Phase Equilibria of Quasi-Ternary Systems Consisting of Multicomponent Polymers in a Binary Solvent Mixture II. Role of Initial Concentration and Relative Amount of Polymers Partitioned in Two Phases

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ABSTRACT: An attempt was made to clarify by computer experiments the role of initial "concentration" v_p^o and relative amounts of polymers, partitioned in two phases at the phase equilibrium of quasi-ternary polymer solutions. For this purpose, a polymer with the Schulz-Zimm type molecular weight distribution (the ratio of the weight- to number-average molar volume of the polymer relative to the molar volume of solvents, $X_w^o/X_n^o=2.0$ and $X_w=300$) was employed under the condition of $v_p^o=1 \times 10^{-5} \sim 0.07$ and the relative amount of the polymer in the polymer-rich phase $\rho_p=1/40 \sim 39/40$. The phase equilibrium of the quasi-ternary polymer solutions can be approximated with that of the quasi-binary system consisting of multicomponent polymers and a single solvent having the negative concentration dependence of the polymer-solvent interaction parameter χ . As ρ_p increases, both the phase volume ratio R and the X_w/X_n of the polymer in the polymer-rich phase decrease and then increase after passing through a minimum.

KEY WORDS Quasi-Ternary Polymer Solution / Phase Equilibrium /
Initial Concentration / Relative Amount of Polymer /

In a previous paper¹ we established a theory and methodology for computer experiments for the two-phase equilibrium of a quasi-ternary system consisting of a multicomponent polymer, solvent 1, and solvent 2 at constant temperature and pressure. We investigated in detail the effects of the solution powers of two solvents on the phase separation characteristics of solutions of a polymer having a Schulz-Zimm molecular weight distribution. The molar volumes of these two solvents were assumed to be identical, and the weight-average molar volume of the polymer relative to that of the solvents, X_w^o , to be 300 (here, the suffix o denotes the original polymer) when the polymer volume fraction of the starting solution, $v_p^s=0.01$ and the relative amount of the polymer partitioned in the polymer-rich phase, $\rho_p=1/15$.

In this paper, we study the role of phase

separation conditions such as the initial polymer volume fraction v_p^o and ρ_p and the relative amount of the polymer partitioned in the polymer-lean phase ρ_s ($\equiv 1 - \rho_p$), in the phase equilibrium of quasi-ternary polymer solutions. These points have already been studied by Kamide *et al.*²⁻¹² in a systematic manner for quasi-binary systems consisting of a multicomponent polymer and single solvent.

Computer Experiment

The simulation procedure, established in the previous paper,¹ was employed with hardly any modification. A polymer having a Schulz-Zimm type molecular weight distribution and $X_w^o=300$ and X_n^o (number average)=150 was used as the starting original polymer in the computer experiments. The hypothetical phase equilibrium calculation was carried out with the electric computer, IBM 4341 II. The total

number of components comprising the original polymer was 1500.

First, one gram of the original polymer (density, 1 g cm^{-3} ; in this case the volume of the polymer $V_3^0 = 1 \text{ ml}$) was dissolved in $V_1^0 \text{ ml}$ of solvent 1 to give a solution of the polymer volume fraction v_p^s ($\equiv 1/(1 + V_1^0)$), to which $V_2 \text{ ml}$ of solvent 2 were added. The solution thus prepared had a total volume V ($= V_3^0 + V_1^0 + V_2$), and v_p^0 given by

$$v_p^0 = V_3^0 / (V_3^0 + V_1^0 + V_2) = 1 / (1 + V_1^0 + V_2) \quad (1)$$

and was allowed to attain phase equilibrium. V_2 is related to the phase volume ratio R , the volume fraction of solvent 2 in the polymer-lean, and -rich phases, $v_{2(1)}$ and $v_{2(2)}$, respectively, and the total volume of solution V by the relation,

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

Using eq 2 we can express the total volume V in the form

$$V = \frac{(R+1)(V_3^0 + V_1^0)}{R+1 - Rv_{2(1)} - v_{2(2)}} \quad (3)$$

Combination of eq 1 and 3 gives

$$\begin{aligned} v_p^0 &= \frac{V_3^0(R+1 - Rv_{2(1)} - v_{2(2)})}{(R+1)(V_3^0 + V_1^0)} \\ &= \frac{R+1 - Rv_{2(1)} - v_{2(2)}}{(R+1)(1 + V_1^0)} \end{aligned} \quad (4)$$

As shown in the previous paper,¹ v_p^0 can be considered constant by using an adequate V_1^0 value in eq 4 as a precondition, if necessary. The computer experiment on a quasi-binary system consisting of a multicomponent polymer in a single solvent was performed by Kamide *et al.* and polymer molecular weight distribution was the same as that employed in the present calculation of a quasi-ternary system and the concentration dependence of χ parameter defined by eq 5 was taken into consideration

$$\chi = \chi_0(1 + pv_p) \quad (5)$$

where χ_0 is a constant independent of v_p .

