

Phase Equilibria of Quasi-Ternary Systems Consisting of Multi-component Polymers in a Binary Solvent Mixture

V. Effects of Concentration Dependence of Thermodynamic Interaction Parameters

Shigenobu MATSUDA

*Fundamental Research Laboratory of Fibers and Fiber-Forming Polymers,
Asahi Chemical Industry Co., Ltd.,
11-7, Hacchonawate, Takatsuki, Osaka 569, Japan*

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ABSTRACT: The concentration dependences of three χ parameters (thermodynamic interaction parameters of solvent 1—2, solvent 1-polymer, and solvent 2-polymer; χ_{12} , χ_{13} , and χ_{23} , respectively) were studied for developing a theory of the two-phase equilibrium of a quasi-ternary system which consists of multicomponent polymers and a binary solvent mixture. χ_{12} , χ_{13} , and χ_{23} were defined by

$$\chi_{12} = \chi_{12}^0 \left(1 + \sum_{s=1}^{n_s} p_{12,s} v_p^s \right)$$

$$\chi_{13} = \chi_{13}^0 \left(1 + \sum_{q=1}^{n_q} p_{13,q} v_p^q \right)$$

$$\chi_{23} = \chi_{23}^0 \left(1 + \sum_{r=1}^{n_r} p_{23,r} v_p^r \right)$$

where χ_{12}^0 , χ_{13}^0 , and χ_{23}^0 are the parameters independent of the total polymer concentration v_p and are dependent on the temperature only, and $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ are the concentration dependent parameters. Computer experiments on solutions of an original polymer with the Schulz-Zimm type molecular weight distribution (the ratio of weight- to number-average molar volume of the polymer to the solvents $X_w^0/X_n^0 = 2.0$ and $X_w^0 = 300$) were carried out to study the effects of concentration dependent parameters on the two phase equilibrium characteristics. Partition coefficient σ , phase volume ratio R , and polymer volume fraction in polymer rich phase $v_{p(2)}$ increase with an increase in $p_{13,1}$ and $p_{23,1}$ and yield maximum near $p_{12,1} = -0.2$. The effects of the concentration dependence of χ -parameter on σ , R , and $v_{p(2)}$ decrease in the following order: $p_{23,1} > p_{13,1} > p_{12,1}$.

KEY WORDS Concentration Dependent Parameter / Thermodynamic Interaction Parameter / Quasi-Ternary System / Binary Solvent Mixture / Partition Coefficient / Phase Volume Ratio /

The phase separation phenomena of monodisperse polymer/solvent/nonsolvent systems had been studied by Flory,¹ Scott,^{2,3} Tompa,⁴ Nakagaki and Sunada,⁵ Krigbaum and Carpenter⁶ and Shu and Liou,⁷ but even for these relatively simple cases, two-phase equilibrium calculation had been based on

crude assumptions: (1) a solvent mixture could be approximated as a "single solvent" (Flory,¹ Scott^{2,3}), (2) polymer molecular weight was infinite (Scott,^{2,3} Nakagaki-Sunada⁵), (3) among three thermodynamic interaction parameters χ_{12} , χ_{13} , and χ_{23} (originally defined in the Flory-Huggins theory.⁸

1, solvent 1; 2, solvent 2; 3, polymer), the relationships that $\chi_{12} = \chi_{13}$ and $\chi_{23} = 0$ held (Tompa,⁴ Nakagaki-Sunada⁵) and (4) polymer did not exist in the polymer-lean phase (Krigbaum-Carpenter,⁶ Shu-Liou⁷). Very recently⁹⁻¹¹, we proposed a rigorous theory of phase equilibrium for a quasi-ternary system consisting of multicomponent polymers, solvent 1 (good solvent) and solvent 2 (poor solvent), where χ_{12} , χ_{13} , and χ_{23} were assumed to be concentration independent. Based on this theory, we carried out systematically a series of computer experiments on the quasi-ternary system to study the effects of (a) three thermodynamic interaction parameters,⁹ (b) the relative amount ρ_p of polymer partitioned in a polymer rich phase and the initial concentration v_p^0 ,¹⁰ and (c) the average molecular weight and molecular weight distribution (MWD) of the original polymer,¹¹ on the phase separation characteristics, and compared the results with those of quasi-binary systems consisting of multicomponent polymers and a single solvent. Aminavhabi and Munk,¹² Altena and Smolders¹³ showed that the magnitude of χ_{12} and its concentration dependence influence thermodynamic properties, such as phase separation characteristics, of monodisperse polymer in binary solvent system. In this communication we have generalized the theory for phase equilibrium of quasi-ternary system studied in the previous papers⁹⁻¹¹ to the case where the three χ parameters (not only χ_{12} but also χ_{13} and χ_{23}) depends significantly on the concentration, and explored the effects of these concentration dependence on the two-phase equilibrium characteristics.

THEORETICAL BACKGROUND

On the basis of Flory-Huggins theory,⁸ Kamide *et al.*⁹⁻¹¹ proposed a theory of quasi-ternary system, assuming that χ_{12} , χ_{13} , and χ_{23} are independent of the polymer molecular weight and concentration. Chemical potentials

of solvent 1, 2, and X_i -mer ($\Delta\mu_1$, $\Delta\mu_2$, and $\Delta\mu_{X_i}$, respectively) were given by following equations.

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

$$\Delta\mu_2 = \tilde{R}T \left\{ \ln v_2 + \left(1 - \frac{1}{X_n}\right)v_p + \chi_{12}v_1(1-v_2) + \chi_{23}v_p(1-v_2) - \chi_{13}v_1v_p \right\} \quad (2)$$

$$\Delta\mu_{X_i} = \tilde{R}T \left[\ln v_{X_i} - (X_i - 1) + X_i \left(1 - \frac{1}{X_n}\right)v_p + X_i \{ \chi_{13}v_1(1-v_p) + \chi_{23}v_2(1-v_p) - \chi_{12}v_1v_2 \} \right] \quad (3)$$

$(i=1, \dots, m)$

where X_i is the molar volume ratio of the i th polymer to solvent 1 or 2, v_1 , v_2 , and v_{X_i} , the volume fraction of solvent 1, 2, and X_i -mer, respectively, v_p , the total polymer volume fraction ($\equiv \sum_{i=1}^m v_{X_i}$), \tilde{R} and T , the gas constant and Kelvin temperature, respectively. m is the total number of polymer component, all belonging to the same chemical homologue. We assume that (a) the molar volume of solvent 1 is the same as that of solvent 2, (b) solvent 1, 2, and polymer are volumetrically additive, and (c) the densities of solvent 1, 2, and polymer are the same.⁹ These assumptions do not limit the validity of the theory. For the quasi-binary system consisting of multicomponent polymers dissolved in a single solvent, we considered the concentration dependence of χ parameter, as follows.¹⁴

$$\chi = \chi_0 \left(1 + \sum_{j=1}^n p_j v_p^j \right) \quad (4)$$

Here, χ_0 is the temperature dependent factor and p_j ($j=1, \dots, n$) are the concentration dependent parameters. From the analogy to the quasi-binary system, concentration dependence of χ_{12} , χ_{13} , and χ_{23} for the quasi-ternary system should be written as

$$\chi_{12} = \chi_{12}^0 \left(1 + \sum_{s=1}^{n_s} p_{12,s} v_p^s \right) \times \left\{ 1 + \sum_{i=1}^{n_t} (p_{1,t} v_1^t + p_{2,t} v_2^t) \right\} \quad (5)$$

$$\chi_{13} = \chi_{13}^0 \left(1 + \sum_{q=1}^{n_q} p_{13,q} v_p^q \right) \quad (6)$$

$$\chi_{23} = \chi_{23}^0 \left(1 + \sum_{r=1}^{n_r} p_{23,r} v_p^r \right) \quad (7)$$

where χ_{12}^0 , χ_{13}^0 , and χ_{23}^0 are parameters independent of the concentration and the degree of polymerization ($\sim X_i$) and are dependent on temperature only. $p_{12,s}$, $p_{13,q}$, and $p_{23,r}$ are independent of X_i and temperature. $p_{1,t}$ and $p_{2,t}$ are the solvent composition dependent parameters. Here, we neglected the theoretical and experimental possibility of the dependence of χ_{12} parameters on the composition of binary solvent mixture.

$$\chi_{12} = \chi_{12}^0 \left(1 + \sum_{s=1}^{n_s} p_{12,s} v_p^s \right) \quad (5')$$

Gibbs's free energy of mixing of these solvents and polymer, ΔG can be divided into four parts; Gibbs free energy of ideal solution, ΔG^{id} , excess free energy of solvent 1-2, ΔG_{12}^E , excess free energy of solvent 1-polymer, ΔG_{13}^E , and excess free energy of solvent 2-polymer, ΔG_{23}^E :

$$\Delta G = \Delta G^{id} + \Delta G_{12}^E + \Delta G_{13}^E + \Delta G_{23}^E \quad (8)$$

Using eq 4, the excess chemical potential of solvent $\partial \Delta G^E / \partial N_0$ for quasi-binary system becomes,¹⁴

$$\frac{\partial \Delta G^E}{\partial N_0} = \tilde{R}T \chi_0 \left(1 + \sum_{j=1}^n p_j v_p^j \right) v_p^2 \quad (9)$$

where N_0 is the number of solvent molecules.

In the same way as for quasi-binary system, eq 6 and 7 are combined with the original equations of the excess chemical potential of solvents 1 and 2 ($\partial \Delta G_{13}^E / \partial N_1$ and $\partial \Delta G_{23}^E / \partial N_2$), to give

$$\frac{\partial \Delta G_{13}^E}{\partial N_1} = \tilde{R}T \chi_{13}^0 \left(1 + \sum_{q=1}^{n_q} p_{13,q} v_p^q \right) v_p (1 - v_1) \quad (10)$$

$$\frac{\partial \Delta G_{23}^E}{\partial N_2} = \tilde{R}T \chi_{23}^0 \left(1 + \sum_{r=1}^{n_r} p_{23,r} v_p^r \right) v_p (1 - v_2) \quad (11)$$

Here N_1 and N_2 are number of solvent 1 and 2, respectively. Equation 5' was directly put into an equation of ΔG_{12}^E (eq 12) in order to satisfy the symmetry with respect to the exchange of solvents 1 and 2,

$$\Delta G_{12}^E \equiv \tilde{R}TL \chi_{12} v_1 v_2 \quad (12)$$

$$= \tilde{R}TL \chi_{12}^0 \left(1 + \sum_{s=1}^{n_s} p_{12,s} v_p^s \right) v_1 v_2 \quad (12')$$

where $L = N_1 + N_2 + \sum X_i N_{X_i}$ and N_{X_i} is the number of X_i -mer. Combining eq 8, 10—12, we can determine ΔG of the quasi-ternary system and derivate $\Delta \mu_1$, $\Delta \mu_2$, and $\Delta \mu_{X_i}$ ($i=1, \dots, m$), respectively (see Appendix A), as

$$\begin{aligned} \Delta \mu_1 = & \tilde{R}T \left[\ln v_1 - \left(1 - \frac{1}{X_n} \right) v_p \right. \\ & + \chi_{12}^0 \left\{ v_2 (1 - v_1) + \sum_{s=1}^{n_s} p_{12,s} v_2 v_p^s (1 - (s+1)v_1) \right\} \\ & + \chi_{13}^0 v_p (1 - v_1) \left\{ 1 + \sum_{q=1}^{n_q} p_{13,q} v_p^q \right\} \\ & - \chi_{23}^0 v_2 v_p \left\{ 1 + \sum_{r=1}^{n_r} p_{23,r} v_p^r + \sum_{r=1}^{n_r} p_{23,r} \left(\frac{r}{r+1} \right) \right. \\ & \left. \times \frac{v_p^r}{(1-v_2)^{r+1}} \left(\frac{1 - (v_1 + v_p)^{r+1}}{v_2} \right) \right\} \left. \right] \quad (13) \end{aligned}$$

$$\begin{aligned} \Delta \mu_2 = & \tilde{R}T \left[\ln v_2 - \left(1 - \frac{1}{X_n} \right) v_p \right. \\ & + \chi_{12}^0 \left\{ v_1 (1 - v_2) + \sum_{s=1}^{n_s} p_{12,s} v_1 v_p^s (1 - (s+1)v_2) \right\} \end{aligned}$$

$$\begin{aligned}
& + \chi_{23}^0 v_p (1 - v_2) \left\{ 1 + \sum_{r=1}^{n_r} p_{23,r} v_p^r \right\} - \chi_{13}^0 v_1 v_p \\
& \times \left\{ 1 + \sum_{q=1}^{n_q} p_{13,q} v_p^q + \sum_{q=1}^{n_q} p_{13,q} \left(\frac{q}{q+1} \right) \right. \\
& \times \left. \frac{v_p^q}{(1-v_1)^{q+1}} \left(\frac{1-(v_2+v_p)^{q+1}}{v_1} \right) \right\} \quad (14) \\
\Delta \mu_{X_i} = & RT \left[\ln v_{X_i} - (X_i - 1) + X_i \left(1 - \frac{1}{X_n} \right) v_p \right. \\
& - X_i \chi_{12}^0 v_1 v_2 \left\{ 1 - \sum_{s=1}^{n_s} p_{12,s} s v_p^{s-1} \right. \\
& \times \left. \left(1 - \frac{s+1}{s} v_p \right) \right\} \\
& + X_i \chi_{13}^0 v_1 \left\{ 1 - v_p \left(1 + \sum_{q=1}^{n_q} p_{13,q} v_p^q \right) \right. \\
& + \sum_{q=1}^{n_q} p_{13,q} \left(1 - \left(\frac{q}{q+1} \right) \frac{v_p}{1-v_1} \right) \left(\frac{v_p}{1-v_1} \right)^q \\
& \times \left. \left(\frac{1-(v_2+v_p)^{q+1}}{v_1} \right) \right\} \\
& + X_i \chi_{23}^0 v_2 \left\{ 1 - v_p \left(1 + \sum_{r=1}^{n_r} p_{23,r} v_p^r \right) \right. \\
& + \sum_{r=1}^{n_r} p_{23,r} \left(1 - \left(\frac{r}{r+1} \right) \frac{v_p}{1-v_2} \right) \left(\frac{v_p}{1-v_2} \right)^r \\
& \times \left. \left(\frac{1-(v_1+v_p)^{r+1}}{v_2} \right) \right\} \quad (i=1, \dots, m) \quad (15)
\end{aligned}$$

