

Phase Equilibria of Quasi-Ternary Systems Consisting of Multi-Component Polymers in a Binary Solvent Mixture VII. Co-Solvency

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ABSTRACT: An attempt was made to study theoretically the conditions of occurrence of co-solvency phenomena for quasi-ternary components systems consisting of a multicomponent polymer dissolved in a binary solvent mixture. For this purpose, Kamide and Matsuda theory on spinodal curve (SC) and critical solution point (CSP) for the quasi-ternary systems [*Polym. J.*, **18**, 347 (1986)] was employed. The co-solvency occurs generally only when the total polymer volume fractions v_p at two spinodal points ($v_1=0$ and $v_2=0$), $v_p^{(1)}$ and $v_p^{(2)}$ satisfy the following two inequalities concurrently: $0 < v_p^{(1)} < 1$ and $0 < v_p^{(2)} < 1$. (Here, v_1 and v_2 are the volume fractions of solvents 1 and 2.) SC, CSP, and the cloud point curve (CPC) were calculated for a wide range of three thermodynamic interaction parameters χ_{12} , χ_{13} , and χ_{23} (the suffixes 1 and 2 mean solvents 1 and 2, respectively, the suffix 3, the polymer). Co-solvency occurs generally in the cases when (1) original polymer has smaller weight-average degree of polymerization X_w^0 , (2) the polymer has the smaller ratio of X_w^0 to the number-average degree of polymerization X_n^0 (i.e., X_w^0/X_n^0), and (3) the initial polymer volume fraction v_p^0 is smaller than that of the critical concentration v_p^c . There exists a specific χ_{12} value yielding the most wide composition range of co-solvency of the system concerned (for example $\chi_{12} = 1.4$ for $X_w^0 = 300$). When $\chi_{12} = 0$, no co-solvency occurs. For larger χ_{12} (but not larger than 2.0), smaller χ_{13} , and smaller χ_{23} , co-nonsolvency was theoretically predicted to occur and in this case the system has two Flory solvent compositions.

KEY WORDS Co-Solvency / Quasi-Ternary System / Binary Solvent Mixture / Spinodal Curve / Critical Solution Point / Thermodynamic Interaction Parameters /

Even if two solvents are poor against a given polymer when they are used separately, a binary mixture consisting of these two solvents sometimes dissolves the polymer. In this sense the binary mixture acts as good solvent. This phenomenon is conventionally called as co-solvency, first discovered in 1920's experimentally for cellulose nitrate solution systems.¹ Thereafter, co-solvency has been observed for numerous polymer/two nonsolvents mixture systems including

cellulose acetate (CA)/chloroform/ethyl alcohol,² polystyrene (PS)/acetone/*n*-propyl laurate,³ PS/methylcyclohexane (MCH)/acetone,⁴ PS/acetone/cyclohexanol,⁵ PS/MCH/diethyl ether,⁵ PS/acetone/diethyl ether,^{6,7} poly(methyl methacrylate) (PMMA)/benzyl alcohol/sec-butyl chloride,⁸ poly(*p*-*tert*-butyl phenyl)methacrylate/acetone/CH,⁹ PMMA/CCl₄/*tert*-butyl chloride,¹⁰ PMMA/CCl₄/butyl chloride.^{10,11}

Scott¹² calculated co-existing curve for

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ternary system of monodisperse polymer/binary solvent mixture, showing that under the conditions of infinite molecular weight polymer with $\chi_{12}=2.0$ and $\chi_{13}=\chi_{23}=0.75$, there exist two binodal curves (in other words, there are two two-phase separation regions).

Bamford and Tompa¹³ showed, using the conditional equation giving critical solution point (CSP), proposed by Scott,¹² that two CSP are theoretically expected to exist for CA/chloroform/ethyl alcohol system. Noting chloroform as solvent 1 and ethyl alcohol as solvent 2 and assuming three thermodynamic interaction parameters between solvent 1 and solvent 2 (χ_{12}), solvent 1 and polymer (χ_{13}), and solvent 2 and polymer (χ_{23}) to be 1.10, 0.56 and 1.00, respectively and the degree of polymerization of the polymer $X=953$, they calculated the volume fractions of solvent 1, solvent 2, and the polymer at CSP. These critical volume fractions, v_1^c , v_2^c and v_x^c (c denotes CSP) were 0.912, 0.057, and 0.031 for one CSP, and 0.511, 0.464, and 0.025 for another, respectively. Note that χ_{23} parameter employed by them was not experimentally determined and Scott equations of CSP do not satisfy the thermodynamic requirement. In other words, these equations are not correct, as very recently pointed out by Kamide and Matsuda.¹⁴ Using Scott's equations of CSP (eq 26 and 27 in ref 12) for the ternary system ($X=953$, $\chi_{12}=1.10$, $\chi_{13}=0.56$, and $\chi_{23}=1.00$) we obtain $(v_1^c, v_2^c, v_x^c)=(0.985, 0.0580, 0.0335)$ and $(0.5089, 0.4604, 0.0307)$. By use of Tompa's equation of CSP (eq 7.27 and 7.29 in ref. 15) for the same system we obtain not only a correct CSP $(v_1^c, v_2^c, v_x^c)=(0.9110, 0.0583, 0.0307)$ and $(0.5112, 0.4630, 0.0258)$ but also an incorrect CSP $(v_1^c, v_2^c, v_x^c)=(0.3483, 0.6494, 0.00228)$. If we use Kamide-Matsuda's equation of CSP (eq 10' and 11' in ref 14) for the above system we obtain correct (v_1^c, v_2^c, v_x^c) only.