RESULTS AND DISCUSSION

For any quasi-ternary system consisting of a multicomponent polymer, solvent 1 and solvent 2, three thermodynamic interaction parameters between solvent 1, solvent 2 and the polymer 3, χ_{12} , χ_{13} , and χ_{23} , can be clearly determined at constant temperature and pressure. The phase equilibrium may or may not occur under the given preconditions of ρ_p and v_p^0 . Note that the volume ratio of solvent 1 to solvent 2, at phase equilibrium, V_1/V_2 is not always constant when v_p^0 is changed while keeping ρ_p constant. This is exemplified in Figure 1. With diminishing v_p^0 , the content of solvent 1 decreases, indicating the composition of a binary solvent mixture to change depending on the operating conditions and, in this regard, the quasi-ternary system to be much more complicated than a quasi-binary system.

Figure 2 shows the change in the total composition (*i.e.*, the composition of the sum of the polymer-lean and -rich phases and that immediately before the phase separation) with v_p^s . Here v_1 and v_2 are the volume fractions of solvent 1 and solvent 2 in a quasi-ternary system as defined by $v_1 = V_1^0 / (V_1^0 + V_2 + V_3^0)$ and $v_2 = V_2 / (V_1^0 + V_2 + V_3^0)$. The phase equilibrium conditions are the same as those in Figure 1. A rapid increase in v_2 with a increase in ρ_p is observed at constant v_p^s .

Figure 3 shows the phase diagrams obtained for solutions with $v_p^s = 0.001 \sim 0.07$. In this figure coexistence curves and tie-lines for $\rho_p = 1/15 \sim 14/15$ are shown. The same set of χ_{12} , χ_{13} , and χ_{23} as those in Figures 1 and 2 are employed also. As v_p^s decreases, the coexistence curves slightly shift to the v_2 apex. A significant variation in coexistence curves with v_p^s (or v_p^0) sharply reflects the polymolecularity of the original polymer sample. Note that the coexistence curve of the strictly mo-

Figure 1. Change in volume ratio, V_1/V_2 , of solvent 1 to solvent 2 with the initial volume fraction v_p^o of the solution in which the two phase separation occurs. The original polymer, Schulz-Zimm distr., $X_w^o=300$, $X_w^o/X_n^o=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.20$.

Figure 2. Change in total composition of the solution in which the phase separation occurs, with the starting polymer volume fraction v_p^s . The original polymer, Schulz-Zimm distr., $X_w^o=300$, $X_w^o/X_n^o=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.20$; v_p^s , 0.09 ($\blacktriangledown$), 0.07 ($\blacklozenge$), 0.05 ($\bullet$), 0.03 ($\blacksquare$), 0.01 ($\blacktriangle$), 0.003 ($\circ$), 0.001 ($\square$).

nodisperse polymer solution is, of course, absolutely independent of v_p^o and v_p^s . The coexistence curve at the polymer rich phase side is almost parallel to the v_1 axis, irrespective of v_p^s , suggesting that the volume fraction of solvent 2 in the polymer-rich phase $v_{2(2)}$ is nearly constant, regardless of ρ_p .

In two coexisting phases, v_2 can be regarded

Figure 3. Effects of the starting polymer volume fraction v_p^s and the relative amount of the polymer in a polymer-rich phase ρ_p on the phase diagram of quasi-ternary polymer solutions. The original polymer, Schulz-Zimm distr., $X_w^o=300$, $X_w^o/X_n^o=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; $v_p^s=0.07$ (broken line), 0.01 (chain line), 0.001 (full line); a) $\rho_p=1/15$, b) $\rho_p=1/5$, c) $\rho_p=3/10$, d) $\rho_p=1/2$, e) $\rho_p=7/10$, f) $\rho_p=14/15$.

as roughly the same, but v_1 and v_p in the polymer-rich phase differ remarkably from those in the polymer-lean phase. That is, in the polymer-rich phase v_p is larger and v_1 , smaller than in the polymer lean phase.

As v_p^s decreases, a tie-line for a given ρ_p shifts to the v_2 - v_p axis. Of course, this effect of v_p^s on the tie line can be explained reasonably by the polymolecularity of the original polymer sample. At $v_p^s=0.001$, the polymer volume fraction in the polymer-lean phase, $v_{p(1)}$, can be approximated as zero, but this approximation can never be approved for higher v_p^s solutions. Even for a solution with $v_p^s=0.001$, we cannot calculate, with good accuracy, other physical quantities characterizing the phase equilibrium assuming $v_{p(1)}=0$.

The above-mentioned characteristics of a

Figure 4. Effects of the χ_{12} , χ_{13} , and χ_{23} parameters on the σ or R vs the initial polymer volume fraction v_p^0 relations. The original polymer, Schulz-Zimm distr., $X_w^0=300$, $X_w^0/X_n^0=2.0$; $\rho_p=1/15$; a, $\chi_{12}=1.30$, $\chi_{13}=0.20$, $\chi_{23}=1.0$; b, $\chi_{12}=0.05$, $\chi_{13}=0.20$, $\chi_{23}=1.0$; c, $\chi_{12}=0.48$, $\chi_{13}=0.05$, $\chi_{23}=1.0$; d, $\chi_{12}=0.48$, $\chi_{13}=0.50$, $\chi_{23}=1.0$; e, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.0$; f, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.4$.

phase diagram of the quasi-ternary system were qualitatively observed by actual experiments on polyethylene/benzylether/ethanol,¹³ polystyrene/benzyl-benzoate/acetonitrile¹³ and polystyrene/benzene/methanol.¹⁴

