & & & M_{j+1} & \\ \vdots & & & & & \vdots & \\ M & & & & & & M_m \end{vmatrix} \Big]
 \end{aligned}$$

$$\begin{aligned}
 & = \left(\frac{\tilde{R}T}{V_0}\right)^{m+1} \left[ (M+U) \left(\prod_{j=1}^m M_j\right) \left(1 + M \prod_{j=1}^m \frac{1}{M_j}\right) \right. \\
 & \quad \left. - \sum_{j=1}^m (M+K) \left[ (M+K) \left(\frac{1}{M_j} \prod_{i=1}^m M_i\right) \left\{1 + M \left(\sum_{i=1}^m \frac{1}{M_i} - \frac{1}{M_j}\right)\right\} - \sum_{i \neq j}^m (M+K) \frac{M}{M_i M_j} \left(\prod_{k=1}^m M_k\right) \right] \right] \\
 & = \left(\frac{\tilde{R}T}{V_0}\right)^{m+1} \left(\prod_{j=1}^m M_j\right) \left[ (M+U) \left\{1 + M \sum_{j=1}^m \frac{1}{M_j}\right\} - (M+K)^2 \sum_{j=1}^m \frac{1}{M_j} \right] = 0 \tag{A-1}
 \end{aligned}$$

Equation A-1 can be rewritten as

$$(M+U) \left\{1 + M \sum_{j=1}^m \frac{1}{M_j}\right\} - (M+K)^2 \sum_{j=1}^m \frac{1}{M_j} = 0 \tag{A-2}$$

Combining eq A-2 with eq 9a—d, we obtain eq 10. Here, in deriving eq A-2, we employed the relation given by<sup>1</sup>

$$\begin{vmatrix} x_1 & a & \cdots & a \\ a & x_2 & \cdots & a \\ \vdots & \vdots & & \vdots \\ a & a & \cdots & x_m \end{vmatrix} = f(a) - a \frac{df(x)}{dx} \Big|_{x=a} \tag{A-3}$$

Partial differentiation of eq A-1 with  $v_{xi}$  ( $i = N, 1, 2, \dots, m; v_{xN} = v_2$ ) yields

$$\left(\frac{\partial|\Delta G'|}{\partial v_{x_i}}\right)_{T,P,v_{x_k}} = \left(\frac{\tilde{R}T}{V_0}\right)^{m+1} \left(\prod_{j=1}^m M_j\right) \frac{\partial}{\partial v_{x_i}} \{(M+U)(1+Mv_p X_w^0) - (M+K)^2 v_p X_w^0\}_{T,P,v_{x_k}}$$

$$\equiv W_i \quad (k \neq i, k = N, 1, 2, \dots, m; v_{x_N} = v_2) \tag{A-4}$$

Substituting eq 9a—d and A-4 into eq 4, we obtain eq A-5;

$$\left(\frac{V_0}{\tilde{R}T}\right)^{m+1} |\Delta G''| = \begin{vmatrix} W_N & W_1 & W_2 & \cdots & W_m \\ M+K & M+M_1 & M & \cdots & M \\ M+K & M & M+M_2 & \cdots & M \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ M+K & M & M & \cdots & M+M_m \end{vmatrix}$$

$$= (-1)^2 W_N \begin{vmatrix} M+M_1 & M & \cdots & M \\ M & M+M_2 & \cdots & M \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ M & M & \cdots & M+M_m \end{vmatrix}$$

$$+ \sum_{j=1}^m (-1)^{2j+3} W_j \left[ (-1)^2 (M+K) \right.$$

$$\times \begin{vmatrix} M+M_1 & M & \cdots & M & M & \cdots & M \\ M & M+M_2 & \cdots & M & M & \cdots & M \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ M & M & \cdots & M+M_{j-1} & M & \cdots & M \\ M & M & \cdots & M & M+M_{j+1} & \cdots & M \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ M & M & \cdots & M & M & \cdots & M+M_m \end{vmatrix}$$

$$\begin{aligned}
& + \sum_{i \neq j}^m (-1)^{2i+3} (M+K) \\
& \times \left[ \begin{array}{cccccccc}
M & & & & & & & \\
M & M_1 & & & & & & \\
M & & M_2 & & & & 0 & \\
\vdots & & & \ddots & & & & \\
M & & & & M_{i-1} & & & \\
M & & & & & M_{i+1} & & \\
\vdots & & & & & & \ddots & \\
M & & & & & & & M_{j-1} \\
M & & 0 & & & & & & M_{j+1} \\
\vdots & & & & & & & & \\
M & & & & & & & & & M_m
\end{array} \right] \\
& = W_N \left( \prod_{j=1}^m M_j \right) \left( 1 + M \sum_{j=1}^m \frac{1}{M_j} \right) \\
& \quad - \sum_{j=1}^m W_j \left\{ (M+K) \left( \frac{1}{M_j} \prod_{i=1}^m M_i \right) \left( 1 + M \sum_{i \neq j}^m M_i \right) - \sum_{i \neq j}^m (M+K) \left( \frac{M}{M_i M_j} \right) \prod_{i=1}^m M_i \right\} \\
& = \left( \prod_{j=1}^m M_j \right) \left[ W_N \left( 1 + M \sum_{j=1}^m \frac{1}{M_j} \right) - (M+K) \sum_{j=1}^m \frac{W_j}{M_j} \right] = 0 \tag{A-5}
\end{aligned}$$

In deriving eq A-5, we utilized eq A-3 and A-4. Equation A-5 can be rewritten in the form,

$$W_N \left( 1 + M \sum_{j=1}^m \frac{1}{M_j} \right) - (M+K) \sum_{j=1}^m \frac{W_j}{M_j} = 0 \tag{A-6}$$

Equation 11 can be derived from eq A-7, considering eq 9a—d and eq A-4.