Tompa¹⁵ predicted without showing detailed derivation that for infinite molecular weight polymer, co-solvency occurs if the

following conditions are satisfied.

$$2(\chi_{12}\chi_{13} + \chi_{13}\chi_{23} + \chi_{23}\chi_{12}) - (\chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2) > 0 \quad (1)$$

$$2 > \chi_{12} > \chi_{13} + \chi_{23} - 1 + (2\chi_{13} - 1)^{1/2}(2\chi_{23} - 1)^{1/2} \quad (2)$$

Tompa explained co-solvency as follows: when the cohesive energy density of the polymer lies between those of two solvents, the solvent mixture may have on average the cohesive energy density near to that of the polymer and in consequence the binary mixture of two nonsolvents dissolves the polymer.¹⁵

The second virial coefficient A_2 by the light scattering and the limiting viscosity number $[\eta]$ have been investigated in correlation to co-solvency phenomena.^{4-11,16-21} A_2 and $[\eta]$ were shown to exhibit maximum at a specific composition of binary mixture and these were discussed in terms of selective adsorption coefficient λ .²² The solubility parameter δ ,^{4,5} the excess free energy of mixing ΔG_{12}^E ,^{4,16} the long range intermolecular interaction parameter B^{10} in the two-parameter theory estimated by Stockmayer-Fixman plot,²³ coil size^{4,5,8} and the linear expansion factor α^{24} were also studied as a function of binary mixture composition. In particular, Katime and Ochoa¹¹ attempted to explain co-solvency by using the solubility parameter defined by Koenhen and Smolders.²⁵ It should be noted that the physical quantities such as A_2 , $[\eta]$, λ , δ , ΔG_{12}^E , B , and α do not have "the relation of cause and effect" against occurrence of co-solvency, but may be indirectly correlated with the co-solvency.

This article intends to disclose the thermodynamical conditions of occurrence of co-solvency using the Kamide-Matsuda theory^{14,26} of phase equilibria of polydisperse polymer/solvent 1/solvent 2 (*i.e.*, quasi-ternary) systems and to demonstrate theoretically that co-solvency is very generally ob-

servable phenomena for the quasi-ternary systems.

THEORETICAL BACKGROUND

The conditions of spinodal and neutral equilibrium of the quasi-ternary system are given by eq 3 and 4, respectively.¹⁴

$$\left(\frac{1}{v_1} + \frac{1}{v_2} - 2\chi_{12}\right) \left(\frac{1}{v_p X_w^0} + \frac{1}{v_1} - 2\chi_{13}\right) - \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12}\right)^2 = 0 \quad (3)$$

$$\left[\frac{1}{v_p X_w^0} \left(\frac{1}{v_1^2} - \frac{1}{v_2^2}\right) + \frac{1}{v_1^2} \left(\frac{1}{v_2} - 2\chi_{23}\right) - \frac{1}{v_2^2} \left(\frac{1}{v_1} - 2\chi_{13}\right) \right] \left(\frac{1}{v_p X_w^0} + \frac{1}{v_1} - 2\chi_{13}\right) - \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12}\right) \left[\frac{1}{v_1^2} \left(\frac{1}{v_2} - 2\chi_{23}\right) + \frac{1}{v_1^2 v_p X_w^0} + \frac{X_z^0}{v_p X_w^0} \left\{ \frac{1}{v_1 v_2} - \frac{2\chi_{13}}{v_2} - \frac{2\chi_{23}}{v_1} + 2(\chi_{12}\chi_{13} + \chi_{13}\chi_{23} + \chi_{23}\chi_{12}) - (\chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2) \right\} \right] = 0 \quad (4)$$