For quasi-binary system, Koningsveld *et al.*^{16,17} defined the thermodynamic interaction parameter g in the expression of ΔG . For quasi-ternary system, thermodynamic interaction parameters between solvent 1—2, solvent 1-polymer, and solvent 2-polymer g_{12} , g_{13} , and g_{23} can also be defined as,

$$g_{12} = \Delta G_{12}^E / (\tilde{R} T L v_1 v_2) \quad (16)$$

$$g_{13} = \Delta G_{13}^E / (\tilde{R} T L v_1 v_p) \quad (17)$$

$$g_{23} = \Delta G_{23}^E / (\tilde{R} T L v_2 v_p) \quad (18)$$

g_{12} , g_{13} , and g_{23} are related to χ_{12} , χ_{13} , and

χ_{23} , respectively, through the equations (see, Appendix B).

$$g_{12} = \chi_{12} \quad (19)$$

$$g_{13} = \frac{1}{v_1} \int_{1-v_1}^1 \chi_{13} d(1-v_1) \quad (20)$$

$$g_{23} = \frac{1}{v_2} \int_{1-v_2}^1 \chi_{23} d(1-v_2) \quad (21)$$

Equation 20 and 21 are readily written in the differential forms.

$$\chi_{13} = g_{13} - v_1 \frac{\partial g_{13}}{\partial (1-v_1)} \quad (22)$$

$$\chi_{23} = g_{23} - v_2 \frac{\partial g_{23}}{\partial (1-v_2)} \quad (23)$$

Conditions of two-phase equilibrium of the quasi-ternary system at constant temperature and pressure are given by eq 24—26,

$$\Delta \mu_{1(1)} = \Delta \mu_{1(2)} \quad (24)$$

$$\Delta \mu_{2(1)} = \Delta \mu_{2(2)} \quad (25)$$

$$\Delta \mu_{X_i(1)} = \Delta \mu_{X_i(2)} \quad (26)$$

where subscripts (1) and (2) denote the polymer-lean and -rich phases, respectively. Partition coefficient σ is defined by:

$$\sigma = \frac{1}{X_i} \ln \frac{v_{X_i(2)}}{v_{X_i(1)}} \quad (27)$$

Combination of eq 15, 26, and 27 gives

$$\begin{aligned}
\sigma = & (v_{p(1)} - v_{p(2)}) + \left(\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}} \right) \\
& + \chi_{12}^0 [v_{1(2)} v_{2(2)} - v_{1(1)} v_{2(1)}] \\
& - \sum_{s=1}^{n_s} p_{12,s} s \left\{ v_{1(2)} v_{2(2)} v_{p(2)}^{s-1} \left(1 - \frac{s+1}{s} v_{p(2)} \right) \right. \\
& - v_{1(1)} v_{2(1)} v_{p(1)}^{s-1} \left(1 - \frac{s+1}{s} v_{p(1)} \right) \left. \right\} \\
& - \chi_{13}^0 \left[(v_{1(2)} - v_{1(1)}) - (v_{1(2)} v_{p(2)} - v_{1(1)} v_{p(1)}) \right. \\
& - \sum_{q=1}^{n_q} p_{13,q} (v_{1(2)} v_{p(2)}^{q+1} - v_{1(1)} v_{p(1)}^{q+1})
\end{aligned}$$

$$\begin{aligned}
& + \sum_{q=1}^{n_q} \frac{p_{13,q}}{q+1} \left\{ v_{1(2)} \left(q+1 - \frac{qv_{p(2)}}{1-v_{1(2)}} \right) \right. \\
& \times \left(\frac{v_{p(2)}}{1-v_{1(2)}} \right)^q \frac{1-(v_{2(2)}+v_{p(2)})^{q+1}}{v_{1(2)}} \\
& - v_{1(1)} \left(q+1 - \frac{qv_{p(1)}}{1-v_{1(1)}} \right) \left(\frac{v_{p(1)}}{1-v_{1(1)}} \right)^q \\
& \left. \times \frac{1-(v_{2(1)}+v_{p(1)})^{q+1}}{v_{1(1)}} \right\} \\
& - \chi_{23}^0 \left[(v_{2(2)} - v_{2(1)}) - (v_{2(2)}v_{p(2)} - v_{2(1)}v_{p(1)}) \right. \\
& - \sum_{r=1}^{n_r} p_{23,r} (v_{2(2)}v_{p(2)}^{r+1} - v_{2(1)}v_{p(1)}^{r+1}) \\
& + \sum_{r=1}^{n_r} \frac{p_{23,r}}{r+1} \left\{ v_{2(2)} \left(r+1 - \frac{rv_{p(2)}}{1-v_{2(2)}} \right) \right. \\
& \times \left(\frac{v_{p(2)}}{1-v_{2(2)}} \right)^r \frac{1-(v_{1(2)}+v_{p(2)})^{r+1}}{v_{2(2)}} \\
& - v_{2(1)} \left(r+1 - \frac{rv_{p(1)}}{1-v_{2(1)}} \right) \left(\frac{v_{p(1)}}{1-v_{2(1)}} \right)^r \\
& \left. \times \frac{1-(v_{1(1)}+v_{p(1)})^{r+1}}{v_{2(1)}} \right\} \quad (28)
\end{aligned}$$

Substitution of eq 13 into 24 yields eq 29 (the left-hand side of eq 29 is put with A),

$$\begin{aligned}
A \equiv & \ln \frac{v_{1(2)}}{v_{1(1)}} + (v_{p(2)} - v_{p(1)}) - \left(\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}} \right) \\
& + \chi_{12}^0 \left[(v_{2(2)} - v_{2(1)}) - (v_{1(2)}v_{2(2)} - v_{1(1)}v_{2(1)}) \right. \\
& + \sum_{s=1}^{n_s} p_{12,s} \{ (v_{2(2)}v_{p(2)}^s - v_{2(1)}v_{p(1)}^s) \\
& \left. - (s+1)(v_{1(2)}v_{2(2)}v_{p(2)}^s - v_{1(1)}v_{2(1)}v_{p(1)}^s) \right] \\
& + \chi_{13}^0 \left[(v_{p(2)} - v_{p(1)}) - (v_{1(2)}v_{p(2)} - v_{1(1)}v_{p(1)}) \right. \\
& + \sum_{q=1}^{n_q} p_{13,q} \{ v_{p(2)}^{q+1}(1-v_{1(2)}) \\
& \left. - v_{p(1)}^{q+1}(1-v_{1(1)}) \right\}
\end{aligned}$$

$$\begin{aligned}
& - \chi_{23}^0 \left[(v_{2(2)}v_{p(2)} - v_{2(1)}v_{p(1)}) \right. \\
& + \sum_{r=1}^{n_r} p_{23,r} (v_{2(2)}v_{p(2)}^{r+1} - v_{2(1)}v_{p(1)}^{r+1}) \\
& + \sum_{r=1}^{n_r} p_{23,r} \left(\frac{r}{r+1} \right) \left\{ v_{2(2)} \left(\frac{v_{p(2)}}{1-v_{p(2)}} \right)^{r+1} \right. \\
& \times \frac{1-(v_{1(2)}+v_{p(2)})^{r+1}}{v_{2(2)}} - v_{2(1)} \left(\frac{v_{p(1)}}{1-v_{p(1)}} \right)^{r+1} \\
& \left. \times \frac{1-(v_{1(1)}+v_{p(1)})^{r+1}}{v_{2(1)}} \right\} = 0 \quad (29)
\end{aligned}$$

Substitution of eq 14 into 25 gives eq 30 (the left-hand side of eq 30 is put with B):

$$\begin{aligned}
B \equiv & \ln \frac{v_{2(2)}}{v_{2(1)}} + (v_{p(2)} - v_{p(1)}) - \left(\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}} \right) \\
& + \chi_{12}^0 \left[(v_{1(2)} - v_{1(1)}) - (v_{1(2)}v_{2(2)} - v_{1(1)}v_{2(1)}) \right. \\
& + \sum_{s=1}^{n_s} p_{12,s} \left\{ (v_{1(2)}v_{p(2)}^s - v_{1(1)}v_{p(1)}^s) \right. \\
& \left. - (s+1)(v_{1(2)}v_{2(2)}v_{p(2)}^s - v_{1(1)}v_{2(1)}v_{p(1)}^s) \right\} \\
& + \chi_{23}^0 \left[(v_{p(2)} - v_{p(1)}) - (v_{2(2)}v_{p(2)} - v_{2(1)}v_{p(1)}) \right. \\
& + \sum_{r=1}^{n_r} p_{23,r} \{ v_{p(2)}^{r+1}(1-v_{2(2)}) - v_{p(1)}^{r+1}(1-v_{2(1)}) \} \\
& - \chi_{13}^0 \left[(v_{1(2)}v_{p(2)} - v_{1(1)}v_{p(1)}) \right. \\
& + \sum_{q=1}^{n_q} p_{13,q} (v_{1(2)}v_{p(2)}^{q+1} - v_{1(1)}v_{p(1)}^{q+1}) \\
& + \sum_{q=1}^{n_q} p_{13,q} \left(\frac{q}{q+1} \right) \left\{ v_{1(2)} \left(\frac{v_{p(2)}}{1-v_{p(2)}} \right)^{q+1} \right. \\
& \times \frac{1-(v_{2(2)}+v_{p(2)})^{q+1}}{v_{1(2)}} - v_{1(1)} \left(\frac{v_{p(1)}}{1-v_{p(1)}} \right)^{q+1} \\
& \left. \times \frac{1-(v_{2(1)}+v_{p(1)})^{q+1}}{v_{1(1)}} \right\} = 0 \quad (30)
\end{aligned}$$

If both (a) χ_{12}^0 , χ_{13}^0 , and χ_{23}^0 and (b) $p_{12,s}$, $p_{13,q}$, and $p_{23,r}$ ($s=1, \dots, n_s$; $q=1, \dots, n_q$; $r=1, \dots, n_r$) are given in advance, σ , A , and B are functions

having six variables, $X_{n(1)}$, $X_{n(2)}$, $v_{2(1)}$, $v_{2(2)}$, $v_{p(1)}$, and $v_{p(2)}$.

