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

VI. Theoretical Prediction of the Flory Solvent Composition

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ABSTRACT: An attempt was made to present a theoretical background for calculating the Flory (theta) solvent composition of quasi-ternary systems consisting of multicomponent polymers dissolved in a binary solvent mixture. For this purpose, Kamide and Matsuda's theory on the critical point of the quasi-ternary system [*Polym. J.*, **18**, 347 (1986)] was used as a basic principle. The volume fractions of solvents 1 and 2 at Flory solvent conditions v_1^F and v_2^F can be regarded as those at the critical solution points v_1^c and v_2^c at limit of an infinite molecular weight and the following equation was derived:

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

where χ_{12} , χ_{13} , and χ_{23} are the thermodynamic interaction parameters between the two components chosen among solvents 1, 2, and the polymer (3). By solving the equation $v_1^F (=1-v_2^F)$ can be theoretically calculated from knowledge on χ_{12} , χ_{13} , and χ_{23} . Effects of χ_{12} , χ_{13} , and χ_{23} on v_1^F were investigated systematically with computer experiments. It is predicted that double Flory solvent compositions have a possibility to exist for some polymer-solvents system. When $\chi_{12} > 0$, mixing of two good solvents is expected to yield a Flory solvent mixture.

KEY WORDS Quasi-Ternary System / Flory (Theta) Solvent / Thermodynamic Interaction Parameter / Computer Experiment / Critical Solution Point /

The Flory solvent composition or the Flory temperature of binary solvent mixture consisting of solvent 1 and solvent 2 for a given polymer is usually experimentally determined¹ by (1) the second virial coefficient A_2 in light scattering, membrane osmometry or sedimentation equilibrium,^{2,3} (2) cloud point titration,⁴⁻⁶ (3) phase equilibrium^{1,2,7-9} (4) the exponent of the Mark-Houwink-Sakurada equation,^{2,3,10} and (5) concentration dependence of hydrodynamic parameters such as

sedimentation and diffusion coefficients.¹¹

The article attempts to present an alternative theoretical method for evaluating the Flory solvent composition (*i.e.*, the volume fraction of the solvent 1 v_1^F and that of the solvent 2 v_2^F) at a given temperature from three thermodynamic interaction parameters $\chi(\chi_{12}, \chi_{13}, \text{ and } \chi_{23})$ (Here, suffix 1, 2, and 3 denote solvent 1, solvent 2 and the polymer, respectively).

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THEORETICAL BACKGROUND

Very recently, we showed for multicomponent polymers/solvent 1/solvent 2 system that the spinodal and the neutral equilibrium conditions are expressed by¹²

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

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

with

$$v_1 + v_2 + v_p = 1 \quad (3)$$

v_p is the polymer volume fraction, X_w^0 and X_z^0 the weight- and z-average molar volume ratio of the original polymer to the solvent (the molar volume of the two solvents are assumed to be identical). In deriving eq 1 and 2, the concentration dependences of χ_{12} , χ_{13} , and χ_{23} were neglected. Equation 1 gives the spinodal curve and from combination of eq 1 and 2 we can determine the v_1 , v_2 , and v_p at the critical point as expressed by v_1^c , v_2^c , and v_p^c .¹²

Regardless the molecular weight distribution (MWD) of the original polymer, at the limit of $X_w^0 \rightarrow \infty$ (and also, $X_z^0 \rightarrow \infty$) v_p^c reduces to zero and concurrently v_1^c and v_2^c become v_1^F and v_2^F , respectively: In the case of $X_w^0 \rightarrow \infty$, it follows that $v_1^c \rightarrow v_1^F$, $v_2^c \rightarrow v_2^F$, and $v_p^c \rightarrow 0$.

At the limit of $X_w^0 \rightarrow \infty$, eq 1 reduces to

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

In deriving eq 4 we assumed v_p^c approaches to zero with order of $(X_w^0)^{-a}$ ($0 < a < 1$) with increasing X_w^0 : $v_p^c \sim O((X_w^0)^{-a})$. Accordingly, $1/(v_p^c X_w^0)$ is of order of $(X_w^0)^{a-1}$ (i.e., $1/(v_p^c X_w^0) \sim O((X_w^0)^{a-1})$ and at limit of $X_w^0 \rightarrow \infty$ $1/(v_p^c X_w^0)$ approaches to zero.