Here, v_p ($\equiv \sum_x v_x$) is the polymer volume fraction, and X_w^0 , the weight-average degree of polymerization X (o means the original polymer). We neglected the concentration dependence of χ_{12} , χ_{13} , and χ_{23} . v_p is related to v_1 and v_2 through the relation

$$v_1 + v_2 + v_p = 1 \quad (5)$$

By solving eq 3 the spinodal curve (SC) can be directly calculated and by solving the simultaneous equations (eq 3 and 4) the volume fractions at CSP, v_1^c , v_2^c , and v_p^c are evaluated. Equation of SC at $v_1=0$ is obtained from eq 3 in the form:¹⁴

$$v_p + \frac{v_2}{X_w^0} - 2\chi_{23}v_2v_p = 0 \quad (6)$$

SP at $v_1=0$ is evidently independent of χ_{12} and χ_{13} and is determined by χ_{23} alone.

The compositions of SP ($v_2^{(2)}$, $v_p^{(2)}$) at $v_1=0$ are given by solving eq 6 as

$$v_p^{(2)} = \frac{1}{2} \left[1 - \frac{1}{2\chi_{23}} + \frac{1}{2\chi_{23}X_w^0} + \left\{ \left(1 - \frac{1}{2\chi_{23}} + \frac{1}{2\chi_{23}X_w^0} \right)^2 - \frac{2}{\chi_{23}X_w^0} \right\}^{1/2} \right] \quad (7a)$$

with

$$v_2^{(2)} = 1 - v_p^{(2)} \quad (7b)$$

At $v_2=0$ SC and SP are independent of χ_{12} and χ_{23} and a single function of χ_{13} in the form:

$$v_p + \frac{v_1}{X_w^0} - 2\chi_{13}v_1v_p = 0 \quad (8)$$

By solving eq 8, the composition of SP ($v_1^{(1)}$, $v_p^{(1)}$) at $v_2=0$ are given by eq 9

$$v_p^{(1)} = \frac{1}{2} \left[1 - \frac{1}{2\chi_{13}} + \frac{1}{2\chi_{13}X_w^0} + \left\{ \left(1 - \frac{1}{2\chi_{13}} + \frac{1}{2\chi_{13}X_w^0} \right)^2 - \frac{2}{\chi_{13}X_w^0} \right\}^{1/2} \right] \quad (9a)$$

with

$$v_1^{(1)} = 1 - v_p^{(1)} \quad (9b)$$

Then eq 7a and eq 9a give $v_p^{(1)}$ and $v_p^{(2)}$, separately and the co-solvency occurs only when $v_p^{(1)}$ and $v_p^{(2)}$, evaluated thus, satisfy the following two inequalities concurrently.

$$0 < v_p^{(1)} < 1 \quad \text{and} \quad 0 < v_p^{(2)} < 1 \quad (10)$$

Without complete satisfaction of eq 10 the co-solvency never occur. In this sense, the reverse is rigorously true.

In other words, the necessary condition of co-solvency can also be obtained by putting X_w^0 value into eq 7a and 9a, combined with eq 10. If an additional crude approximation of $X_w^0 \rightarrow \infty$ is applied to eq 10 the necessary condition reduces to the well-known inequalities,

$$\chi_{13} > 0.5 \quad \text{and} \quad \chi_{23} > 0.5 \quad (11)$$

Moreover, when two CSP are obtained from eq 3 and 4 the system has two two-phase equilibria regions and unavoidably co-solvency occurs. Then, the existence of two CSP is the sufficient condition. We denote the compositions of a CSP at solvent 1 side by $v_1^{c(1)}$, $v_2^{c(1)}$, and $v_p^{c(1)}$ and those of another CSP at solvent 2 side by $v_1^{c(2)}$, $v_2^{c(2)}$, and $v_p^{c(2)}$. When the system has larger χ_{12} , smaller χ_{13} and smaller χ_{23} , $v_1^{c(1)}$ increases and $v_1^{c(2)}$ decreases (*i.e.*, $v_2^{c(1)}$ decreases and $v_2^{c(2)}$ increases) and the interval between two CSPs has a

tendency to expand and the region of co-solvency widens significantly.

COMPUTER EXPERIMENT

SC and CSP were calculated according to the method of Kamide and Matsuda (eq 18 and 19 of ref 14). The cloud point curve (CPC) was indirectly estimated from the binodal curve (see Figures 1 and 2 of ref 14).