Dissolve original polymer into solvent (ordinally, solvent 1) and add non-solvent (ordinally, solvent 2), two-phase separation finally occurs. If volumes of solvent 1, 2, and polymer are V_1^0 , V_2 , and V_3^0 , respectively, the volume of starting solution V_0 is given by $V_1^0 + V_3^0$ and the starting concentration v_p^s is given by

$$v_p^s = \frac{V_3^0}{V_0} = \frac{V_3^0}{V_1^0 + V_3^0} \quad (31)$$

Under the two phase equilibrium, the total volume of the system is $V_1^0 + V_2 + V_3^0 (=V)$ and the initial concentration v_p^0 is expressed by

$$v_p^0 = \frac{V_3^0}{V} = \frac{V_3^0}{V_1^0 + V_2 + V_3^0} \quad (32)$$

Normalized molecular weight distribution (MWD) of original polymer $g_0(X_i)$ is a summation of the relative amounts of X_i -mer separated into polymer-lean and -rich phase, $g_{(1)}(X_i)$ and $g_{(2)}(X_i)$:

$$g_0(X_i) = g_{(1)}(X_i) + g_{(2)}(X_i) \quad (i=1, \dots, m) \quad (33)$$

The weight fraction ρ_s of the polymer in the polymer-lean phase to the total polymer and the fraction $\rho_p (=1-\rho_s)$ of the polymer in the polymer-rich phase are given by eq 34a and 34b.

$$\rho_s = \sum_{i=1}^m g_{(1)}(X_i) \quad (34a)$$

$$\rho_p = \sum_{i=1}^m g_{(2)}(X_i) \quad (34b)$$

Using σ , phase volume ratio $R (=V_{(1)}/V_{(2)}$; $V_{(1)}$ and $V_{(2)}$, volume of the polymer-lean and rich phases) and $g_0(X_i)$, $g_{(1)}(X_i)$, and $g_{(2)}(X_i)$ are expressed as (see, Appendix C):

$$g_{(1)}(X_i) = \frac{R}{R + \exp(\sigma X_i)} g_0(X_i) \quad (35a)$$

$$g_{(2)}(X_i) = \frac{\exp(\sigma X_i)}{R + \exp(\sigma X_i)} g_0(X_i) \quad (35b)$$

$v_{p(1)}$, $v_{p(2)}$, and $X_{n(1)}$ are finally expressed by eq 36a, b, and 37 (see, Appendix C).

$$v_{p(1)} = v_p^s \frac{R+1-Rv_{2(1)}-v_{2(2)}}{R} \rho_s \quad (36a)$$

$$v_{p(2)} = v_p^s (R+1-Rv_{2(1)}-v_{2(2)}) \rho_p \quad (36b)$$

$$\frac{1}{X_{n(1)}} = \frac{1}{\rho_s} \left(\frac{1}{X_n^0} - \frac{1}{X_{n(2)}} \right) \quad (37)$$

Here, X_n^0 is the number-average X_i of original polymer. If ρ_p is set as initial condition ρ_p^g , σ , A , and B become the functions of four variables $v_{2(1)}$, $v_{2(2)}$, R^a , and $X_{n(2)}^a$.

$$\sigma = \sigma(v_{2(1)}, v_{2(2)}, R^a, X_{n(2)}^a) \quad (38)$$

$$A = A(v_{2(1)}, v_{2(2)}, R^a, X_{n(2)}^a) = 0 \quad (39)$$

$$B = B(v_{2(1)}, v_{2(2)}, R^a, X_{n(2)}^a) = 0 \quad (40)$$

where R^a and $X_{n(2)}^a$ are the assumed value of R and $X_{n(2)}$, $X_{n(2)}$ in eq 38–40 is given by

$$X_{n(2)} = \sum_{i=1}^m g_{(2)}(X_i) \left/ \left(\sum_{i=1}^m g_{(2)}(X_i) / X_i \right) \right. \quad (41)$$

Combining eq 34b, 35b, and 41, ρ_p and $X_{n(2)}$ are finally the functions of σ and R^a . We define C and D by eq 42 and 43, respectively.

$$C \equiv \rho_p(\sigma(v_{2(1)}, v_{2(2)}, R^a, X_{n(2)}^a), R^a) - \rho_p^g \quad (42)$$

$$D \equiv X_{n(2)}(\sigma(v_{2(1)}, v_{2(2)}, R^a, X_{n(2)}^a), R^a) - X_{n(2)}^a \quad (43)$$

By solving non-linear simultaneous equations 39, 40, 42, and 43, $v_{2(1)}$, $v_{2(2)}$, R , and $X_{n(2)}$ are determined. Substituting these four values into eq 38, we can calculate σ and other phase separation characteristics (see, Appendix C).

COMPUTER SIMULATION

Computer experiments were carried out according to the procedure, established in the previous papers.⁹⁻¹¹

1. As prerequisites, (a) χ_{12}^0 , χ_{13}^0 , and χ_{23}^0 , (b) $p_{12,s}$, $p_{13,q}$, and $p_{23,r}$ ($s=1, \dots, n_s$; $q=1, \dots,$

$n_q; r=1, \dots, n_r$), (c) $V_1^0, V_3^0, g_0(X_i)$ ($i=1, \dots, m$), and ρ_p ($=1-\rho_s$) are given.

2. At first, $X_{n(2)}^a$ and three values of R^a (low, middle, and high value of $R^a, R_L, R_M,$ and R_H , respectively) are assumed. True R should be between R_L and R_M or R_M and R_H .

3. For the assumed $X_{n(2)}$ and R^a , simultaneous equations 44 and 45,

$$A = A(v_{2(1)}, v_{2(2)}) = 0 \quad (44)$$

$$B = B(v_{2(1)}, v_{2(2)}) = 0 \quad (45)$$

are solved by using two variable Newton's method.

4. Substituting three sets of $(v_{2(1)}, v_{2(2)})$, which correspond to $R_L, R_M,$ and R_H , into eq 42, we get $C_L, C_M,$ and C_H . Reset (R_L, R_H) by (R_L, R_M) for $C_L \cdot C_M < 0$ and by (R_M, R_H) for $C_M \cdot C_H < 0$. $\sigma_L, \sigma_M,$ and σ_H are also obtained.

5. Using interhalving method (repetition

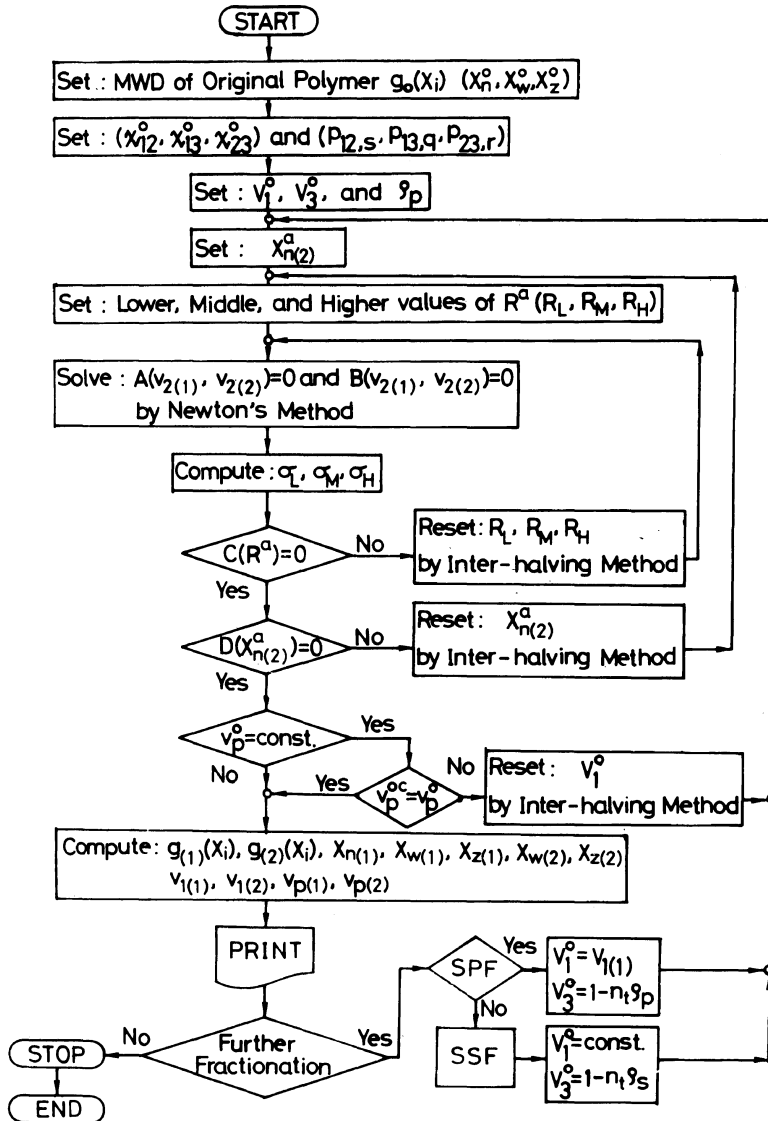


Figure 1. Flow chart of the simulation.

of step 3—4),

$$C = C(R^a) = 0 \quad (46)$$

can be attained. Thus, R and σ (accordingly, $g_{(1)}(X_i)$ and $g_{(2)}(X_i)$) are determined for the assumed value of $X_{n(2)}$.

6. When D (given by eq 43) $\neq 0$ for calculated σ and R , replace $X_{n(2)}^a$ by $(X_{n(2)} + X_{n(2)}^a)/2$.

7. Repeating step 3—6 (interhalving method),

$$D = D(X_{n(2)}^a) = 0 \quad (47)$$

can be solved for $X_{n(2)}^a$ and therefore an equilibrium state is finally determined.

8. When a constant initial polymer volume fraction ($v_p^0 = \text{constant}$, v_p^{0g}) is needed, we solve the following equation

$$v_p^0(v_{2(1)}, v_{2(2)}, R^a, V_1^0) - v_p^{0g} = 0 \quad (48)$$

by replacing V_1^0 (repetition of step 1—7).

9. Compute other phase separation characteristics (a) V_2 , V , $V_{(1)}$, and $V_{(2)}$, (b) $v_{1(1)}$, $v_{1(2)}$, $v_{p(1)}$, and $v_{p(2)}$, and (c) $X_{n(1)}$, $X_{w(1)}$, $X_{w(2)}$ and so on.

This simulation procedure is superior to others^{1-7,13} with respect to following point.

(i) MWD of polymer in both phases can directly be obtained, in addition to the volume fractions of solvents and polymer.

(ii) ρ_p can be determined rigorously. For example, Altena and Smolders¹³ did not write clearly ρ_p in their computer experiments on the phase separation of mono-disperse polymer/binary solvent mixture.

(iii) Calculations under constant v_p^0 are feasible. Constant v_p^0 is important to compare quasi-ternary system with quasi-binary system. Figure 1 shows the main flow chart of simulation.

COMPUTER EXPERIMENT

Original polymer was assumed to have the Schulz-Zimm (SZ) type MWD,

$$g_0(X_i) = \frac{y^{h+1}}{\Gamma(h+1)} X_i^h \exp(-yX_i) \quad (49)$$

where

$$y = h/X_n^0 \quad (50)$$

and

$$h = 1/(X_w^0/X_n^0 - 1) \quad (51)$$

with $X_w^0 = 300$ and $X_w^0/X_n^0 = 2$. $\Gamma(h+1)$ is the gamma function. We have already ascertained that the conclusion obtained for the SZ type polymer with $X_w^0 = 300$ has very general character applicable for common polymer solution.¹¹ The calculations were made under following conditions: (a) $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, (b) $p_{12,1} = -1.0 \sim 2.0$, $p_{13,1} = -0.6 \sim 0.6$, and $p_{23,1} = -0.15 \sim 0.15$ ($p_{12,s} = p_{13,q} = p_{23,r} = 0$ for $s, q, r \geq 2$), (c) $\rho_p = 1/100 \sim 99/100$, $V_3^0 = 1$, and $v_p^0 = 0.005$. For comparison, calculations of quasi-binary system, under the conditions of $p_1 = -0.6$, 0 , and 0.6 ($p_j = 0, j \geq 2$), $V_3^0 = 1$, and $v_p^0 = 0.005$, were also carried out. When coexisting curves were calculated, we put $v_p^s = 0.01$ in place of $v_p^0 = 0.005$. Equations 46—48 were considered to be solved, if $|C(R^a)| < E_1$, $|D(X_{n(2)}^a)| < E_2$, and $|v_p^0 - v_p^{0g}| < E_3$ were satisfied. E_1 , E_2 , and E_3 are allowance errors. Here, $E_1 = 0.001$, $E_2 = 0.01$, and $E_3 = 0.001$.

RESULTS AND DISCUSSION

Figure 2 shows the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the normalized X distribution of the polymer partitioned in the polymer-rich phase $g_{(2)}(X_i)$ at $\rho_p = 1/15$. $p_{12,1}$ was found to have small but still significant effect on $g_{(2)}(X_i)$ and the breadth in $g_{(2)}(X)$ attains minimum at $p_{12,1} = -0.2$ when $p_{13,1} = p_{23,1} = 0$. The polydispersity of the polymer in a polymer-rich phase becomes lower with an increase in $p_{13,1}$ or $p_{23,1}$, at least in the range $p_{13,1} \leq 0.6$ and $p_{23,1} \leq 0.07$. Particularly, a small change in

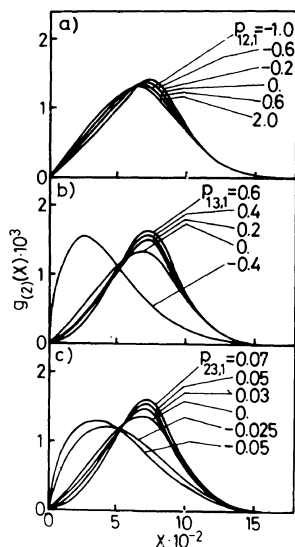


Figure 2. Effects of the 1st order concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the normalized molecular weight distribution of the polymer partitioned in polymer rich phase $g_{(2)}$. Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $\rho_p = 1/15$ and $v_p^0 = 0.005$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$.

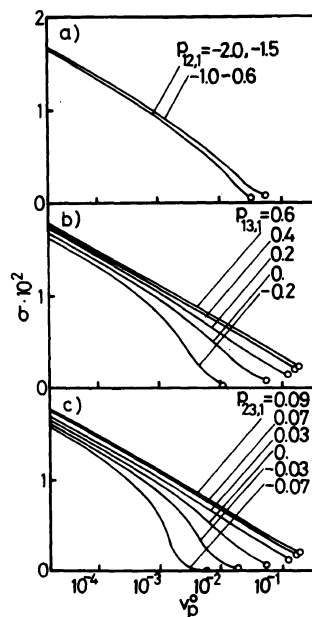


Figure 3. Effects of the 1st order concentration dependent parameters $p_{12,1}$, $p_{13,1}$ and $p_{23,1}$ on the relations between partition coefficient σ and v_p^0 . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $\rho_p = 1/15$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. Unfilled circle denotes $v_{p,c}^0$.