Figure 4 shows the relations among the partition coefficient σ , phase volume ratio R and v_p^0 . The full line in the figure corresponds to a given combination of three χ parameters. Figure 4 also shows the data (as broken line) for quasi-binary solutions, in which the molecular characteristics of the original polymer

Figure 5. Effects of the χ_{12} , χ_{13} , and χ_{23} parameters of the relations between the partition coefficient σ or the phase volume ratio R and the relative amount of polymer partitioned in a polymer-rich phase ρ_p . The original polymer, Schulz-Zimm distr., $X_w^0=300$, $X_w^0/X_n^0=2.0$; $v_p^0=0.005$; —, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.0$; ---, $\chi_{12}=0$, $\chi_{13}=0.2$, $\chi_{23}=1.0$; - - - - , $\chi_{12}=0.9$, $\chi_{13}=0.2$, $\chi_{23}=1.0$; — · — · — , $\chi_{12}=1.4$, $\chi_{13}=0.2$, $\chi_{23}=1.0$; — · · — · — , $\chi_{12}=0.48$, $\chi_{13}=0.5$, $\chi_{23}=1.0$; — · · · — · · — , $\chi_{12}=0.48$, $\chi_{13}=0.2$, $\chi_{23}=0.8$; · · · · · , $\chi_{12}=0.48$, $\chi_{13}=0.2$, $\chi_{23}=1.3$.

are the same as those used for quasi-ternary solutions and the number on each line is a p parameter. The relations between χ_0 and v_p^0 for quasi-binary solutions have already been discussed in detail by Kamide and Sugamiya.¹⁵ The σ as well as R decreases with an increase in v_p^0 . As χ_{12} and χ_{23} become smaller and χ_{13} larger, both σ and R increase. For any combination of χ_{12} , χ_{13} , and χ_{23} , the same σ vs. v_p^0 or R vs. v_p^0 relations as those for quasi-binary solutions assuming $p=0$ can be obtained. That is, for a given ρ_p and a given v_p^0 , the quasi-ternary system always affords smaller σ and R than does the quasi-binary system. The lines for the quasi-binary system with $p=0$ can be regarded as asymptotic lines attainable by the quasi-ternary system. The higher fractionation efficiency for a quasi-binary system was experimentally demonstrated by Kamide *et al.*¹⁶ using polystyrene.

Figure 5 shows the effect of ρ_p on σ and R for the quasi-ternary (full line) and -binary (broken line) solutions of $v_p^0=0.005$ of the polymer having the Schulz-Zimm distribution ($X_w^0=300$, $X_n^0=150$). As ρ_p increases from zero to unity, σ increases monotonously, but R

decreases first and increases after passing through a minimum ($\rho_{\min}$). As described before, σ and R , both calculated for the quasi-ternary solution, do not exceed, by any combination of the three χ parameters, those for the quasi-binary solution with $p=0$. A decrease in χ_{12} and χ_{23} and an increase in χ_{13} bring about an increase in σ and R .

Figure 6 shows the effect of v_p° on the relations between σ (or R) and ρ_p . In this case, $\chi_{12}=0.48$, $\chi_{13}=0.2$, and $\chi_{23}=1.3$ were assumed. The characteristic feature of σ (or R) vs. ρ_p relations in Figure 5 holds its validity over a wide range of v_p° , from 1×10^{-5} to 1×10^{-2} . That is, as ρ_p increases, σ as well as $d\sigma/d\rho_p$ increases monotonously, but R decreases first and increases after passing through minimum $\rho_{p,\min}$ at any v_p° investigated. $\rho_{p,\min}$ is maintained almost constant, irrespective of v_p° .

Figure 7 shows the relationship between ρ_p and v_p° , which yield the same value of σ or R . In a smaller v_p° region, σ is evidently ρ_p -dependent and in the larger v_p° region (particularly at smaller ρ_p) σ is dependent of v_p° and of ρ_p . Over an extremely wide v_p° range, R is strongly v_p° -dependent and the feature of its

dependence is almost the same. The dependence of ρ_p on v_p° at a given R , $(d\rho_p/dv_p^\circ)_R$ changes its sign from positive to negative as ρ_p decreases.

For any value of ρ_p , both σ and R increases with v_p° and for any value of v_p° , σ increases with ρ_p , but R is minimum at $\rho_p \approx 0.7$. This confirms the general characteristics in Figure 6. Figure 8 shows the relationships among v_p° , ρ_p , σ and R obtained at phase equilibrium. As Kamide and his coworkers pointed out for a quasi-binary system,¹⁰ under given external

Figure 6. Effect of the initial polymer volume fraction v_p° on the relations between the partition coefficient σ or the phase volume ratio R and the relative amount of the polymer in a polymer-rich phase ρ_p . The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.30$.

Figure 7. Relationships among ρ_p , v_p° , and σ (upper part) and among ρ_p , v_p° , and R (lower part) for a quasi-ternary polymer solutions. The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.30$.

Figure 8. Relations among the initial polymer fraction v_p° , the relative amount of the polymer in a polymer-rich phase ρ_p , the partition coefficient σ , and the phase volume ratio R for quasi-ternary polymer solution. The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.30$.