The calculations of SC, CSP and CPC for the quasi-ternary systems consisting of multicomponent polymers with the Schulz-Zimm (SZ) type molecular weight distribu-

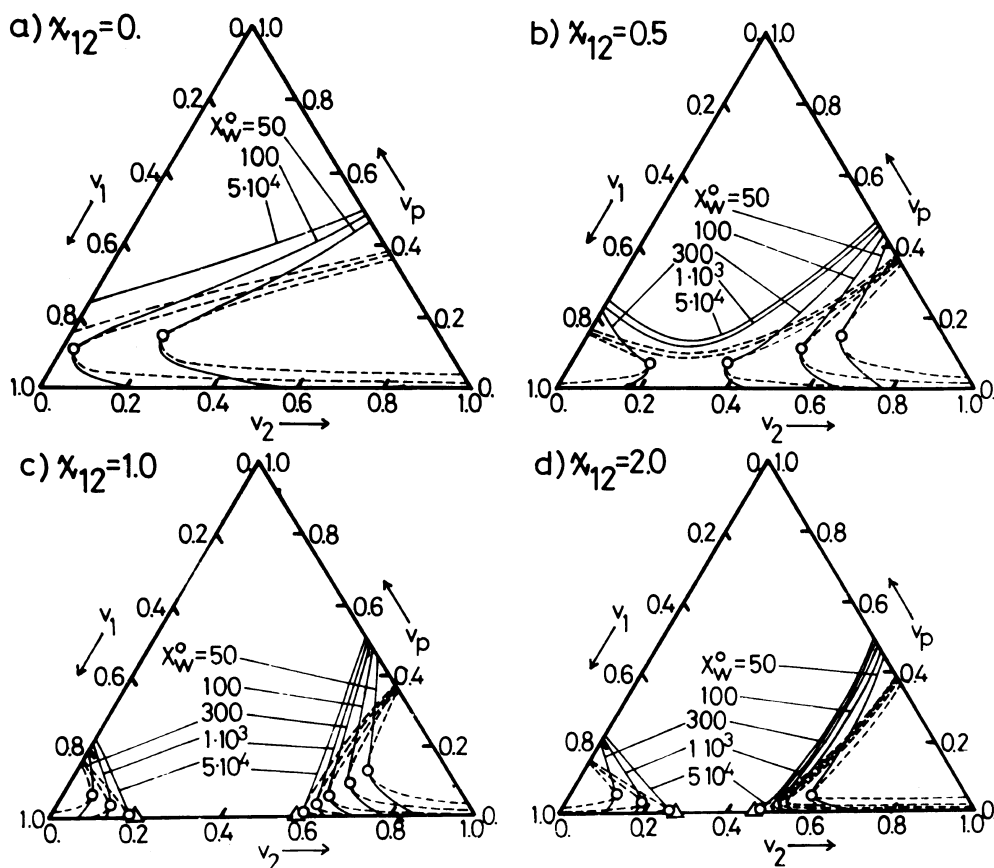


Figure 1. Effect of the weight-average degree of polymerization of the original polymer X_w^0 on the co-solvency of quasi-ternary solution systems consisting of the multicomponent polymer (Schulz-Zimm distribution, $X_w^0/X_n^0=2$) dissolved in a binary mixture: a) $\chi_{12}=0$, $\chi_{13}=0.6$, $\chi_{23}=0.8$; b) $\chi_{12}=0.5$, $\chi_{13}=0.6$, $\chi_{23}=0.8$; c) $\chi_{12}=1.0$, $\chi_{13}=0.6$, $\chi_{23}=0.8$; d) $\chi_{12}=2.0$, $\chi_{13}=0.6$, $\chi_{23}=0.8$; full line, cloud point curve; broken line, spinodal curve; unfilled circle, critical solution point; unfilled triangle, Flory solvent.

tion ($X_w^0 = 50 \sim 5 \times 10^4$ and $X_w^0/X_n^0 = 1 \sim 5$ (X_n^0 is the number average X)) dissolved in binary solvent mixture were carried out in the ranges of $\chi_{12} = 0 \sim 2$, $\chi_{13} = 0 \sim 1.4$, and $\chi_{23} = 0 \sim 1.4$.

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of X_w^0 on CPC, SC, and CSP. In the figure, the full and broken lines are CPC and SC, respectively and CSP is shown as an unfilled circle. In the case of $\chi_{12} = 1.0$ and 2.0 with $\chi_{13} = 0.6$ and $\chi_{23} = 0.8$ (Figure 1c and 1d), the co-solvency occurs over an entire range of X_w^0 and the systems have two Flory solvent compositions:²⁷ The volume fraction of solvent 1 at the Flory solvent, $v_1^F = 0.4248$ and 0.8024 for $\chi_{12} = 1.0$ and $v_1^F = 0.5281$ and 0.7283 for $\chi_{12} = 2.0$ (for these cases, $\chi_{13} = 0.6$ and $\chi_{23} = 0.8$). At limit of $X_w^0 = \infty$ two CSP coincide with their Flory solvent compositions. In the case of $\chi_{12} = 0.5$, the Flory solvent composition does not exist, but in the range of relatively smaller X_w^0 ($= 300$) two CSPs are observed and consequently the co-solvency occurs. Two two-phase equilibrium regions overlap heavily with each other for polymer solutions with larger X_w^0 .