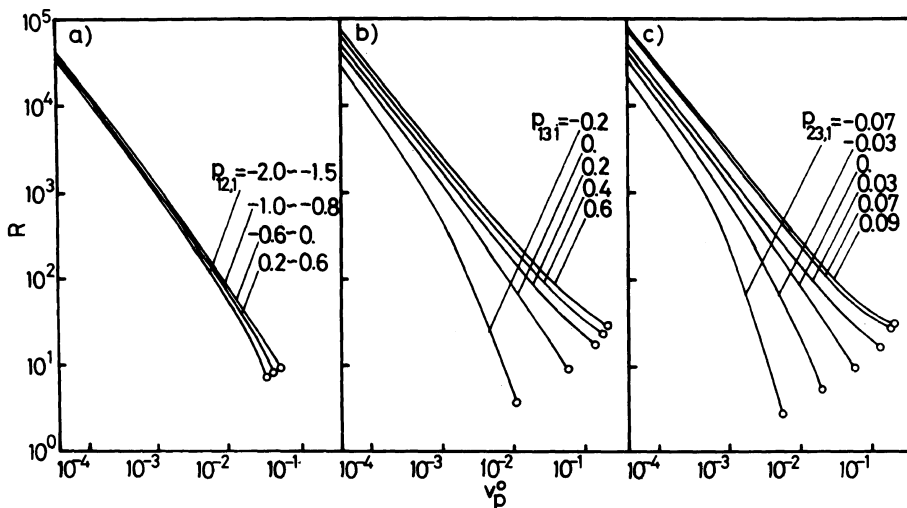


Figure 4. Effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between the two phase volume ratio R and v_p^0 . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $\rho_p = 1/15$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. Unfilled circle denotes $v_{p,c}^0$.

$p_{23,1}$ brings about a large change in $g_{(2)}(X)$. The effect of the concentration dependence of χ -parameters on $g_{(2)}(X)$ decreases in the following order: $p_{23,1} > p_{13,1} > p_{12,1}$.

In Figures 3 and 4, the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the σ (or R) vs. v_p^0 relations at $\rho_p = 1/15$ are shown. Unfilled circle indicates the point at which both σ and R reach a minimum. Above v_p^0 at minimum, two-phase separation under given conditions becomes impossible and this v_p^0 was defined as "critical point" by Kamide *et al.*¹⁸ for quasi-binary system and referred to as $v_{p,c}^0$. Unfilled circle approaches critical solution point (CSP) in the limit of $\rho_p \rightarrow 0$. Volume fractions

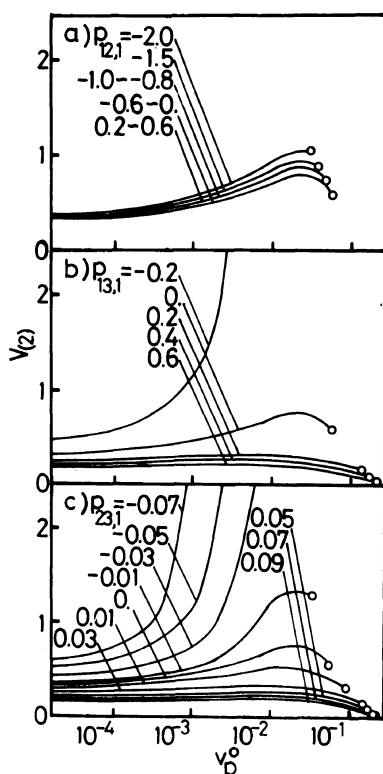


Figure 5. Effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between the volume of the polymer rich phase $V_{(2)}$ and v_p^0 . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $\rho_p = 1/15$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. Unfilled circle denotes $v_{p,c}^0$.

of solvents 1, 2, and polymer at CSP (v_1^c , v_2^c , and v_p^c , respectively) can be calculated from the spinodal and neutral-equilibrium conditions according to the method proposed by Kamide and Matsuda.¹⁹ (v_1^c , v_2^c , v_p^c) is (0.4880, 0.4609, 0.0511) under the conditions of (χ_{12}^0 , χ_{13}^0 , χ_{23}^0) = (0.5, 0.2, 1.0) with $p_{12,1} = p_{13,1} = p_{23,1} = 0$. When $p_{12,1} = p_{13,1} = p_{23,1} = 0$, $v_{p,c}^0$ at $\rho_p = 1/15$ is *ca.* 0.05 and is close to v_p^c . Both σ and R decrease with an increase in v_p^0 . Generally, σ and R , at given ρ_p , increase with increasing $p_{13,1}$, and $p_{23,1}$. The effects of $p_{12,1}$ on σ (or R) vs. v_p^0 curve are small.

Relations between $V_{(2)}$ and v_p^0 under the conditions of $\rho_p = 1/15$ are shown in Figure 5. In this figure, unfilled circle, is $v_{p,c}^0$. As v_p^0 increases, $V_{(2)}$ increases first and shows the maximum. v_p^0 at this maximum of $V_{(2)}$ vs. v_p^0 curve, corresponds to v_p^0 , which gives the maximum of $v_{1(2)}$ or $v_{2(2)}$ vs. v_p^0 curve and also corresponds to the minimum of $v_{p(2)}$ vs. v_p^0 curve (for example, see Figure 13). With a decrease in $p_{13,1}$ and $p_{23,1}$ $V_{(2)}$ increases suddenly. The effects of $p_{12,1}$ on $V_{(2)}$ is relatively small. And $V_{(2)}$ shows a minimum at a specific $p_{12,1}$, between $p_{12,1} = -0.6$ and 0. On the other hand, V and $V_{(1)}$ decrease almost linearly with an increase in v_p^0 . $V_{(1)}/V_{(2)}$ (namely R) vs. v_p^0 curve is little influenced by the maximum of $V_{(2)}$ vs. v_p^0 curve because of a rapid change in $V_{(1)}$ (see, Figure 4).

Figure 6 shows the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between V_1 (or V_2) and ρ_p relations, when v_p is constant (in this case, $v_p^0 = 0.005$). At constant v_p^0 (namely, constant V), we can compare $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ with p_1 , which is the concentration dependent parameter of χ for quasi-binary solutions (see eq 4). Between V_1 vs. ρ_p curve and V_2 vs. ρ_p curve, there is a mirror symmetry with respect to the broken line of $V_1 = V_2 = (V - V_3^0)/2$ (in this case $V = 200$ and $V_3^0 = 1$). As $p_{13,1}$ and $p_{23,1}$ increase V_1 decreases and V_2 increases. In other words, solvent power of solvent 1 grows stronger with an increase in $p_{13,1}$, and precipitating power of solvent 2

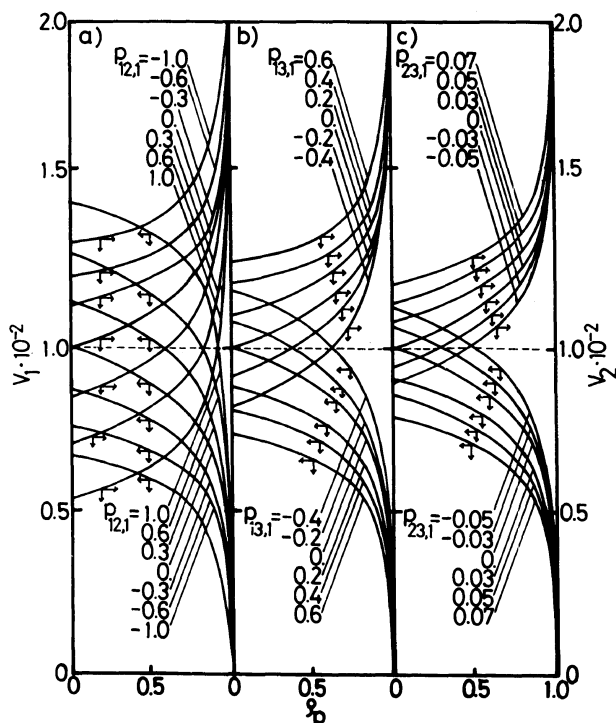


Figure 6. Effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations of the volume of solvent 1 (or 2), V_1^0 (or V_2) and ρ_p . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $v_p^0 = 0.005$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. Broken line denotes the line of $V_1 = V_2 = (V - V_3^0)/2$.

gets weaker with an increase in $p_{23,1}$. As $p_{12,1}$ decreases, solvent power of binary solvent mixture becomes stronger. The figure shows that V_1 reduces to zero at $\rho_p = 1.0$.

The effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between σ (or R) and ρ_p are shown in Figure 7. In the figure, results of quasi-binary system with $p_1 = -0.6, 0$, and 0.6 ($p_j = 0$, $J \geq 2$) are also shown by the broken line.²⁰⁻²⁷ In the case of $p_{12,1}$, $p_{13,1}$, and $p_{23,1} = 0$, σ and R for quasi-ternary system are smaller than those for quasi-binary system with $p_1 = 0$ for any combination of χ_{12}^0 , χ_{13}^0 , and χ_{23}^0 .⁹ When $p_{13,1} \geq 0.2$ (with $p_{12,1} = p_{23,1} = 0$) or $p_{23,1} \geq 0.03$ (with $p_{12,1} = p_{23,1} = 0$), σ (or R) for the quasi-ternary system exceeds σ (or R) for the quasi-binary system with $p_1 = 0$. Especially, σ and R for the quasi-ternary system

with $p_{23,1} = 0.09$ ($p_{12,1} = p_{13,1} = 0$) are larger than σ and R for the quasi-binary system with $p_1 = 0.6$. In consequence, under specific conditions, a better fractionation efficiency is expected to be obtained for the quasi-ternary solution than for the quasi-binary solutions. This prediction however has not been experimentally confirmed and clearly more detailed experimental examination is called for. The effect of $p_{12,1}$ on σ (or R) is not so large.

We denote σ , R , and the volume fractions of each phase at $\rho_p = 1$ with an asterisk as σ^* , R^* , ($v_{1(1)}^*$, $v_{2(1)}^*$, $v_{p(1)}^*$) and ($v_{1(1)}^*$, $v_{2(2)}^*$, $v_{p(1)}^*$). $v_{p(2)}^*$ can be calculated by the following equation.

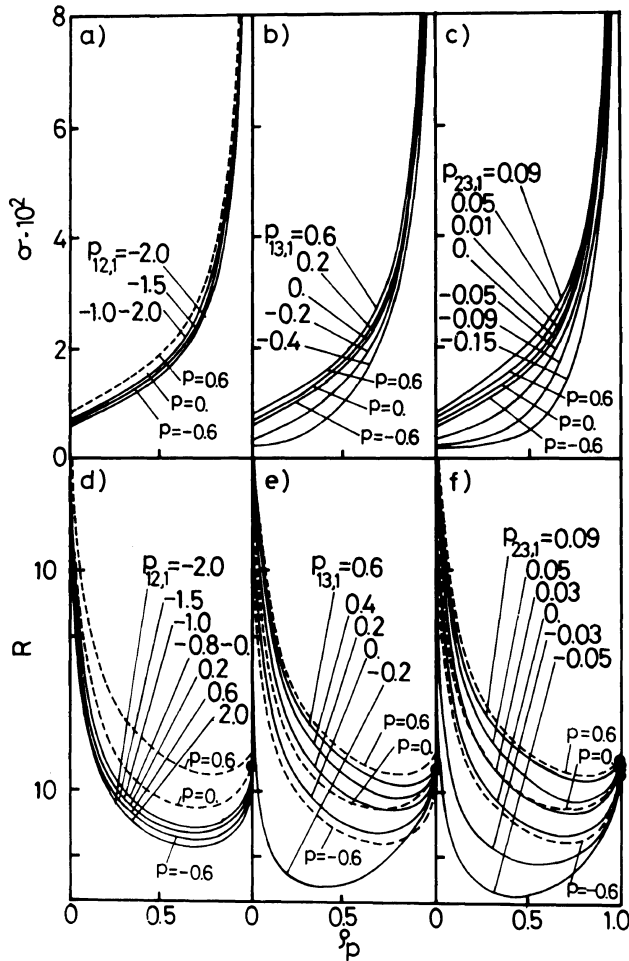


Figure 7. Effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between partition coefficient σ or the phase volume ratio R and ρ_p . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $v_p^0 = 0.005$. a) and d) $p_{13,1} = p_{23,1} = 0$, b) and e) $p_{12,1} = p_{23,1} = 0$, c) and f) $p_{12,1} = p_{13,1} = 0$. The broken lines are the results for quasi-binary system. p is denoted on curve. Filled circle denotes R at $\rho_p = 1.0$.

$$\ln(1 - v_{p(2)}^*) + v_{p(2)}^* - \frac{v_{p(2)}^*}{X_n^0} + \chi_{23}^0 \left[v_{p(2)}^{*2} + \sum_{r=1}^{n_r} p_{23,r} v_{p(2)}^{*r+2} \right] = 0 \quad (52)$$

and R^* is expressed by

$$R^* = \frac{v_{p(2)}^*}{v_p^0} - 1 \quad (53)$$

As is known from eq 52 and 53, $v_{p(2)}^*$ and

R^* are independent of χ_{12}^0 , χ_{13}^0 , $p_{12,s}$, and $p_{13,q}$ ($s = 1, \dots, n_s$; $q = 1, \dots, n_q$) and determined by χ_{23}^0 and $p_{23,r}$ ($r = 1, \dots, n_r$). The extrapolated values of R for $\rho_p \rightarrow 1$ are given by filled circle in Figure 7d, e, and f, and are consistent with R^* calculated from eq 52. From the combination of $v_{x_i(1)} = 0$ ($i = 1, \dots, 0$) for $\rho_p = 1$ and the definition of σ (eq 27), σ for $\rho_p = 1$ (σ^*) becomes infinite. Figure 8 shows the effect of $p_{23,1}$ on R^* , $v_{2(2)}^*$, and $v_{p(2)}^*$. With an increase in $p_{23,1}$, R^* and $v_{p(2)}^*$ increase and $v_{2(2)}^*$ decreases.