## APPENDIX B

*Symmetry of eq 10 and 11*

Equation A-2 can be rewritten as follows,

$$\{(M+K)(U-K) + (U-K)(Q_w - K) + (Q_w - K)(M+K)\} = 0 \tag{B-1}$$

where

$$1/Q_w = \sum_{j=1}^m \frac{1}{M_j} = v_p X_w^0 \tag{B-2}$$

Substitution of eq 9a—c and B-2 into eq B-1 yields

$$\begin{aligned} & \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12}\right) \left(\frac{1}{v_2} + \chi_{13} - \chi_{23} - \chi_{12}\right) \\ & + \left(\frac{1}{v_2} + \chi_{13} - \chi_{23} - \chi_{12}\right) \\ & \times \left(\frac{1}{v_p X_w^0} + \chi_{12} - \chi_{13} - \chi_{23}\right) \\ & + \left(\frac{1}{v_p X_w^0} + \chi_{12} - \chi_{13} - \chi_{23}\right) \\ & \times \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12}\right) = 0 \end{aligned} \quad (\text{B-3})$$

We can rearrange eq A-7 into the form,

$$\begin{aligned} & W_N \{(M+K) + (Q_w - K)\} \\ & - (M+K) \left(\frac{1}{v_p X_w^0} \sum_{i=1}^m \frac{W_i}{M_i}\right) \\ & = \frac{W_N}{U-K} \{(M+K)(U-K) \\ & + (U-K)(Q_w - K) + (Q_w - K)(M+K)\} \\ & - \frac{M+K}{U-K} \left\{ \left(\frac{1}{v_p X_w^0} \sum_{j=1}^m \frac{W_j}{M_j}\right) (U-K) \right. \\ & \left. + W_N(Q_w - K) \right\} = 0 \end{aligned} \quad (\text{B-4})$$

Equation B-4 can be simplified using eq B-1 as

$$\frac{1}{Q_w - K} \left(\frac{1}{v_p X_w^0} \sum_{i=1}^m \frac{W_i}{M_i}\right) + \frac{W_N}{U-K} = 0 \quad (\text{B-5})$$

Combination of eq B-1 and eq A-5 gives

$$\begin{aligned} W_i &= \left(\frac{\tilde{R}T}{V_0}\right)^{m+1} \left(\prod_{j=1}^m M_j\right) \left[ \frac{(Q_w - K) + (U - K)}{v_1^2} \right. \\ & \left. - \frac{X_i \{(M+K) + (U-K)\}}{(v_p X_w^0)^2} \right] \end{aligned} \quad (\text{B-6})$$

$$\begin{aligned} W_N &= \left(\frac{\tilde{R}T}{V_0}\right)^{m+1} \left(\prod_{j=1}^m M_j\right) \left[ \frac{(Q_w - K) + (U - K)}{v_1^2} \right. \\ & \left. - \frac{(M+K) + (Q_w - K)}{v_2^2} \right] \end{aligned} \quad (\text{B-7})$$

From eq B-5, B-6, and B-7, we obtain

$$\begin{aligned} & \frac{\{(Q_w - K) + (U - K)\}^2}{v_1^2 (Q_w - K)(U - K)} - \frac{(M+K) + (U - K)}{(v_p X_w^0)^2 (Q_w - K)} \\ & - \frac{(M+K) + (Q_w - K)}{v_2^2 (U - K)} = 0 \end{aligned} \quad (\text{B-8})$$

By combining B-1 with B-8, we can derive eq B-9.

$$\begin{aligned} & \frac{1}{M+K} \left(1 - \frac{\chi_{12} + \chi_{13} - \chi_{23}}{M+K}\right)^2 \\ & + \frac{1}{U-K} \left(1 + \frac{\chi_{12} + \chi_{23} - \chi_{13}}{U-K}\right)^2 \\ & + \frac{X_z}{Q_w - K} \left(1 - \frac{\chi_{13} + \chi_{23} + \chi_{12}}{Q_w - K}\right)^2 = 0 \end{aligned} \quad (\text{B-9})$$

Equation B-9 can be rewritten, using eq 9a-c and B-2, as

$$\begin{aligned} & \frac{1}{v_1^2} \left(\frac{1}{v_2} - \chi_{12} - \chi_{23} + \chi_{13}\right)^3 \\ & \times \left(\frac{1}{X_w^0 v_p} - \chi_{13} - \chi_{23} + \chi_{12}\right)^3 \\ & + \frac{1}{v_2^2} \left(\frac{1}{v_1} - \chi_{12} - \chi_{13} + \chi_{23}\right)^3 \\ & \times \left(\frac{1}{X_w^0 v_p} - \chi_{13} - \chi_{23} + \chi_{12}\right)^3 \\ & + \frac{X_z}{(X_w^0 v_p)^2} \left(\frac{1}{v_1} - \chi_{12} - \chi_{13} + \chi_{23}\right)^3 \\ & \times \left(\frac{1}{v_2} - \chi_{12} - \chi_{23} + \chi_{13}\right)^3 = 0 \end{aligned} \quad (\text{B-10})$$

Equations B-3 and B-10 are obviously symmetrical with respect to the exchange of solvents 1 and 2 and are consistent with eq 10 and 11, respectively.