In the case of $\chi_{12} = 0$ (Figure 1a), solvent 1 having $\chi_{13} = 0.6$ behaves as good solvent for smaller X_w^0 (for example, 50 and 100). For larger X_w^0 solvent 1 with $\chi_{13} = 0.6$ becomes of course poorer and no co-solvency occurs.

Even in the case when two two-phase equilibrium regions overlap as demonstrated in Figure 1a ($X_w^0 = 5 \times 10^4$) and 1b ($X_w^0 = 1 \times 10^3$ and 5×10^4), one phase region exists at higher v_p . This region can also be, in a broad sense, regarded as that of co-solvent if the region maintains the liquid phase. But, in this article, we deal only with the case when two two-phase equilibrium regions are observed. Tompa¹⁵ predicted that for $\chi_{12} = 2.0$ solvents 1 and 2 become critical consolute state and for $\chi_{12} > 2.0$ three-phase separation region exists. A

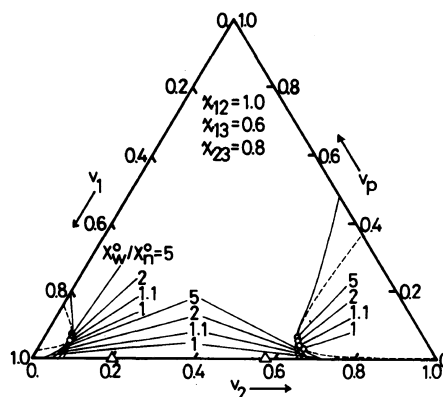


Figure 2. Effect of the ratio of the weight- to the number-average degree of polymerization of the original polymer X_w^0/X_n^0 on the co-solvency of quasi-ternary solution systems consisting of multicomponent polymer (Schulz-Zimm distribution, $X_w^0 = 300$) in a binary solvent mixture: $\chi_{12} = 1.0$, $\chi_{13} = 0.6$, $\chi_{23} = 0.8$; full line, cloud point curve; broken line, spinodal curve; unfilled circle, critical solution point; unfilled triangle, Flory solvent.

sign of the occurrence of three phase separation can be observed at $\chi_{12} = 2.0$. In Figure 1d ($\chi_{12} = 2.0$) CSP exists on CPC at solvent 2 side for $X_w^0 = 50$ and 5×10^4 , but no CSP exists on CPC at solvent 2 side for $X_w^0 = 100$, 300 and 1×10^3 . This singular property is considered to be closely correlated with three-phase separation phenomena and will be discussed in more detail in a forthcoming paper.

Figure 2 shows the effect of the polymolecularity of the polymer (SZ, $X_w^0 = 300$) on co-solvency for the case of $\chi_{12} = 1.0$, $\chi_{13} = 0.6$, and $\chi_{23} = 0.8$. As eq 3 shows, SC (broken line) is independent of the polymolecularity. As X_w^0/X_n^0 increases, v_p^c increases in both two-phase equilibrium regions. In the region $v_p^0 > v_p^c$ (v_p^0 is the initial polymer volume fraction) CPC is sensitive to X_w^0/X_n^0 and two-phase equilibrium region widens with increasing X_w^0/X_n^0 . These effects are similar to the effect of X_w^0/X_n^0 on CPC and CSP of the quasi-binary systems consisting of multicomponent polymers dissolved in a single solvent, first noticed by Kamide *et al.*²⁸ Note that in the quasi-ternary systems v_p^c is much smaller than that in the quasi-binary systems