We can evaluate χ_{23}^0 and $p_{23,r}$ from R^* experimentally determined.

The effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on relations between X_w/X_n and v_p^0 (for $\rho_p=1/15$) are shown in Figure 9. With an increase in $p_{13,1}$ and $p_{23,1}$, X_w/X_n decreases abruptly.

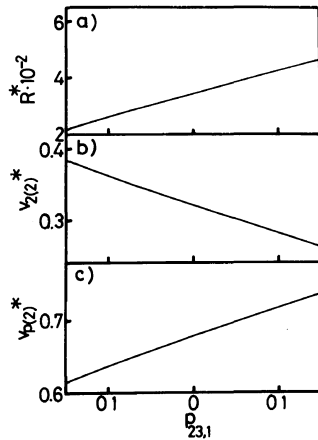


Figure 8. The effects of $p_{23,1}$ on the R , $v_{2(2)}$, and $v_{p(2)}$ for $\rho_p=1.0$ (R^* , $v_{2(2)}^*$, and $v_{p(2)}^*$, respectively). Original polymer, Schulz-Zimm type distribution ($X_w^0=300$, $X_w^0/X_n^0=2$); $\chi_{12}^0=0.5$, $\chi_{13}^0=0.2$, and $\chi_{23}^0=1.0$. $p_{12,1}=p_{13,1}=0$, $v_p^0=0.005$.

X_w/X_n of the polymer in polymer-lean and -rich phases ($X_{w(1)}/X_{n(1)}$ and $X_{w(2)}/X_{n(2)}$) increases with an increase in v_p^0 and coincides with each other for $v_{p,c}^0$. As ρ_p decreases from 1/15 to zero, $v_{p,c}^0$ approaches to the critical polymer concentration.

Figure 10 shows the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relation between the ratio X_w/X_n of the two phases and ρ_p . In this figure the results¹⁴ for quasi-binary solutions with various p_1 are shown as broken lines for comparison. For any combination of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$, X_w/X_n of the polymer in the polymer-lean phase $X_{w(1)}/X_{n(1)}$ decreases monotonically from 2.0 to 1.0 as an increase in ρ_p . X_w/X_n of the polymer in a polymer-rich phase $X_{w(2)}/X_{n(2)}$ reveals minimum at a specific ρ_p , approaching to X_w^0/X_n^0 at $\rho_p=1.0$. Over a whole range of ρ_p $X_{w(2)}/X_{n(2)}$ attains minimum at $p_{12,1}=-0.2$ when $\chi_{12}^0=0.5$, $\chi_{13}^0=0.2$ and $\chi_{23}^0=1.0$ and becomes smaller for larger $p_{13,1}$ and $p_{23,1}$. Note that the relation between $X_{w(2)}/X_{n(2)}$ and ρ_p for the quasi-ternary systems agrees with that of the quasi-binary systems with $p_1=0.6$. For exam-

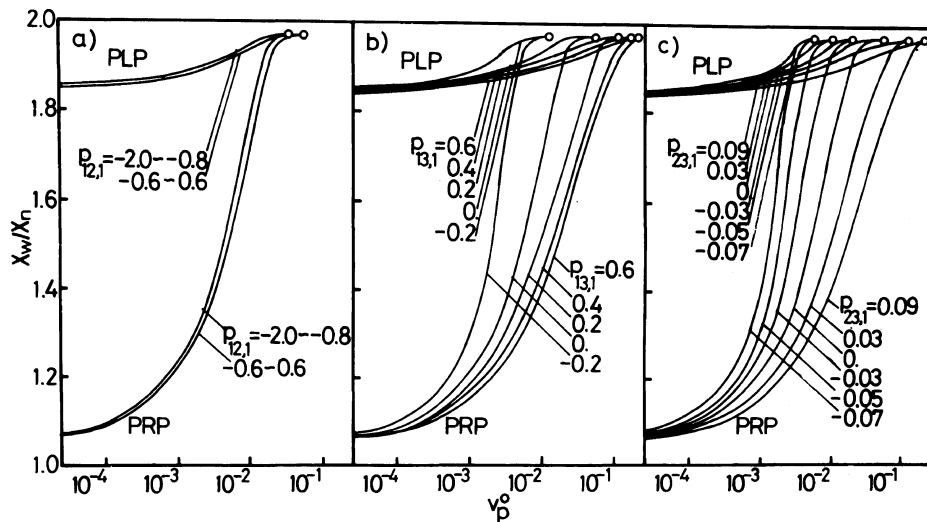


Figure 9. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between X_w/X_n of the polymers in polymer-lean phase (PLP) or polymer-rich phase (PRP) and v_p^0 . Original polymer, Schulz-Zimm type distribution ($X_w^0=300$, $X_w^0/X_n^0=2$); $\chi_{12}^0=0.5$, $\chi_{13}^0=0.2$, and $\chi_{23}^0=1.0$, $\rho_p=1/15$. a) $p_{13,1}=p_{23,1}=0$, b) $p_{12,1}=p_{23,1}=0$, c) $p_{12,1}=p_{13,1}=0$. Unfilled circle denotes $v_{p,c}^0$.

ple, when $p_{13,1}=0.6$ ($p_{12,1}=p_{23,1}=0$) or $p_{23,1}=0.05$ ($p_{12,1}=p_{13,1}=0$) for the quasi-ternary systems (SZ polymer, $X_w^0=300$, $X_w^0/X_n^0=2$, $v_p^0=0.005$), $X_{w(2)}/X_{n(2)}$ vs. ρ_p relation almost coincides with that for the quasi-binary systems (SZ polymer, $X_w^0=300$, $X_w^0/X_n^0=2$, $v_p^0=0.005$). In a previous paper,⁹ we demonstrated that simply by a proper choice of χ_{12}^0 , χ_{13}^0 , and χ_{23}^0 values, polymers could not be prepared having narrower MWD than those obtained from a quasi-binary solution with $p_1=0$. Combination of solvents 1 and 2 with larger values of $p_{13,1}$ and $p_{23,1}$ (in this case, $p_{13,1} \geq 0.6$ and $p_{23,1} \geq 0.05$, respectively) will afford us polymer having narrower MWD than that obtained from quasi-binary system in a polymer fractionation experiment. It has been shown that the effects of χ_{13}^0 on $g_{(2)}(X_i)$ is small but χ_{23}^0 has a large effect on $g_{(2)}(X_i)$.¹⁰ Figure 10 in-

dicates that $p_{23,1}$ has a strong influence on $g_{(2)}(X_i)$, accordingly $X_{w(2)}/X_{n(2)}$. In other words, a suitable choice of solvent 2 (*i.e.*, non-solvent) is required to separate the polymers with sharp MWD from quasi-ternary systems.

Figure 11 shows the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relation between the standard deviation of MWD σ' ($\equiv \{X_w(X_z - X_w)\}^{1/2}$, X_z , the z -average of X_i) of the polymers partitioned in two phases and v_p^0 in the case of $\rho_p=1/15$. Broken line in the figure shows the σ' of original polymer [σ'_0 ($=212.1$)]. In the figure unfilled circle is the $v_{p,c}^0$. $\sigma'_{(1)}$ of the polymer in PLP ($\sigma'_{(1)}$) increases with an increase in v_p^0 and almost coincides with σ'_0 at $v_{p,c}^0$, which approaches to v_p^0 for $\rho_p \rightarrow 0$. $X_{n(1)}$, $X_{w(1)}$, and $X_{z(1)}$ increase with an increase in v_p^0 . $\sigma'_{(1)}$ is very close to σ'_0 at $v_p^0 = v_{p,c}^0$. On the other hand, $X_{n(2)}$, $X_{w(2)}$, and

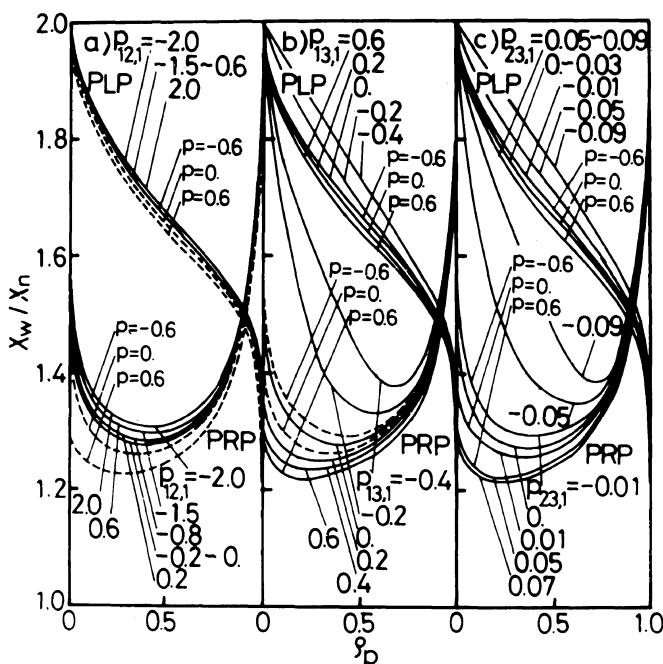


Figure 10. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between X_w/X_n of the polymers in polymer-lean phase (PLP) or polymer-rich phase (PRP) and ρ_p . Original polymer, Schulz-Zimm type distribution ($X_w^0=300$, $X_w^0/X_n^0=2$); $\chi_{12}^0=0.5$, $\chi_{13}^0=0.2$, and $\chi_{23}^0=1.0$, $v_p^0=0.005$. a) $p_{13,1}=p_{23,1}=0$, b) $p_{12,1}=p_{23,1}=0$, c) $p_{12,1}=p_{13,1}=0$. The broken lines are the results for quasi-binary system. p is denoted on curve.

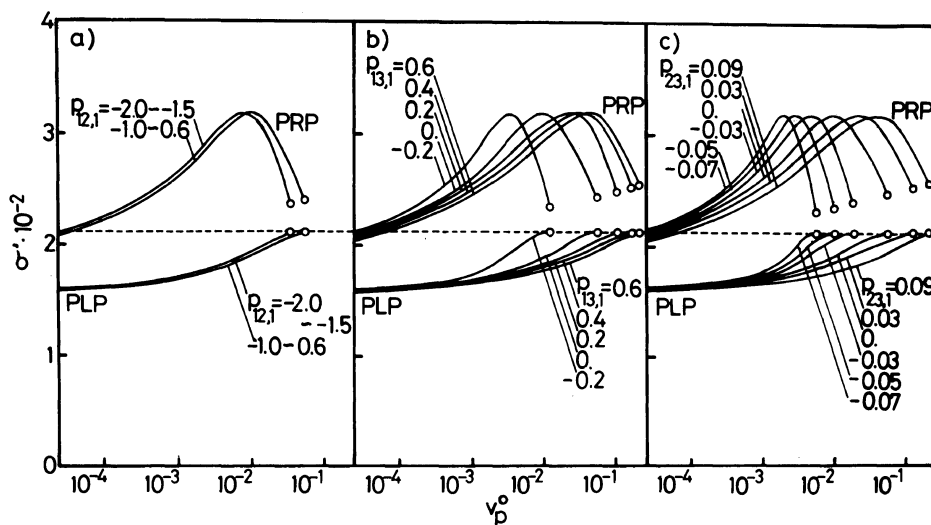


Figure 11. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between σ' of the polymers in polymer-lean phase (PLP) or polymer-rich phase (PRP) and v_p^0 . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $\rho_p = 1/15$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. Unfilled circle denotes $v_{p,c}^0$.