Figure 9. Differential MWD curve $g_{(i)}(X)$ of the polymers in a polymer-rich phase ($i=2$) or in a polymer-lean phase ($i=1$), separated at $\rho_p=1/15$ (a) or $14/15$ (i.e., $\rho_s=1/15$) (b) from different v_p^0 quasi-ternary solutions (numbers at curves). The original polymer, Schulz-Zimm distr., $X_w^0=300$, $X_w^0/X_n^0=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.30$.

operating conditions (v_p^0 and ρ_p), σ together with R are unambiguously determined. In other words, a given pair of v_p^0 and ρ_p corresponds rigorously to a specialized pair of σ and R as independent separation variables even for a quasi-ternary system, provided the molecular characteristics of the original polymer and three χ parameters are given in advance.

It should be remarked that σ and R may vary within a network structure in Figure 8 corresponding to a change in v_p^0 ranging from 1×10^{-5} to 1×10^{-2} and to a change in ρ_p from $1/40$ to $19/20$. As v_p^0 reduces with keeping ρ_p constant, both σ and R (particularly, R) increase progressively and with increasing ρ_p at a given v_p^0 , σ increase monotonously and R decreases in a small ρ_p region, then increases slightly after passing through the minimum.

Figure 9a exemplifies the normalized molecular weight distribution (MWD) curves $g_{(2)}(X)$ in some polymers remained in the polymer-rich phase, which is phase-separated,

keeping $\rho_p=1/15$, from the solutions of various concentration v_p^0 . $g_{(2)}(X)$ for the polymers isolated from a comparatively concentrated solution shows a peak at a lower X (and this X is designed as X_p), and approximated as X_p for the original polymer. As v_p^0 decrease, the peak of the MWD curve moves from a lower to higher X region, without changing practically the upper and lower limits of MWD and this shift results in a sharpening of a MWD.

Figure 9b shows a normalized MWD curve $g_{(1)}(X)$ of some polymers partitioned in the polymer-lean phase, which is phase-separated, keeping $\rho_s=1/15$ (i.e., $\rho_s=14/15$), from the solutions of various v_p^0 . The higher X region in MWD is notably changed by v_p^0 and as v_p^0 is lowered, X_p of $g_{(1)}(X)$ decreases with a remarkable peak sharpening. The shift of X_p and peak sharpening contribute in reverse manner to MWD and in this case, the effect of the latter is significantly larger on MWD than that of the

Figure 10. Dependence of X_p of the polymers in a polymer-rich phase a) or in a polymer-lean phase b) on the initial polymer volume fraction v_p^0 . The original polymer, Schulz-Zimm distr., $X_w^0 = 300$, $X_w^0/X_n^0 = 2.0$; $\circ$, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; $\bullet$, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.2$; $\triangle$, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 0.80$; $\square$, $\chi_{12} = 0.48$, $\chi_{13} = 0.05$, $\chi_{23} = 1.00$; $\blacksquare$, $\chi_{12} = 0.48$, $\chi_{13} = 0.50$, $\chi_{23} = 1.00$; ∇ , $\chi_{12} = 0.20$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; $\blacktriangledown$, $\chi_{12} = 1.30$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$. Full lines are for quasi-binary solutions and the concentration dependence of χ -parameter, p is denoted on the curve.

Figure 11. Effect of the initial polymer volume fraction v_p^0 on X_w/X_n of the polymer in a polymer-rich phase. The original polymer, Schulz-Zimm distr., $X_w^0 = 300$, $X_w^0/X_n^0 = 2.0$; full line, quasi-ternary solution with $\chi_{13} = 0.20$, $\chi_{23} = 1.00$, χ_{12} denoted on curves; broken line, quasi-binary solution with the concentration dependence of χ -parameter, p is denoted on curves; the relative amount of polymer $\rho_p = 1/15$.

former, resulting in a decrease in the breadth of the MWD of the polymer with a decrease in v_p^0 . Similar dependence of MWD on v_p^0 was observed for a multicomponent polymer-single solvent system.

In Figure 10, the X_p - v_p^0 relations, obtained at constant ρ_p or ρ_s ($1/15$) for various combinations of χ_{12} , χ_{13} , and χ_{23} are shown.

Similar relations for quasi-binary solutions with various concentration dependence parameters p in eq 5 are also shown as full lines for comparison. All the data for the quasi-ternary solutions yield a single master curve, irrespective of the combination of χ_{12} , χ_{13} , and χ_{23} values, lying between those for the quasi-binary solutions with $p = 0$ and -0.6 . These

Figure 12. Effects of the relative amounts of polymers in a polymer-lean phase, ρ_s , (number of curve in a)) and in a polymer-rich phase, ρ_p , (number on curve in b)) on the relations between X_w/X_n of the polymers and the initial polymer volume fraction. The original polymer, Schulz-Zimm distr., $X_w^\circ = 300$, $X_w^\circ/X_n^\circ = 2.0$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$.

plots demonstrate as asymptotic approach of X_p to a maximum value at lower v_p° and to a minimum at higher v_p° . X_p can be regarded as roughly constant in the range $v_p^\circ < 2 \times 10^{-3}$ for the polymer in the polymer-rich phase and $v_p^\circ < 2 \times 10^{-2}$ for the polymer in the polymer-lean phase and X_p transits rapidly in a comparatively narrow v_p° range.

The value of X_w/X_n of the polymer in the polymer-rich phase is plotted in Figure 11 vs. $\log v_p^\circ$. In this figure, the results of a quasi-binary solution are shown as broken lines for comparison. Simply by a proper choice χ_{12} , χ_{13} , and χ_{23} values, polymers could not be prepared having narrower MWD than those obtained from a quasi-binary solution assuming $p = 0$.