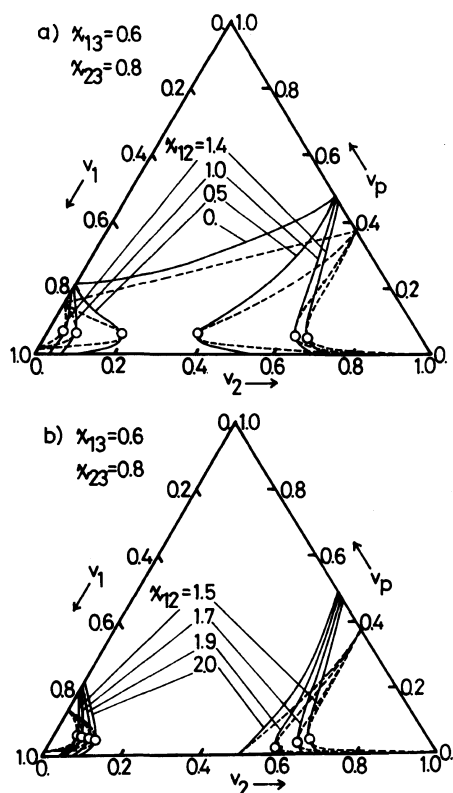


Figure 3. Effect of χ_{12} on the co-solvency of quasi-ternary solution systems consisting of multicomponent polymer in a binary solution: Original polymer, Schulz-Zimm distribution, $X_w^0 = 300$, $X_w^0/X_n^0 = 2$; $\chi_{13} = 0.6$ and $\chi_{23} = 0.8$; full line, cloud point curve; broken line, spinodal curve; unfilled circle, critical solution point.

and the role of CPC on the total phase diagrams in the former systems is significantly small as compared with that in the latter systems.

Figure 3 shows the effect of χ_{12} on co-solvency for the quasi-ternary systems consisting of the polymer (SZ, $X_w^0 = 300$) in a binary solvent mixture ($\chi_{13} = 0.6$ and $\chi_{23} = 0.8$). In the case of $\chi_{12} = 0$ no co-solvency occurs. SC at $\chi_{12} = 0$ can be accurately represented by a straight line connecting the two points: $(0, v_2^{(2)}, v_p^{(2)})$ (SP given by eq 6) and $(v_1^{(1)}, 0, v_p^{(1)})$ (SP given by eq 8). Co-solvency occurs at $\chi_{12} = 0.5$ and the region of co-solvency becomes wide as χ_{12} increases, approaching the maximum at $\chi_{12} = 1.4$. Further in-

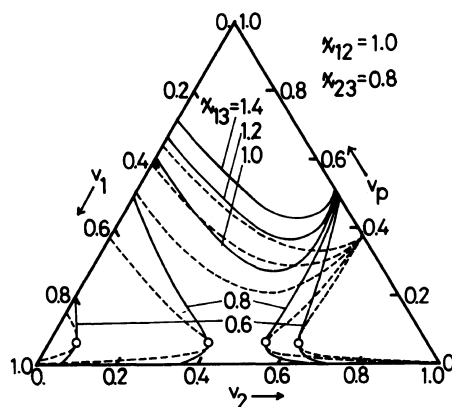


Figure 4. Effect of χ_{13} on the co-solvency of quasi-ternary solution systems consisting of multicomponent polymer in a binary solution: Original polymer, Schulz-Zimm distribution, $X_w^0 = 300$, $X_w^0/X_n^0 = 2$; $\chi_{12} = 1.0$ and $\chi_{23} = 0.8$; full line, cloud point curve; broken line, spinodal curve; unfilled circle, critical solution point.

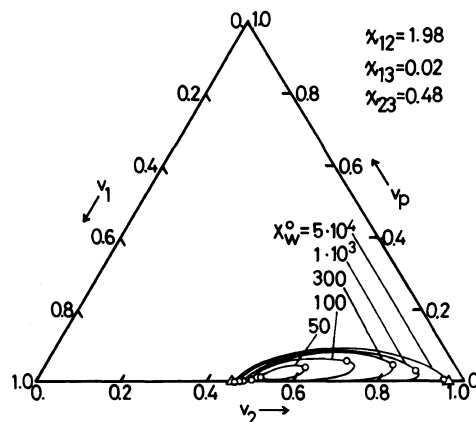


Figure 5. Effect of the weight-average degree of polymerization of the original polymer X_w^0 on the co-solvency of quasi-ternary solution systems consisting of multicomponent polymer (Schulz-Zimm distribution, $X_w^0/X_n^0 = 2$) in a binary solvent mixture: $\chi_{12} = 1.98$, $\chi_{13} = 0.05$, $\chi_{23} = 0.48$; full line, spinodal curve; unfilled circle, critical solution point; unfilled triangle, Flory solvent.

crease in χ_{12} beyond 1.4 makes the co-solvency region smaller again, increasing two-phase equilibrium region. Two v_p^c decrease slowly, but monotonously with an increase in χ_{12} .

Figure 4 shows the effect of χ_{13} on co-solvency for the quasi-ternary systems consisting of the polymers (SZ, $X_w^0 = 300$) in a

binary solvent mixture ($\chi_{12}=1.0$ and $\chi_{23}=0.8$). A decrease in χ_{13} brings about an expansion of a single phase region, yielding co-solvency at $\chi_{13}=0.8$ and 0.6 . At $\chi_{13}=0.8$ the system does not have two Flory solvent compositions, but at $\chi_{13}=0.6$ the system has two Flory solvent compositions ($v_1^F=0.4249$ and 0.8024).²⁷ The effect of χ_{23} on the co-solvency is principally the same as that of χ_{13} .