Equation 2 can be rewritten by dividing both sides by X_z^0 as

$$\begin{aligned} & \left[\frac{1}{v_p X_w^0 (X_z^0)^{1/2}} \left(\frac{1}{v_1^2} - \frac{1}{v_2^2} \right) + \frac{1}{v_1^2} \left(\frac{1}{v_2} - 2\chi_{23} \right) \right. \\ & \times \left. \frac{1}{(X_z^0)^{1/2}} - \frac{1}{v_2^2} \left(\frac{1}{v_1} - 2\chi_{13} \right) \frac{1}{(X_z^0)^{1/2}} \right] \\ & \times \left[\frac{1}{v_p X_w^0 (X_z^0)^{1/2}} + \frac{1}{v_1 (X_z^0)^{1/2}} - \frac{2\chi_{13}}{(X_z^0)^{1/2}} \right] - \left(\frac{1}{v_1} + \chi_{23} - \chi_{13} - \chi_{12} \right) \\ & \times \left[\frac{1}{v_1^2} \left(\frac{1}{v_2} - 2\chi_{23} \right) \frac{1}{X_z^0} + \frac{1}{v_1^2 v_p X_w^0 X_z^0} + \frac{1}{v_p X_w^0} \left\{ \frac{1}{v_1 v_2} - \frac{2\chi_{13}}{v_2} - \frac{2\chi_{23}}{v_1} \right. \right. \\ & \left. \left. + 2(\chi_{12}\chi_{13} + \chi_{13}\chi_{23} + \chi_{23}\chi_{12}) - (\chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2) \right\} \right] = 0 \quad (5) \end{aligned}$$

The left hand side of eq 5 reduces to zero at limit of $X_w^0 \rightarrow \infty$ regardless of v_1 and v_2 . Therefore, v_1^c and v_2^c at limit of infinite X_w^0 (in other words, v_1^F and v_2^F) can be calculated by solving eq 4 alone for a given combination of χ_{12} , χ_{13} , and χ_{23} under the condition that $0 < v_1 < 1$ and $0 < v_2 < 1$.

COMPUTER EXPERIMENT

Replace v_1 and v_2 in eq 4 with v_1^F and $1 - v_1^F$

(v_2^F), respectively and denote the left-hand side term of the equation by A in the following manner:

$$A \equiv \left(\frac{1}{v_1^F} + \frac{1}{1-v_1^F} - 2\chi_{12} \right) \left(\frac{1}{v_1^F} - 2\chi_{13} \right) - \left(\frac{1}{v_1^F} + \chi_{23} - \chi_{13} - \chi_{12} \right)^2 = 0 \quad (6)$$

For a given combination of χ_{12} , χ_{13} , and χ_{23} , v_1^F (and accordingly, v_2^F) can be evaluated from eq 6 using the Newton method. The calculations were carried out under the conditions that $0 < \chi_{12} < 2.0$, $0 < \chi_{13} < 2.0$ and $0 < \chi_{23} < 2.0$ with the aid of a Hitac-E600.

RESULTS AND DISCUSSION

Figure 1 shows the effect of X_w^0 on v_1^c , v_2^c , and v_p^c in the case of $\chi_{12}=0.5$, $\chi_{13}=0.2$, and $\chi_{23}=1.0$ by full lines. The basic data were reproduced from Figure 5 of ref 12. The

Figure 1. Relations between the critical solution point (v_1^c , v_2^c , and v_p^c) and X_w^0 for quasi-ternary polymer solutions: Original polymer, Schulz-Zimm type distribution, $X_w^0/X_n^0=1, 2$, and 4 ; $\chi_{12}=0.5$, $\chi_{13}=0.2$, and $\chi_{23}=1.0$; broken line, Flory solvent compositions.

Figure 2. Relations between Flory solvent composition v_1^F ($=1-v_2^F$) and χ_{13} : a) $\chi_{12}=0$, b) $\chi_{12}=0.5$, c) $\chi_{12}=1.0$, d) $\chi_{12}=1.5$, e) $\chi_{12}=1.9$, f) $\chi_{12}=2.0$; number on curve means χ_{23} .

broken line in the figure is the Flory solvent composition ($v_1^F=0.57773$ and $v_2^F=0.42227$), calculated from eq 6. As the theory predicts, with increasing X_w^0 , the quantities v_1^c , and v_2^c approach to v_1^F and v_2^F , respectively and v_p^c reduces to zero. This indicates clearly that the mathematical assumption employed in deriving eq 4 is acceptable and eq 6 enables us to calculate v_1^F and v_2^F with good accuracy.

Figure 2 shows the relations between v_1^F and χ_{13} for fixed values of χ_{12} and χ_{23} . In the figure the broken line denotes the case of $\chi_{23}=0.5$. For $\chi_{12}=0$ (Figure 2a), the v_1^F decreases rapidly with increasing χ_{13} in the range $\chi_{23} < 0.5$, but it increases with increasing χ_{13} if $\chi_{23} > 0.5$. For a specific combination of χ_{12} and χ_{23} ($\chi_{12}=0$ and $\chi_{23}=0.5$), $\partial v_1^F / \partial \chi_{13}$ changes its sign at $\chi_{13}=0.5$. In the case of $\chi_{12}=0$ and $\chi_{13}=\chi_{23}=0.5$, eq 4 (or 6) is satisfied for any combination of v_1 and v_2 . Note that in a system of $\chi_{12}=0$ and $\chi_{13}=\chi_{23}=0.5$ solvents 1 and 2 are thermodynamically identical