Unexpectedly, X_w/X_n vs. v_p° relations for quasi-ternary solutions were found to be very similar in shape to those for quasi-binary solutions calculated with $p \leq 0$. This suggests that a multicomponent polymer-solvent 1-solvent 2 system can be approximated with a multicomponent polymers-solvent system (i.e., single solvent approximation) if the negative concentration dependence of χ -parameter is assumed. For any system of polymer and solvent investigated, a negative p

has never been reported and hence is a hypothetical system.

Figure 12 shows the relation between X_w/X_n of the polymer in the polymer-lean and -rich phases and v_p° for a given combination of three χ parameters when a constant ρ_p ($\equiv 1 - \rho_s$) of the polymers is separated. The MWD of the polymer in the polymer-lean phase becomes sharp without limit as ρ_s decreases and the effect of ρ_s predominates over v_p° on the polydispersity of the polymer-lean phase. As ρ_p decreases, the v_p° dependence of X_w/X_n of the polymer in the polymer-rich phase becomes remarkable, as expected. The ρ_p value, at which the minimum X_w/X_n is obtained at a given v_p° , $\rho_{p,\min}$, depends on v_p° , becoming smaller as v_p° diminishes.

Figure 13 shows the normalized MWD curve of the polymers in the polymer-rich and -lean phases, $g_{(2)}(X)$ and $g_{(1)}(X)$, isolated from a quasi-ternary solution. With a decrease in ρ_p , a remarkable increase in its content in a larger X region and a significant lowering of the peak height are observed in both $g_{(2)}(X)$ and $g_{(1)}(X)$ and in the former, X_p shifts, noticeably to a larger X region, but in the latter remains constant, roughly identical with X_p of the original polymer.

Figure 13. Effects of the relative amounts of polymers in a polymer-rich phase ρ_p (a) and in a polymer-lean phase ρ_s (b) on the MWD curve $g_{(i)}(X)$ ($i=1$ and 2) of the polymers. The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; the initial polymer volume fraction $v_p^\circ=0.005$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; ρ_p and ρ_s are denoted on the curve.

Figure 14. Effects of the parameters χ_{12} (a), χ_{13} (b) and χ_{23} (c) on the relations between X_w/X_n of the polymers in a polymer-rich phase ρ_p . The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; a) χ_{12} is denoted on curve, $\chi_{13}=0.2$, $\chi_{23}=1.0$; b) $\chi_{12}=0.48$, χ_{13} is denoted on curve, $\chi_{23}=1.0$; c) $\chi_{12}=0.48$, $\chi_{13}=0.20$ and χ_{23} is denoted on curve; broken line, quasi-binary solution, the concentration dependence of χ -parameter p is denoted on curve.

Figure 14 shows the effects of χ_{12} , χ_{13} , and χ_{23} on the relationships between X_w/X_n of the polymer dissolving in the polymer-rich phase and that remaining in the polymer-lean phase and ρ_p for $v_p^\circ = 0.005$. Figure 14 also shows the data for a quasi-binary system. X_w/X_n of the polymer in the polymer-rich phase decreases first and then increases after passing through a minimum of X_w/X_n ($(X_w/X_n)_{\min}$). ρ_p , yielding $(X_w/X_n)_{\min}$, is defined as $\rho_{p,\min}$. In contrast to this, X_w/X_n of the polymer in the polymer-lean phase decreases monotonously with a decrease in ρ_s , approaching 1.0 at the limit of $\rho_s = 0$ (i.e., $\rho_p = 1$). Figure 14 indicates that the characteristics observed in a quasi-binary systems hold even in a quasi-ternary (and probably much higher order) system. The X_w/X_n of the polymers in both phases is without exception smaller in a quasi-binary system with $p > 0$ than in quasi-ternary systems, suggesting that fractionation using quasi-binary system is much more effective compared to a quasi-ternary system.

Figure 15 shows the standard deviation σ' of the polymers in both phases as a function of ρ_p for quasi-ternary and -binary systems. In this case, for the former system, various combinations of χ_{12} , χ_{13} , and χ_{23} are assumed. For the same value of ρ_p , the combination of these χ parameters controls to some extent the polydispersity of the polymers. A decrease in χ_{12} improves the separation efficiency. It should be noted that σ' , a much more adequate parameter representing the polydispersity than the ratio X_w/X_n , is always larger in the polymer-rich phase than in the polymer-lean phase. This clearly indicates the superiority of the solution method against the precipitation method, even for quasi-ternary solutions as well as quasi-binary solutions.

Figure 16 illustrates the effect of v_p° on the polydispersity of the polymers in both phases. This effect is conspicuous for polymers remaining in the polymer-rich phase, especially at extremely small ρ_p . A striking decrease in $\rho_{p,\min}$ for both X_w/X_n and σ' is noted with a

Figure 15. The standard deviation σ' of the polymers in a polymer-rich phase and in a polymer-lean phase separated from a quasi-ternary solution (full line) and quasi-binary solution (broken line), plotted vs. the relative amounts of polymers in a polymer-rich phase ρ_p . The original polymer, Schulz-Zimm distr., $X_w^\circ = 300$, $X_w^\circ/X_n^\circ = 2.0$; χ_{12} , number on curve, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; initial polymer volume fraction $v_p^\circ = 0.005$; for quasi-binary solution, the concentration dependence of χ -parameter p , number on curve.

decrease in v_p° .