As Tompa¹⁵ predicted as early as 1956, the theory indicates that a mixture of solvent 1 having $\chi_{13}<0.5$ and solvent 2 having $\chi_{23}<0.5$ (in other words, the both solvents are good solvents when used separately) may be

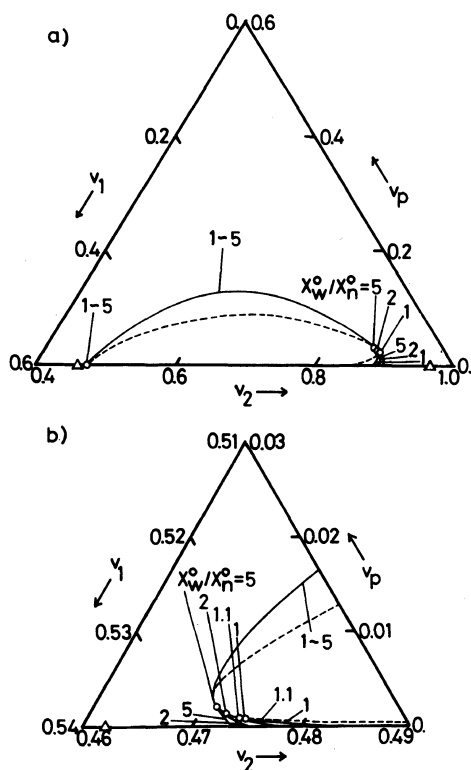


Figure 6. Effect of the ratio of the weight- to the number-average degree for polymerization of the original polymer X_w^0/X_n^0 on the co-nonsolvency of quasi-ternary solution systems consisting of multicomponent polymer (Schulz-Zimm distribution, $X_w^0=1000$) in a binary solvent mixture: $\chi_{12}=1.98$, $\chi_{13}=0.02$, $\chi_{23}=0.48$; full line, cloud point curve; broken line, spinodal curve; unfilled circle, critical solution point; unfilled triangle, Flory solvent.

sometimes nonsolvent for the polymer. Unfortunately, this phenomenon has not yet been experimentally confirmed. The phenom-

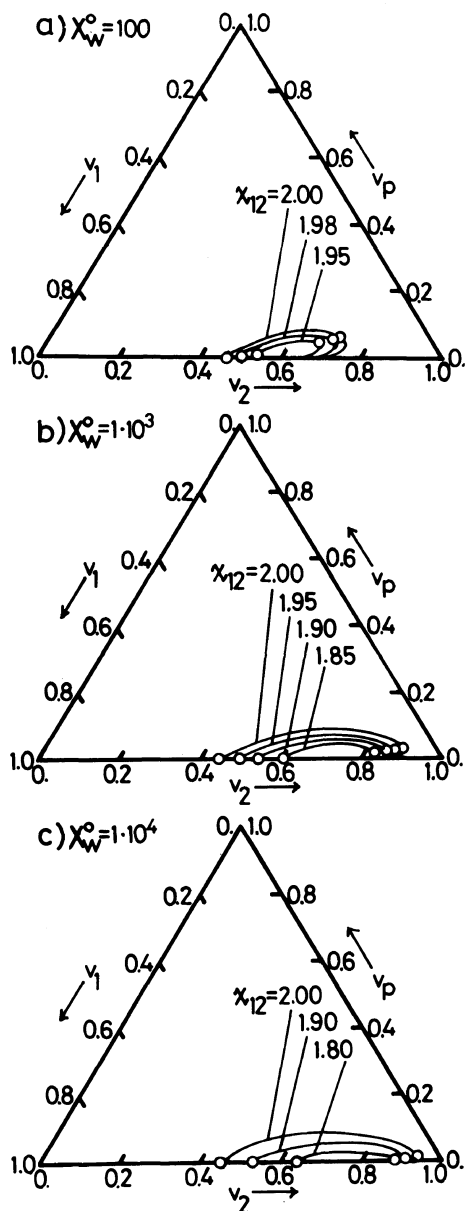


Figure 7. Effect of χ_{12} on the co-nonsolvency of quasi-ternary solution systems consisting of multicomponent polymer in a binary solvent mixture: Original polymer, Schulz-Zimm distribution, $X_w^0/X_n^0=2$, $X_w^0=1 \times 10^2$ (a), 1×10^3 (b), and 1×10^4 (c); $\chi_{13}=0.02$, $\chi_{23}=0.48$; full line, spinodal curve; unfilled circle, critical solution point.

enon is just reverse to co-solvency and we define this hereafter co-nonsolvency. Co-nonsolvency is apparently accompanied with two CSPs as co-solvency is.