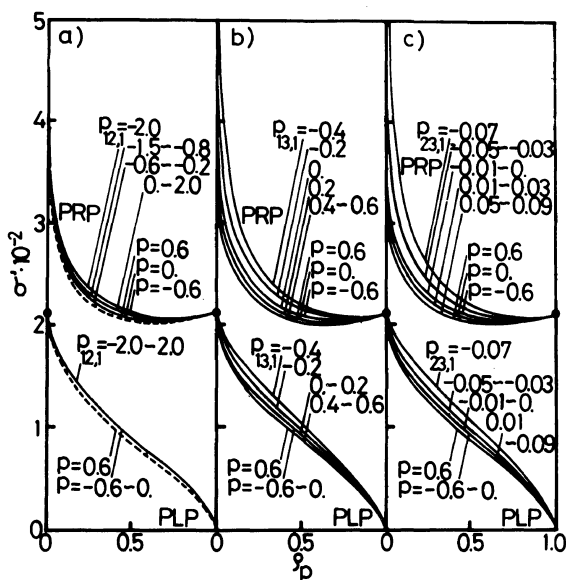


Figure 12. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between σ' of the polymers in polymer-lean phase (PLP) or polymer-rich phase (PRP) and ρ_p . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $v_p^0 = 0.005$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. The broken lines are the results for quasi-binary system. p is denoted on curve.

$X_{z(2)}$ decrease and $X_{z(2)} - X_{w(2)}$ increases monotonically as v_p^0 increases. In the range of $v_p^0 \leq 1 \cdot 10^{-4}$, $\sigma'_{(2)}$ is smaller than σ'_0 . With an

increase in $X_{z(2)} - X_{w(2)}$, $\sigma'_{(2)}$ gradually increases and coincides with σ'_0 at $v_p^0 \sim 1 \times 10^4$. In spite of the agreement of $\sigma'_{(2)}$ with σ'_0

at $v_p^0 \sim 1 \times 10^{-4}$, neither $X_{w(2)} = X_w^0$ nor $X_{z(2)} = X_z^0$ hold even at $v_p^0 \sim 1 \times 10^{-4}$ but $X_{w(2)} \gg X_w^0$ and $X_{z(2)} \gg X_z^0$ hold. $\sigma'_{(2)}$ attains a maximum at specific v_p^0 ($\equiv v_p^0, \text{max}$) because the effect of decrease in $X_{w(2)}$ becomes larger than those of increase in $X_{z(2)} - X_{w(2)}$. Fur-

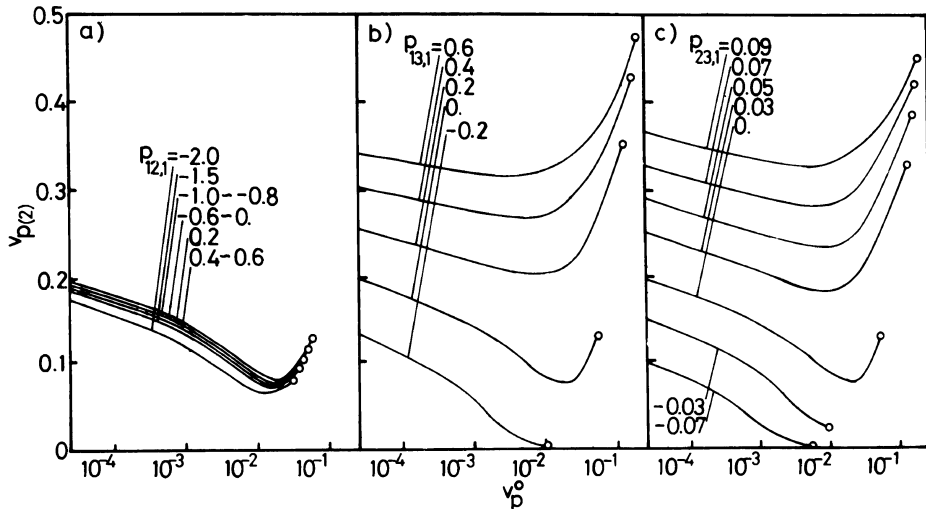


Figure 13. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between polymer volume fraction in polymer-rich phase $v_{p(2)}$ and v_p^0 . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $\rho_p = 1/15$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. Unfilled circle denotes $v_{p,c}$.

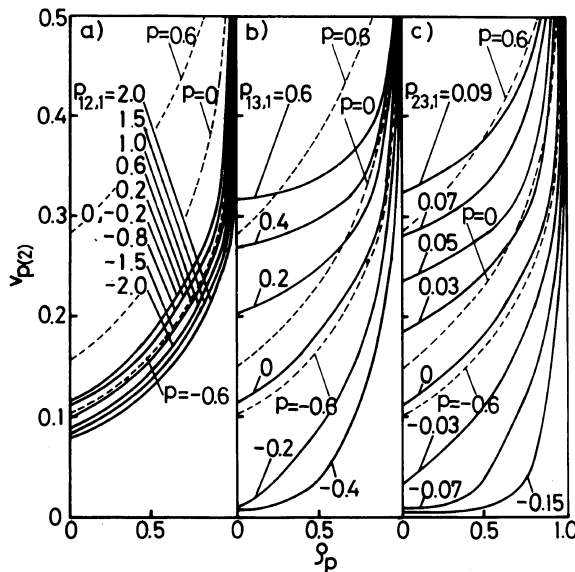


Figure 14. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between polymer volume fraction in polymer-rich phase $v_{p(2)}$ and ρ_p . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $v_p^0 = 0.005$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. The broken lines are the results for quasi-binary system. p is denoted on curve.

ther, $\sigma'_{(2)}$ rapidly decreases with an increase in v_p^0 . When $v_p^0 = v_{p,c}^c$, $X_{n(2)}$, $X_{w(2)}$, and $X_{z(2)}$ are fairly larger than X_n^0 , X_w^0 , and X_z^0 , respectively and $\sigma'_{(2)}$ is larger than σ'_0 . At $v_p^0 = v_{p,c}^c$, $X_{w(2)}/X_{n(2)}$ coincides with $X_{w(1)}/X_{n(1)}$ as shown in Figure 9, but note that $X_{n(2)} \gg X_{n(1)}$ and $X_{w(2)} \gg X_{n(1)}$ always hold. As $v_{p,c}^c$ increases with an increase in $p_{13,1}$ and $p_{23,1}$, we can predict that v_p^c slowly increases with an increase in $p_{13,1}$ and $p_{23,1}$.

Figure 12 shows the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on σ' vs. ρ_p curve. The figure also includes the results²⁰⁻²⁷ of quasi-binary system as broken line for comparison. Filled circle denotes the value for the original polymer (σ'_0). As well as $X_{w(2)}/X_{n(2)}$ vs. ρ_p curve, $\sigma'_{(2)}$ vs. ρ_p curve has a minimum at some ρ_p . $\sigma'_{(1)}$ and $\sigma'_{(2)}$ gradually decrease with an increase in $p_{13,1}$ and $p_{23,1}$. $\sigma'_{(2)}$ of the quasi-ternary system with $p_{13,1} = 0.4 \sim 0.6$ ($p_{12,1} = p_{23,1} = 0$) or $p_{23,1} = 0.05 \sim 0.09$ ($p_{12,1} = p_{13,1} = 0$) agrees fairly with $\sigma'_{(2)}$ of the quasi-binary system with $p_1 = 0.6$. Similar behavior is observed for $\sigma'_{(1)}$.

Figures 13 and 14 show the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the $v_{p(2)}$ vs. v_p^0 curve and $v_{p(2)}$ vs. ρ_p curve, respectively. The effect of $p_{12,1}$ on $v_{p(2)}$ is small but innegligible and $v_{p(2)}$ for a given ρ_p shows a maximum at $p_{12,1}$, ranging between -0.6 and 0 . The effects of $p_{13,1}$ and $p_{23,1}$ are remarkable and $v_{p(2)}$ increases abruptly with an increase in $p_{13,1}$ and $p_{23,1}$. Especially, $v_{p(2)}$ increases suddenly with a small increase in $p_{23,1}$. $v_{p(2)}$ vs. v_p^0 curve has a minimum at the point corresponding to the maximum of $V_{(2)}$ vs. v_p^0 curve. $v_{p(2)}$ increases with an increase in ρ_p , and coincides with $v_{p(2)}^*$ at $\rho_p = 1$ (see Figure 8). By use of eq C-8b, relation between R and ρ_p is expressed by:

$$R = \frac{v_{p(2)}}{v_p^0 \rho_p} - 1 \quad (54)$$

In the range of the small ρ_p (*i.e.*, $\rho_p < 0.3$), R decreases abruptly with an increase in ρ_p because $v_{p(2)}$ changes slowly with ρ_p . In con-

trast to this, in the large ρ_p region R increases gradually with ρ_p because of the rapid change of $v_{p(2)}$ with ρ_p .

Equation C-8a can be rewritten as follows.

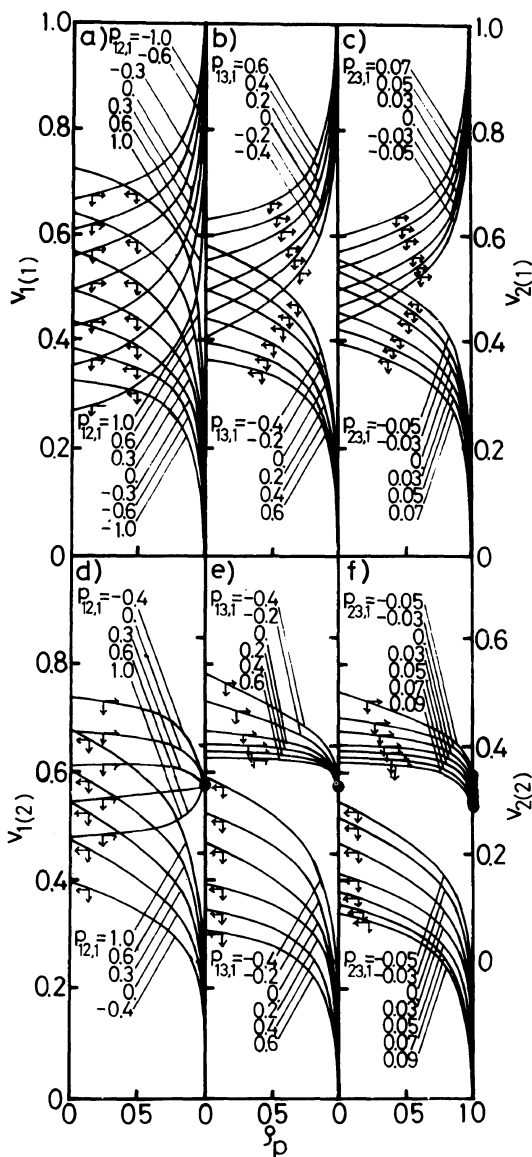


Figure 15. Effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on $v_{1(1)}$, $v_{2(1)}$, $v_{1(2)}$, and $v_{2(2)}$ vs. ρ_p curves. Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $v_p^0 = 0.005$. a) and d) $p_{13,1} = p_{23,1} = 0$, b) and e) $p_{12,1} = p_{23,1} = 0$, c) and f) $p_{12,1} = p_{13,1} = 0$. The broken lines are the results for quasi-binary system. p is denoted on curve.

$$v_{p(1)} = v_p^0 \rho_s \left(1 + \frac{1}{R} \right) \quad (55)$$

If $1/R \ll 1$, $v_{p(1)}$ is independent of χ_{12}^0 , χ_{13}^0 , χ_{23}^0 , $p_{12,s}$, $p_{13,q}$, and $p_{23,r}$ and dependent on ρ_p and v_p^0 (see for example, Figure 19 of ref 10).

The effects of $p_{12,1}$, and $p_{13,1}$, and $p_{23,1}$ on $v_{1(1)}$, $v_{2(1)}$, $v_{1(2)}$, and $v_{2(2)}$ vs. ρ_p curves are shown in Figure 15. Generally, with a decrease in $p_{12,1}$ and an increase in $p_{13,1}$ and $p_{23,1}$, $v_{1(1)}$, $v_{1(2)}$, and $v_{2(2)}$ decrease and $v_{2(1)}$ increases. The effect of concentration dependence of χ -parameters increases in the following order: $p_{12,1} < p_{13,1} < p_{23,1}$. The effect of $p_{12,1}$ on $v_{1(2)}$ is just reverse to that on $v_{2(2)}$ and $v_{1(2)} + v_{2(2)}$ is insignificantly influenced by $p_{12,1}$. $v_{1(1)}$ (or $v_{1(2)}$) vs. ρ_p curve is similar to V_1 vs. ρ_p curve in shape and $v_{2(1)}$ vs. ρ_p curve has a similar shape to V_2 vs. ρ_p curve. As ρ_p increases, $v_{1(1)}$ and $v_{1(2)}$ decrease rapidly, approaching to zero at $\rho_p = 1.0$ and $v_{2(1)}$ increases remarkably, approaching to unity at $\rho_p = 1.0$. Extrapolated value of $v_{2(2)}$ to $\rho_p = 1$ is denoted by filled circle, which coincides with $v_{2(2)}^*$ calculated by eq 52.