Figure 17 shows the relationships between ρ_p and v_p° , which yield the polymers, in the polymer-rich and -lean phases, having the same value of X_w/X_n . As expected from Figure 14 and 16, two different values of ρ_p at a given value of v_p° yield the same X_w/X_n of the polymer-rich phase. In the range of small ρ_p (strictly speaking, in a region lower than the broken line), $X_{w(2)}/X_{n(2)}$ of the polymer depends mainly on v_p° , while in the higher ρ_p range (i.e., a region higher than the broken line), $X_{w(2)}/X_{n(2)}$ is predominantly governed by ρ_p alone. $X_{w(1)}/X_{n(1)}$ is ρ_p - (i.e., ρ_s -) dependent over the whole range of v_p° . Figure 17 offers the fundamental information necessary for

Figure 16. Effect of the initial polymer volume fraction v_p^0 (number on curve) on relations between X_w/X_n or σ' of the polymers in a polymer-rich and -lean phases and ϕ_p for quasi-ternary solution. The original polymer, Schulz-Zimm distr., $X_w^0=300$, $X_w^0/X_n^0=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.30$.

Figure 17. Relations between initial polymer volume fraction v_p^0 , the relative amount of the polymer-rich phase ρ_p and X_w/X_n of the polymer in a polymer-rich phase (upper part) and in a polymer-lean phase (lower part), both separated from quasi-ternary solution. The original polymer, Schulz-Zimm distr., $X_w^0=300$, $X_w^0/X_n^0=2.0$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.30$.

designing a detailed fractionation scheme for a given polymer and a given combination of solvent 1 and solvent 2.

Figure 18 shows the v_p^0 dependence of the

volume fractions of solvent 1 in the polymer-lean phase and in the polymer-rich phase, $v_{1(1)}$ and $v_{1(2)}$, and the volume fraction of solvent 2 in the two phases, $v_{2(1)}$ and $v_{2(2)}$ for a given combination of χ_{12} , χ_{13} , and χ_{23} . $v_{1(1)}$, $v_{1(2)}$, and $v_{2(2)}$ increase, but $v_{2(1)}$ decreases with an increase in v_p^0 . The volume fractions of solvents in the two phases are markedly influenced by the χ_{23} parameter. An increase in χ_{23} (i.e., the precipitation power) brings about a significant increase in $v_{1(1)}$ and $v_{1(2)}$ and a decrease in $v_{2(1)}$ and $v_{2(2)}$.

Figure 19 shows the relations between the polymer volume fraction, $v_{p(1)}$, in the polymer-lean phase, separated from quasi-ternary polymer solutions having various combinations of χ_{12} , χ_{13} , and χ_{23} at various ρ_p . $v_{p(1)}$ is overwhelmingly dependent on ρ_p and v_p^0 and substantially independent of the three χ parameters. The full lines in Figure 19 are the results of a quasi-binary solution, with $p = -0.6 \sim +0.6$ on each line. These lines are completely consistent with those of a quasi-ternary solution. Large variation in p for a

Figure 18. The volume fractions of solvent 1 in polymer-lean and -rich phases $v_{1(1)}$ a) and $v_{1(2)}$ b), and the volume fractions of solvent 2 in polymer-lean and -rich phases $v_{2(1)}$ c) and $v_{2(2)}$ d) plotted against the initial polymer volume fraction v_p° . The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; the relative amount of the polymer in a polymer-rich phase, $\rho_p=1/15$; —, $\chi_{12}=0.48$, $\chi_{13}=0.05$, $\chi_{23}=1.25$; ---, $\chi_{12}=0.48$, $\chi_{13}=0.10$, $\chi_{23}=1.25$; - - - - , $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.25$; ·····, $\chi_{12}=0.48$, $\chi_{13}=0.05$, $\chi_{23}=1.00$; ······, $\chi_{12}=0.48$, $\chi_{13}=0.10$, $\chi_{23}=1.00$; — · —, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$.

quasi-binary solution at given ρ_p does not give a significant change in the $v_{p(1)}-v_p^\circ$ relations.

Figure 20 and 21 depict the relations among the polymer volume fraction, $v_{p(2)}$, in the polymer-rich phase and v_p° and ρ_p . Under the same operating conditions, such as χ_{12} , χ_{13} , and χ_{23} , and ρ_p ($=1/15$) (or $v_p^\circ=0.005$), $v_{p(2)}$ decreases with an increase in v_p° and with a decrease in ρ_p . Unlike $v_{p(1)}$, $v_{p(2)}$ is evidently dependent on the χ parameters, and $v_{p(2)}$, and accordingly, $v_{p(2)}-v_{p(1)}$, are larger for smaller

Figure 19. Plot of the polymer volume fraction of the polymer in a polymer-lean phase $v_{p(1)}$ against the initial polymer volume fraction v_p° at a constant relative amount of the polymer partitioned in a polymer-rich phase ρ_p (number on curve). The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; ●, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=0.80$; ○, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; ■, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.20$; ▽, $\chi_{12}=0.48$, $\chi_{13}=0.05$, $\chi_{23}=1.00$; □, $\chi_{12}=0.48$, $\chi_{13}=0.50$, $\chi_{23}=1.00$; ▲, $\chi_{12}=0.20$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; ◆, $\chi_{12}=1.30$, $\chi_{13}=0.20$, $\chi_{23}=1.00$.