Figure 5 shows the effect of X_w^0 on co-nonsolvency for the quasi-ternary systems ($\chi_{12}=1.98$, $\chi_{13}=0.02$, and $\chi_{23}=0.48$). With an increase in X_w^0 the two-phase equilibrium region expands its space. Two CSPs, denoted as unfilled circles in the figure, reduce to two Flory solvent compositions at the limit of $X_w^0 = \infty$. Note that there are cases when co-solvency occurs, even if the system has no Flory solvent compositions (see, Figures 1b, 3a and 4). The system, in which co-nonsolvency occurs, has always two Flory solvent compositions.

Figure 6a shows the effect of the polymolecularity of the polymer (SZ, $X_w^0=1000$) on co-nonsolvency of the quasi-ternary systems ($\chi_{12}=1.98$, $\chi_{13}=0.02$, and $\chi_{23}=0.48$). The polymolecularity influences co-nonsolvency very slightly. With an increase in X_w^0/X_n^0 , v_p^c increases significantly and in the region of $v_p^0 < v_p^c$ two-phase equilibria region expands very slightly with increasing X_w^0/X_n^0 . Figure 6b is an extended figure of the region enclosed by the lines $0.46 < v_2 < 0.49$ and $0 < v_p < 0.01$ of Figure 6a. From Figure 6a we might erroneously conclude that SC is intercepted with a v_1-v_2 axis, but Figure 6b shows SC does not intercepted with the axis. SC at v_2-v_p axis side also has a peak and gradually approaches to v_1-v_2 axis with decreasing v_p .

Figure 7 shows the effect of χ_{12} on co-nonsolvency for the quasi-ternary systems consisting of the polymers (SZ, $X_w^0/X_n^0=2$) in a binary mixture ($\chi_{13}=0.02$ and $\chi_{23}=0.48$). With a slight increase in χ_{12} the co-solvency region increases remarkably. For larger X_w^0 , this tendency is evidently accelerated and co-nonsolvency occurs at lower χ_{12} . Two v_p^c have a slight tendency to increase with χ_{12} .

Figure 8 shows the effect of χ_{13} and χ_{23} on co-nonsolvency of the quasi-ternary systems consisting of the polymers (SZ, $X_w^0=1 \times 10^4$,

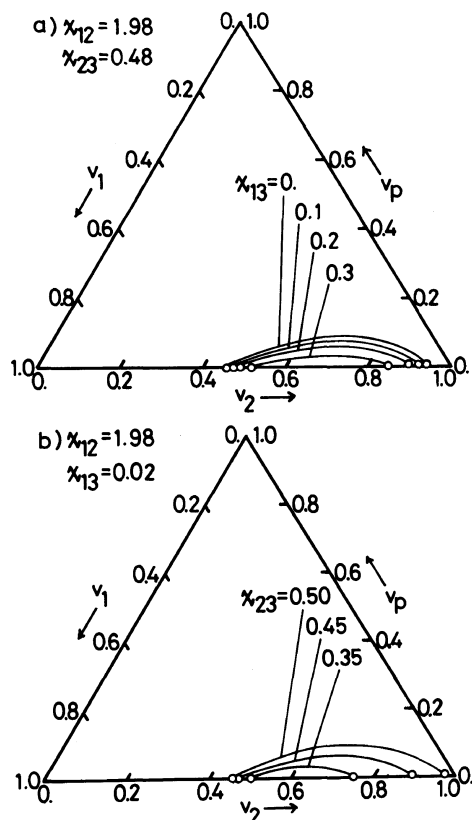


Figure 8. Effect of χ_{13} (a) and χ_{23} (b) on the co-nonsolvency of quasi-ternary solution systems consisting of multicomponent polymer in a binary solvent mixture: Original polymer, Schulz-Zimm distribution, $X_w^0 = 1 \times 10^4$, $X_w^0/X_n^0 = 2$; a) $\chi_{12}=1.98$, $\chi_{23}=0.48$; b) $\chi_{12}=1.98$, $\chi_{13}=0.02$; full line, spinodal curve; unfilled circle, critical solution point.

$X_w^0/X_n^0=2$) dissolved in a binary mixture. In the case of $\chi_{13} < \chi_{23}$, the co-nonsolvency region expands with decreasing χ_{13} and increasing χ_{23} . With a decrease in χ_{13} co-nonsolvency region widens almost symmetrically, but the situation is somewhat different when χ_{23} increases: The expansion of solvent 2 side is much more remarkable. In the case of $\chi_{13} > \chi_{23}$ the effect of χ_{13} and χ_{23} is just reverse to that in the case of $\chi_{13} < \chi_{23}$.

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