Figure 16 shows the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relation between V (or V_2) and ρ_p when solvent 2 (poor solvent) was added to the starting solution consisting of solvent 1 (good solvent) and polymer with $v_p^s = 0.01$. As $p_{12,1}$ decreases and $p_{13,1}$, and $p_{23,1}$ increase, a large amount of solvent 2 is needed to bring about the two phase separation. Especially small change in $p_{23,1}$ causes a drastic change in V_2 . Considering the strong effects of $p_{23,1}$ and χ_{23}^0 on V_2 as first demonstrated by Kamide and Matsuda,¹⁰ a careful choice of non-solvent is an important factor to determine V_2 (or V).

Figure 17 shows the effect of the concentration dependence of three thermodynamic interaction parameters on the coexisting curve. Phase separation is obtained under the same conditions as those in Figure 16. In the figure tie lines for $\rho_p = 1/100$ are shown by the full lines, which can be accurately approximated with tie line for $\rho_p = 0$ (limiting tie-line) and the line of $v_p^s = 0.01$ is shown by the broken line. The cross point of the limiting tie-line and the line of $v_p^s = 0.01$ can be

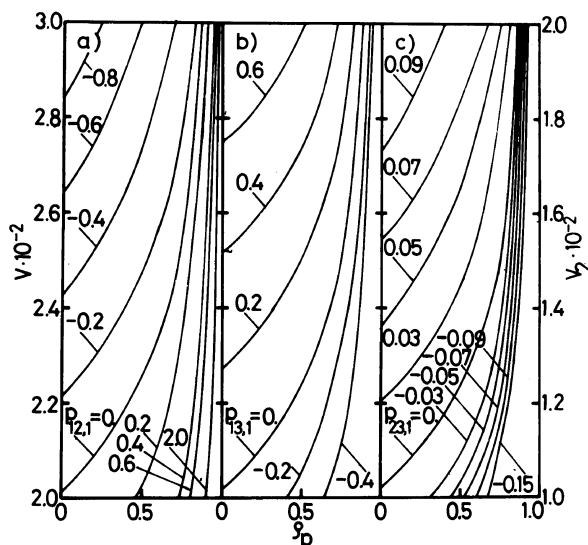


Figure 16. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between the total volume of the system V (or volume of nonsolvent V_2) and ρ_p . Original polymer, Schulz-Zimm type distribution ($X_w^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $v_p^s = 0.01$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$.

regarded as a cloud point. In the previous paper,⁹ the coexisting curve shifted to a direction of decreasing v_2 with a decrease in χ_{12}^0 and a increase in χ_{13}^0 and χ_{23}^0 . With an increase in $p_{12,1}$ from -2.0 to 0.6 , a similar shift in the coexisting curve was observed, but

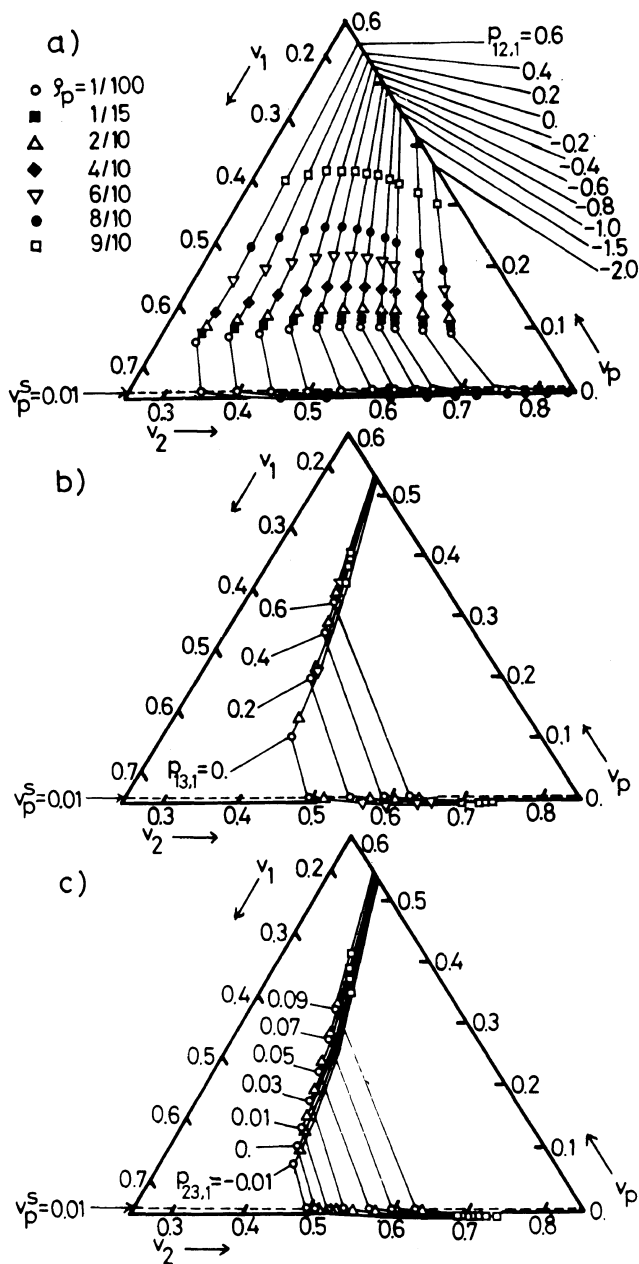


Figure 17. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the coexisting curves and their tie-lines for quasi-ternary system consisting of multicomponent polymer (Schulz-Zimm distribution, $X_w^0 = 300$, $X_w^0/X_n^0 = 2$) in binary solvent mixture. $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $v_p^s = 0.01$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$. \circ , $\rho_p = 1/100$; \blacksquare , $\rho_p = 1/15$; \triangle , $\rho_p = 2/10$; \blacklozenge , $\rho_p = 4/10$; ∇ , $\rho_p = 6/10$; \bullet , $\rho_p = 8/10$; \square , $\rho_p = 9/10$.

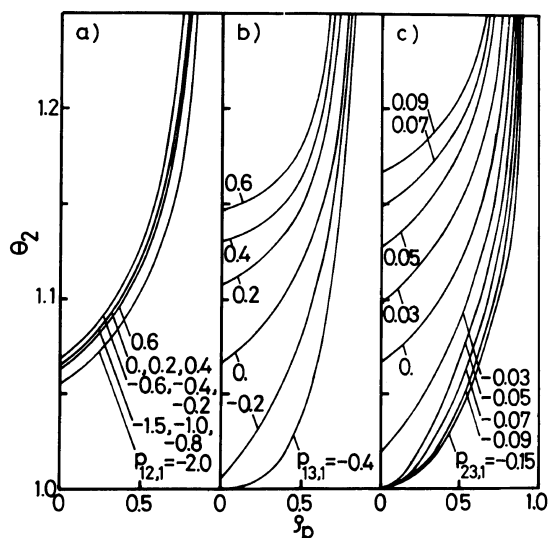


Figure 18. Effects of the concentration dependent parameters $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relations between degree of selective adsorption θ_2 and ρ_p . Original polymer, Schulz-Zimm type distribution ($X_p^0 = 300$, $X_w^0/X_n^0 = 2$); $\chi_{12}^0 = 0.5$, $\chi_{13}^0 = 0.2$, and $\chi_{23}^0 = 1.0$, $v_p^s = 0.01$. a) $p_{13,1} = p_{23,1} = 0$, b) $p_{12,1} = p_{23,1} = 0$, c) $p_{12,1} = p_{13,1} = 0$.

$v_{p(2)}$ changes a little, showing a maximum at $p_{12,1} = -0.2$. With an increase in $p_{13,1}$ and $p_{23,1}$, limiting tie-line approaches to $v_2 - v_p$ axis and $v_{p(2)}$ increases drastically.

Figure 18 shows the effects of $p_{12,1}$, $p_{13,1}$, and $p_{23,1}$ on the relation between θ_2 , which is defined by following equation,

$$\theta_2 = \frac{v_{2(1)}/(v_{1(1)} + v_{2(1)})}{v_{2(2)}/(v_{1(2)} + v_{2(2)})} \quad (56)$$

and ρ_p . As θ_2 is always larger than 1.0, a larger amount of non-solvent is partitioned in polymer-lean phase than -rich phase. The fact that θ increases with an increase in ρ_p suggests strongly that tie-line changes from $v_1 - v_p$ axis parallel to $v_2 - v_p$ axis parallel.

Summarizing, (a) a good separation efficiency can be expected for (i) small χ_{12}^0 and $p_{12,1} \sim -0.2$, (ii) large χ_{13}^0 and large $p_{13,1}$, (iii) small χ_{23}^0 and large $p_{23,1}$. Specially, careful choice of solvent 2 (non-solvent) is important. (b) For large $p_{13,1}$ and $p_{23,1}$, separation efficiency in quasi-ternary system exceeds

that in quasi-binary system. (c) In order to diminish the amount of non-solvent necessary to separate the polymer in the polymer-rich phase at the same ρ_p (i) small χ_{12}^0 and large $p_{12,1}$, (ii) large χ_{13}^0 and small $p_{13,1}$, (iii) large χ_{23}^0 and small $p_{23,1}$ are desired.

Acknowledgements. The author should like to express his most sincere gratitude to Dr. Kenji Kamide, Director of Fundamental Research Laboratory of Fibers and Fiber-Forming Polymers, Asahi Chemical Industry Co., Ltd., for his guidance.

APPENDIX A

Derivation of eq 13—15.

Integrating eq 9, ΔG^E for quasi-binary system is obtained:¹⁴

$$\begin{aligned} \Delta G^E &= \int_0^{N_0} \left(\frac{\partial \Delta G^E}{\partial N_0} \right) dN_0 \\ &= \tilde{R}T \left(N_0 + \sum_{i=1}^m X_i N_{X_i} \right) \\ &\quad \times \left[\chi_0 \left(1 + \sum_{j=1}^n \frac{p_j}{j+1} \frac{1-v_p^{j+1}}{v_0} \right) \right] v_0 v_p \end{aligned} \quad (A-1)$$

Following the procedure of quasi-binary system, ΔG_{13}^E and ΔG_{23}^E for quasi-ternary system can be given by integration of eq 10 and 11, respectively.

$$\begin{aligned} \Delta G_{13}^E &= \int_0^{N_1} \left(\frac{\partial \Delta G_{13}^E}{\partial N_1} \right) dN_1 \\ &= \tilde{R}T \left(N_1 + N_2 + \sum_{i=1}^m X_i N_{X_i} \right) \\ &\quad \times \left[\chi_{13}^0 \left\{ 1 + \sum_{q=1}^{n_q} \frac{p_{13,q}}{q+1} \left(\frac{v_p}{v_2 + v_p} \right)^q \right. \right. \\ &\quad \left. \left. \times \frac{1 - (v_2 + v_p)^{q+1}}{v_1} \right\} \right] v_1 v_p \end{aligned} \quad (A-2)$$

$$\Delta G_{23}^E = \int_0^{N_2} \left(\frac{\partial \Delta G_{23}^E}{\partial N_2} \right) dN_2$$

$$\begin{aligned}
&= \tilde{R}T \left(N_1 + N_2 + \sum_{i=1}^m X_i N_{X_i} \right) \\
&\quad \times \left[\chi_{23}^0 \left\{ 1 + \sum_{r=1}^{n_r} \frac{p_{23,r}}{r+1} \left(\frac{v_p}{v_1 + v_p} \right)^r \right. \right. \\
&\quad \left. \left. \times \frac{1 - (v_1 + v_p)^{r+1}}{v_2} \right\} \right] v_2 v_p \quad (\text{A-3})
\end{aligned}$$

ΔG^{id} is expressed by eq A-4.¹⁵

$$\begin{aligned}
\Delta G^{id} &= \tilde{R}T \left(N_1 + N_2 + \sum_{i=1}^m X_i N_{X_i} \right) \\
&\quad \times \left[v_1 \ln v_1 + v_2 \ln v_2 + \sum_{i=1}^m v_{X_i} \ln v_{X_i} \right] \quad (\text{A-4})
\end{aligned}$$

Substituting eq 12, and A-2~A-4 into eq 8, ΔG is given by eq A-5

$$\begin{aligned}
\Delta G &= \tilde{R}T \left(N_1 + N_2 + \sum_{i=1}^m X_i N_{X_i} \right) \\
&\quad \times \left[v_1 \ln v_1 + v_2 \ln v_2 + \sum_{i=1}^m v_{X_i} \ln v_{X_i} \right. \\
&\quad + \chi_{12}^0 \left(1 + \sum_{s=1}^{n_s} p_{12,s} v_p^s \right) v_1 v_2 \\
&\quad + \chi_{13}^0 \left\{ 1 + \sum_{q=1}^{n_q} \frac{p_{13,q}}{q+1} \left(\frac{v_p}{v_2 + v_p} \right)^q \right. \\
&\quad \left. \times \frac{1 - (v_2 + v_p)^{q+1}}{v_1} \right\} v_1 v_p \\
&\quad + \chi_{23}^0 \left\{ 1 + \sum_{r=1}^{n_r} \frac{p_{23,r}}{r+1} \left(\frac{v_p}{v_1 + v_p} \right)^r \right. \\
&\quad \left. \times \frac{1 - (v_1 + v_p)^{r+1}}{v_2} \right\} v_2 v_p \quad (\text{A-5})
\end{aligned}$$

Differentiations of ΔG by N_1 , N_2 , and N_{X_i} give $\Delta\mu_1$, $\Delta\mu_2$, and $\Delta\mu_{X_i}$ ($i=1, \dots, m$) as eq 13, 14, and 15, respectively.