χ_{12} , larger χ_{13} and smaller χ_{23} . The quantity $v_{p(2)}-v_{p(1)}$ is a measure of the ease of separation of the polymers.⁹ The dotted lines in Figure 20 result from a quasi-binary solution. $v_{p(2)}$ of the quasi-ternary solution can never exceed that of the quasi-binary solution with $p=0$, suggesting an effective separation of the two phases for quasi-ternary system to be comparatively difficult compared to that for quasi-binary system.

It is intuitively expected that solvent 1, which has a large affinity to the polymer, is more or less selectively partitioned into a polymer-rich phase, that is, a so-called selective adsorption will occur in the phase equilibrium of the multicomponent polymer-solvent 1-solvent 2 system.

Here, we define θ_2 as a measure representing the selective adsorption by eq 6

$$\theta_2 = \frac{v_{2(1)}/(v_{1(1)}+v_{2(1)})}{v_{2(2)}/(v_{1(2)}+v_{2(2)})} \quad (6)$$

Figure 20. Plot of the polymer volume fraction in a polymer-rich phase $v_{p(2)}$ versus the initial polymer volume fraction v_p^0 for quasi-ternary (full and broken lines) and quasi-binary (dotted line) solutions at constant relative amount of the polymer ρ_p . The original polymer, Schulz-Zimm distr., $X_w^0 = 300$, $X_w^0/X_n^0 = 2.0$; for a quasi-ternary solution, a) χ_{12} , numbers on curve, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$, b) full line, $\chi_{12} = 0.48$, χ_{13} , numbers on the curve, $\chi_{23} = 1.00$, broken line, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, χ_{23} , numbers on the curve; for a quasi-binary solution, the concentration dependence of χ -parameter, p is denoted on curve.

Figure 22 demonstrates the dependence of θ_2 on v_p^0 . It is of interest to note that the selective adsorption becomes remarkable for larger χ_{12} , smaller χ_{13} and larger χ_{23} (i.e., when very good solvent and very poor solvent are employed), especially in a lower v_p^0 region. The selective adsorption becomes negligible in relatively concentrated solution.

Figure 23 shows the relations between θ_2 and ρ_p for the quasi-ternary solutions of $v_p^0 = 0.005$. The magnitude of θ_2 increases with an increase in ρ_p . The slope of the plots, $d\theta_2/d\rho_p$ is

Figure 21. The polymer volume fraction in a polymer-rich phase $v_{p(2)}$ plotted as a function of the relative amount of the polymer in a polymer-rich phase ρ_p . The original polymer, Schulz-Zimm distr., $X_w^0 = 300$, $X_w^0/X_n^0 = 2.0$, initial polymer volume fraction $v_p^0 = 0.005$; full line, quasi-ternary solution; a, $\chi_{12} = 0$, $\chi_{13} = 0.20$, $\chi_{23} = 1.0$; b, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.0$; c, $\chi_{12} = 0.90$, $\chi_{13} = 0.20$, $\chi_{23} = 1.0$; d, $\chi_{12} = 1.4$, $\chi_{13} = 0.2$, $\chi_{23} = 1.0$; e, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 0.80$; f, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.30$; g, $\chi_{12} = 0.48$, $\chi_{13} = 0.50$, $\chi_{23} = 1.00$; h, $\chi_{12} = 0.48$, $\chi_{13} = 0$, $\chi_{23} = 1.0$.

nearly constant at constant ρ_p over a wide range of three χ parameters. Inspection of Figures 22 and 23 leads to the conclusion that χ_{23} plays the most important role in selective adsorption.

In this study, it has been shown that parameters characterizing the phase separation of the quasi-ternary solutions, such as σ , R , $v_{p(1)}$, $v_{p(2)}$, $X_{w(1)}/X_{n(1)}$, $X_{w(2)}/X_{n(2)}$, $\sigma'_{(1)}$ and $\sigma'_{(2)}$ can be equated to those for quasi-binary solutions by assuming an adequate concentration dependence p of the χ parameter. Then, for various equilibrium parameters, a nearly common p value can be reasonably chosen if the three χ_{ij} parameters are given in advance. For example, for a quasi-ternary system with $\chi_{12} = 0.2$, $\chi_{13} = 0.2$, and $\chi_{23} = 1.0$, $p = -0.26 \pm 0.02$ was estimated, when the polymer with the Schulz-Zimm distribution ($X_w^0 = 300$) and dissolved in a solution of $v_p^0 = 0.005$ was separated into two phases.

Figure 22. Dependence of the selective adsorption θ_2 on the initial polymer volume fraction v_p° for a quasi-ternary system. The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; the relative amount of the polymer in a polymer-rich phase, $\rho_p=1/15$; a, $\chi_{12}=0.2$, $\chi_{13}=0.2$, $\chi_{23}=1.00$; b, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; c, $\chi_{12}=0.90$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; d, $\chi_{12}=1.30$, $\chi_{13}=0.2$, $\chi_{23}=1.00$; e, $\chi_{12}=0.48$, $\chi_{13}=0.50$, $\chi_{23}=1.00$; f, $\chi_{12}=0.48$, $\chi_{13}=0.05$, $\chi_{23}=1.00$; g, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=0.80$; h, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.20$.