ΔG^{id} , ΔG_{12}^E , ΔG_{13}^E , and ΔG_{23}^E satisfy following relations,

$$N_1 d \left(\frac{\partial \Delta G^{id}}{\partial N_1} \right) + N_2 d \left(\frac{\partial \Delta G^{id}}{\partial N_2} \right)$$

$$+ \sum_{i=1}^m N_{X_i} d \left(\frac{\partial \Delta G^{id}}{\partial N_{X_i}} \right) = 0 \quad (\text{A-6})$$

$$\begin{aligned}
&N_1 d \left(\frac{\partial \Delta G_{12}^E}{\partial N_1} \right) + N_2 d \left(\frac{\partial \Delta G_{12}^E}{\partial N_2} \right) \\
&+ \sum_{i=1}^m N_{X_i} d \left(\frac{\partial \Delta G_{12}^E}{\partial N_{X_i}} \right) = 0 \quad (\text{A-7})
\end{aligned}$$

$$\begin{aligned}
&N_1 d \left(\frac{\partial \Delta G_{13}^E}{\partial N_1} \right) + N_2 d \left(\frac{\partial \Delta G_{13}^E}{\partial N_2} \right) \\
&+ \sum_{i=1}^m N_{X_i} d \left(\frac{\partial \Delta G_{13}^E}{\partial N_{X_i}} \right) = 0 \quad (\text{A-8})
\end{aligned}$$

$$\begin{aligned}
&N_1 d \left(\frac{\partial \Delta G_{23}^E}{\partial N_1} \right) + N_2 d \left(\frac{\partial \Delta G_{23}^E}{\partial N_2} \right) \\
&+ \sum_{i=1}^m N_{X_i} d \left(\frac{\partial \Delta G_{23}^E}{\partial N_{X_i}} \right) = 0 \quad (\text{A-9})
\end{aligned}$$

namely, Gibbs-Duhem relation holds among $\Delta\mu_1$, $\Delta\mu_2$, and $\Delta\mu_{X_i}$ ($i=1, \dots, m$).

$$N_1 d(\Delta\mu_1) + N_2 d(\Delta\mu_2) + \sum_{i=1}^m N_{X_i} d(\Delta\mu_{X_i}) = 0 \quad (\text{A-10})$$

Equation A-10 can be converted into eq A-11:

$$\begin{aligned}
&N_1 \left[\left(\frac{\partial \Delta\mu_1}{\partial v_1} \right) dv_1 + \left(\frac{\partial \Delta\mu_1}{\partial v_p} \right) dv_p \right. \\
&\quad \left. + \left(\frac{\partial \Delta\mu_1}{\partial (1/X_n)} \right) d(1/X_n) \right] \\
&+ N_2 \left[\left(\frac{\partial \Delta\mu_2}{\partial v_1} \right) dv_1 + \left(\frac{\partial \Delta\mu_2}{\partial v_p} \right) dv_p \right. \\
&\quad \left. + \left(\frac{\partial \Delta\mu_2}{\partial (1/X_n)} \right) d(1/X_n) \right] \\
&+ \sum_{i=1}^m N_{X_i} \left[\left(\frac{\partial \Delta\mu_{X_i}}{\partial v_1} \right) dv_1 \right. \\
&\quad \left. + \left(\frac{\partial \Delta\mu_{X_i}}{\partial v_p} \right) dv_p + \left(\frac{\partial \Delta\mu_{X_i}}{\partial v_{X_i}} \right) dv_{X_i} \right. \\
&\quad \left. + \left(\frac{\partial \Delta\mu_{X_i}}{\partial (1/X_n)} \right) d(1/X_n) \right] = 0 \quad (\text{A-11})
\end{aligned}$$

Substituting eq 13—15 into A-11, we can readily confirm eq A-10.

APPENDIX B

Relation between χ and g

In the case of quasi-binary system, following relation holds between χ (given by eq 4) and g (introduced by Koningsveld *et al.*^{16,17}):¹⁵

$$g = \frac{1}{v_0} \int_{1-v_0}^1 \chi d(1-v_0) \\ = \chi_0 \left[1 + \sum_{j=1}^n \frac{p_j}{j+1} \frac{1-v_p^{j+1}}{v_0} \right] \quad (\text{B-1})$$

Differential form of the relation between χ and g is

$$\chi = g - v_0 \frac{\partial g}{\partial(1-v_0)} \quad (\text{B-2})$$

where $v_0 (= 1 - v_p)$ is volume fraction of solvent. Equation B-2 is consistent with eq B-1. For quasi-ternary system combination of eq 17 and A-2 gives relation between g_{13} and χ_{13} ,

$$g_{13} = \chi_{13}^0 \left\{ 1 + \sum_{q=1}^{n_q} \frac{p_{13,q}}{q+1} \left(\frac{v_p}{v_2 + v_p} \right)^q \times \frac{1 - (v_2 + v_p)^{q+1}}{v_1} \right\} \\ = \chi_{13}^0 \left[\frac{N_2 + \sum X_i N_{X_i}}{N_1 + N_2 + \sum X_i N_{X_i}} + \sum_{q=1}^{n_q} \frac{p_{13,q}}{q+1} \times \frac{(\sum X_i N_{X_i})^q (N_2 + \sum X_i N_{X_i})}{(N_1 + N_2 + \sum X_i N_{X_i})^{q+1}} \right]_{N_1=N_1}^0 \\ = \frac{\chi_{13}^0}{v_1} \int_{1-v_1}^1 \left[1 + \sum_{q=1}^{n_q} p_{13,q} v_p^q \right] d(1-v_1) \quad (\text{B-3})$$

Equation B-3 is also rewritten in the differential form.

$$g_{13} - v_1 \frac{\partial g_{13}}{\partial(1-v_1)} = g_{13} - v_1 \frac{\partial g_{13}}{\partial N_1} \frac{\partial N_1}{\partial(1-v_1)}$$

$$= \chi_{13}^0 \left[1 + \sum_{q=1}^{n_q} p_{13,q} v_p^q \right] = \chi_{13} \quad (\text{B-4})$$

According to the same procedure, relation between g_{23} and χ_{23} is given by eq 21 and 23.

APPENDIX C

From the definition of R and V , $V_{(1)}$ and $V_{(2)}$ are expressed by eq C-1a and b.

$$V_{(1)} = \frac{R}{R+1} V \quad (\text{C-1a})$$

$$V_{(2)} = \frac{1}{R+1} V \quad (\text{C-1b})$$

Substitution of eq C-1a and b into $V_2 = v_{2(1)} V_{(1)} + v_{2(2)} V_{(2)}$, yields,

$$V_2 = \frac{V}{R+1} (Rv_{2(1)} + v_{2(2)}) \quad (\text{C-2})$$

and combination of eq C-2 and 32 with $V = V_1^0 + V_2 + V_3^0$ gives:

$$v_p^0 = v_p^s \frac{(R+1 - Rv_{2(1)} - v_{2(2)})}{R+1} \quad (\text{C-3})$$

$$V = \frac{(R+1)(V_1^0 + V_3^0)}{R+1 - Rv_{2(1)} - v_{2(2)}} \quad (\text{C-4})$$

Substituting eq C-4 into C-1a and b, we obtain:

$$V_{(1)} = \frac{R(V_1^0 + V_3^0)}{R+1 - Rv_{2(1)} - v_{2(2)}} \quad (\text{C-5a})$$

$$V_{(2)} = \frac{V_1^0 + V_3^0}{R+1 - Rv_{2(1)} - v_{2(2)}} \quad (\text{C-5b})$$

As V_1^0 and V_3^0 are initial conditions, V_2 , v_p^0 , and V (also $V_{(1)}$ and $V_{(2)}$) are obviously functions of three parameters, R , $v_{2(1)}$, and $v_{2(2)}$. By use of eq C-1a and b, $v_{X_i(1)}$ and $v_{X_i(2)}$ are expressed by C-6a and b, respectively.

$$v_{X_i(1)} = \frac{V_3^0 g_{(1)}(X_i)}{V_{(1)}} = v_p^0 \frac{R+1}{R} g_{(1)}(X_i) \quad (\text{C-6a})$$

$$v_{X_i(2)} = \frac{V_3^0 g_{(2)}(X_i)}{V_{(2)}} = v_p^0 (R+1) g_{(2)}(X_i) \quad (\text{C-6b})$$

Combining eq 27, C-3, C-6a, and b, eq 35a and b are derived. $v_{X_i(1)}$ and $v_{X_i(2)}$ are rewritten as follows,

$$v_{X_i(1)} = v_p^0 \frac{R+1}{R + \exp(\sigma X_i)} g_0(X_i) \quad (\text{C-7a})$$

$$v_{X_i(2)} = v_p^0 \frac{(R+1) \exp(\sigma X_i)}{R + \exp(\sigma X_i)} g_0(X_i) \quad (\text{C-7b})$$

Utilizing eq C-6 and 34, eq C-8a and b are obtained.

$$v_{p(1)} = v_p^0 \frac{R+1}{R} \sum_{i=1}^m g_{(1)}(X_i) = v_p^0 \frac{R+1}{R} \rho_s \quad (\text{C-8a})$$

$$v_{p(2)} = v_p^0 (R+1) \sum_{i=1}^m g_{(2)}(X_i) = v_p^0 (R+1) \rho_p \quad (\text{C-8b})$$

Substitution of eq C-3 into eq C-8a and b yields eq 36a and b. Combination of $X_{n(1)} = \sum g_{(1)}(X_i) / (\sum g_{(1)}(X_i) / X_i)$ and eq 33, 34a, and b gives following relation (eq 37):

$$\begin{aligned} \frac{1}{X_{n(1)}} &= \frac{1}{\rho_s} \left\{ \sum_{i=1}^m \frac{g_0(X_i)}{X_i} - \sum_{i=1}^m \frac{g_{(2)}(X_i)}{X_i} \right\} \\ &= \frac{1}{\rho_s} \left\{ \frac{1}{X_n^0} - \frac{\rho_p}{X_{n(2)}} \right\} \end{aligned} \quad (\text{C-9})$$

In the same way, $1/X_{n(2)}$ is represented by eq C-10.

$$\frac{1}{X_{n(2)}} = \frac{1}{\rho_p} \left\{ \frac{1}{X_n^0} - \frac{\rho_s}{X_{n(1)}} \right\} \quad (\text{C-10})$$

APPENDIX D

Derivation of eq 52 and 53

At $v_p^0 = \text{constant}$ and $\rho_p = 1$, $V_1^0 = 0$, $V_2 = V - V_3^0$, $(v_{1(1)}^*, v_{2(1)}^*, v_{p(1)}^*) = (0, 1, 0)$, $(v_{1(2)}^*, v_{2(2)}^*, v_{p(2)}^*) = (0, 1 - v_{p(2)}^*, v_{p(2)}^*)$, $g_{(1)}(X_i) = 0$, and $g_{(2)}(X_i) = g_0(X_i)$ hold, and eq 30 becomes:

$$\begin{aligned} \ln(1 - v_{p(2)}^*) + v_{p(2)}^* + \left(\frac{v_{p(1)}}{X_{n(1)}} \right)_{\rho_p \rightarrow 1} - \frac{v_{p(2)}^*}{X_n^0} \\ + \chi_{23}^0 \left[v_{p(2)}^{*2} + \sum_{r=1}^{n_r} p_{23,r} v_{p(2)}^{*r+2} \right] = 0 \end{aligned} \quad (\text{D-1})$$

By use of eq C-8a and 9,

$$\left(\frac{v_{p(1)}}{X_{n(1)}} \right)_{\rho_p \rightarrow 1} = \lim_{\rho_p \rightarrow 1} \left[v_p^0 \frac{R+1}{R} - \frac{1}{X_{n(2)}} \right] = 0 \quad (\text{D-2})$$

Substitution of eq D-2 into D-1 yields eq 52. Utilizing eq C-4, eq D-3 is obtained,

$$V = \frac{(R^* + 1)V_3^0}{v_{p(2)}^*} \quad (\text{D-3})$$

and eq D-3 is rewritten as eq 53. Combining eq C-1a, b, and 53, we can express $V_{(1)}^*$ and $V_{(2)}^*$ is expressed by eq D-4a and b, respectively.

$$V_{(1)}^* = \left(1 - \frac{v_p^0}{v_{p(2)}^*} \right) V \quad (\text{D-4a})$$

$$V_{(2)}^* = \frac{v_p^0}{v_{p(2)}^*} V \quad (\text{D-4b})$$

If we set solvent 1 as non-solvent and solvent 2 as good solvent, eq 52 becomes:

$$\begin{aligned} \ln(1 - v_{p(2)}^*) + v_{p(2)}^* - \frac{v_{p(2)}^*}{X_n^0} \\ + \chi_{13}^0 \left[v_{p(2)}^{*2} + \sum_{q=1}^{n_q} p_{13,q} v_{p(2)}^{*q+2} \right] = 0 \end{aligned} \quad (\text{D-5})$$

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