Figure 23. Dependence of the selective adsorption θ_2 on the relative amount of the polymer in a polymer-rich phase ρ_p for quasi-ternary solutions with $v_p^\circ=0.005$. The original polymer Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$. Key to lines a—h is given in Figure 22.

Figure 24 shows the relations among χ_{12} , χ_{13} , and χ_{23} , yielding the same phase separation characteristics as those obtained for the

Figure 24. Relationships between χ_{12} , χ_{13} , and χ_{23} , yielding the same phase separation characteristics as those by a quasi-binary solution with the concentration dependence of the χ -parameter p (numbers on the curve). The original polymer, Schulz-Zimm distr., $X_w^\circ=300$, $X_w^\circ/X_n^\circ=2.0$; the initial polymer volume fraction $v_p^\circ=0.005$; relative amount of the polymer-rich phase $\rho_p=1/15$.

Figure 25. The ratio M_w/M_n plotted against M_w of the fractions separated by successive solution fractionation from a quasi-ternary system. $\circ$, experimental data on polystyrene–methyleneethylketone–methanol; full line, theoretical curve ($\chi_{12}=0.20$, $\chi_{13}=0.05$, $\chi_{23}=0.80$ and $\rho_p=1/22$); $v_p^\circ=6.15 \cdot 10^{-3}$.

quasi-binary solutions with fixed p value. The quasi-ternary solutions having small χ_{12} , large χ_{13} , and large χ_{23} can be reasonably approximated with a quasi-binary solution with large negative p . A combination of small χ_{12} and large χ_{13} or that of large χ_{12} and small χ_{13} corresponds to a fixed p , if χ_{23} is maintained constant. This relation between χ_{12} and χ_{13} belongs to a family of hyperbolas. A suitable relation between χ_{13} and χ_{23} , corresponding to a quasi-binary solution with fixed p , is almost χ_{13} -dependent, especially for small p . A large χ_{23} is combined with large χ_{12} at constant χ_{13} if the quasi-ternary solution is approximated with the quasi-binary solution with fixed p . Conclusively, a quasi-ternary polymer solution gives smaller σ , smaller R , and a broader molecular weight distribution of the polymers partitioned in the two phase, compared to a quasi-binary polymer solution in which the polymer having the same molecular characteristics as that used in a quasi-ternary solution is dissolved. This strongly suggests that the fundamental characteristics observed for the two-phase equilibrium of a quasi-binary polymer solution can be generalized quantitatively to a quasi-ternary polymer solution by assuming negative p , which is unrealistic for a quasi-

binary polymer solution. A quasi-ternary polymer solution is inferior in separation efficiency, when the solution is used for fractionation.

Figure 25 shows the plots of M_w/M_n vs. M_w for successive solution fractionation runs. The unfilled circles are a series of polystyrene fractions (total number $n=22$), separated successively using methyleneethylketone as solvent and methanol as non-solvent ($v_p^\circ=6.15 \times 10^{-3}$).¹⁶ The full line is a theoretical curve calculated assuming $\chi_{12}=0.2$, $\chi_{13}=0.05$, $\chi_{23}=0.80$, and $\rho_p \cong 1/n$ ($=1/22$). The coincidence of the experimental data with theoretical calculation is satisfactory. However, note that the three χ_{ij} parameters are not experimentally determined and this figure does not mean a direct comparison between experimental evidence and the theory of phase separation of quasi-ternary solutions. This problem is still open for further research.

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REFERENCES

1. K. Kamide, S. Matsuda, and Y. Miyazaki, *Polym. J.*, **16**, 479 (1984).
2. K. Kamide and K. Sugamiya, *Makromol. Chem.*, **139**, 197 (1970).
3. K. Kamide, Y. Miyazaki, and K. Sugamiya, *Makromol. Chem.*, **173**, 133 (1973).
4. K. Kamide, Y. Miyazaki, and K. Yamaguchi, *Makromol. Chem.*, **173**, 157 (1973).
5. K. Kamide, Y. Miyazaki, and K. Yamaguchi, *Makromol. Chem.*, **173**, 175 (1973).
6. K. Kamide and Y. Miyazaki, *Makromol. Chem.*, **176**, 1029 (1975).
7. K. Kamide and Y. Miyazaki, *Makromol. Chem.*, **176**, 1051 (1975).
8. K. Kamide and Y. Miyazaki, *Makromol. Chem.*, **176**, 1427 (1975).
9. K. Kamide and Y. Miyazaki, *Makromol. Chem.*, **176**, 1447 (1975).
10. K. Kamide and Y. Miyazaki, *Makromol. Chem.*, **176**, 3453 (1975).
11. K. Kamide and Y. Miyazaki, *Polym. J.*, **13**, 325 (1981).
12. K. Kamide, T. Abe, and Y. Miyazaki, *Polym. J.*, **14**, 355 (1982).
13. J. N. Bronsted and K. Volqvartz, *Trans. Faraday Soc.*, **36**, 619 (1940).
14. G. V. Schulz and B. Jirgensons, *Z. Phys. Chem.*, **B46**, 105 (1940).
15. K. Kamide and K. Sugamiya, *Makromol. Chem.*, **156**, 259 (1972).
16. K. Kamide, Y. Miyazaki, and T. Abe, *Br. Polym. J.*, **13**, 168 (1981).