and then, the system can be regarded as a quasi-binary solution whose χ is 0.5. This means that for the system v_1^F can be obtained over the whole range of the composition of v_1 . Even in the case of $\chi_{13} > 0.5$, there exists the region in which v_1^F decreases with an increase in χ_{13} (for example, $\chi_{12}=0.5$ and $\chi_{23}=0.6$). Generally, this region affords us two Flory's compositions for this polymer/solvents system as denoted by shadowed area in the figure. The existence of two Flory's composition for a given polymer/solvent/nonsolvent system has not been unfortunately demonstrated experimentally, but this phenomenon probably is closely correlated with the occurrence of co-solvency. Bamford and Tompa¹³ reported for a cellulose acetate/chloroform/ethyl acetate system the occurrence of co-solvency and two critical solution points. Of course, two critical solution points, corresponding to the infinite polymer, yield two Flory solvent compositions.

Figure 3. Relations between Flory solvent composition v_1^F ($=1-v_2^F$) and χ_{23} : a) $\chi_{12}=0$, b) $\chi_{12}=0.5$, c) $\chi_{12}=1.0$, d) $\chi_{12}=1.5$, e) $\chi_{12}=1.9$, f) $\chi_{12}=2.0$; number on curve means χ_{13} .

As χ_{12} increases beyond 1.0, the area giving two Flory solvent compositions becomes wide remarkably (Figure 2c–f). For example, in the case of $\chi_{12}=1.0$ and $\chi_{23}=0.6$ (Figure 2c),

v_1^F diminishes with increasing χ_{13} even for $\chi_{13}<0.5$. This means that there is a possibility that as the solubility power of solvent 1 decreases, the composition of solvent 1 (good

Figure 4. Relations among Flory solvent composition v_1^F ($=1-v_2^F$), χ_{13} and χ_{23} : a) $\chi_{12}=0$, b) $\chi_{12}=0.5$, c) $\chi_{12}=1.0$, d) $\chi_{12}=1.5$, e) $\chi_{12}=1.9$, f) $\chi_{12}=2.0$; shadowed area has two Flory solvent compositions.

solvent) for the Flory solvent decreases unexpectedly. Figure 2e shows that mixing of two good solvents with $\chi_{13} < 0.5$ and $\chi_{23} < 0.5$ is predicted theoretically to give sometimes a Flory solvent. The area giving the Flory solvent is denoted by hatched area. Inspection of Figure 2 also reveals that in this case, mixing of two good solvents gives two Flory solvent mixtures. This is just reverse of co-solvency phenomena (*i.e.*, co-nonsolvency), but unfortunately it has not yet been confirmed with experiments. In the case of $\chi_{12} = 2.0$ (Figure 2f), all combinations of χ_{13} and χ_{23} , except for $\chi_{13} < 0.5$ and $\chi_{23} > 0.5$ (or $\chi_{13} > 0.5$ and $\chi_{23} < 0.5$), have two Flory solvents compositions.

Figure 3 shows the relations between v_1^F and χ_{23} for the fixed χ_{12} and χ_{13} values. The relations were calculated using eq 6, which

is evidently symmetrical with respect to the exchange of solvent 1 and solvent 2. Figure 3 coincides completely with Figure 2 and no further explanation of Figure 3 is needed.

Figure 4 shows the relations among v_1^F , χ_{13} and χ_{23} , constructed by using the same data as employed in Figures 2 and 3, for fixed χ_{12} value. Curved surface surrounded with bold full lines corresponds to v_1^F for a given combination of three χ parameters. Reflecting on the symmetry of eq 6, the axis determined as an interception of two planes; $\chi_{13} = \chi_{23}$ and $v_1^F = 0.5$ is two-fold axis (not shown in the figure). Any combination of solvent 1 and solvent 2 for a given polymer having three χ parameters, whose values lie in shadowed area in Figure 4, affords us always two Flory solvents compositions. It is clear that for $\chi_{12} = 1.9 \sim 2.0$ two Flory solvents compositions

Figure 5. Relations between χ_{13} and χ_{23} giving Flory solvent: a) $\chi_{12} = 0$, b) $\chi_{12} = 0.5$, c) $\chi_{12} = 1.0$, d) $\chi_{12} = 1.5$, e) $\chi_{12} = 1.9$, f) $\chi_{12} = 2.0$; shadowed area has two Flory solvent compositions.

are expected to exist in the range $\chi_{13} < 0.5$ and $\chi_{23} < 0.5$: For example, for $(\chi_{12}, \chi_{13}, \chi_{23}) = (1.9, 0, 0.4)$ we obtain $v_1^F = 0.2$ and 0.45 and for $(\chi_{12}, \chi_{13}, \chi_{23}) = (1.9, 0.4, 0)$ we obtain $v_1^F = 0.55$ and 0.8 , respectively.

Figure 5 is the relations in figure 4 projected on the χ_{13} - χ_{23} plane. Number on the curve means v_1^F . The relations between χ_{23} and χ_{13} for a given χ_{12} is symmetrical with respect to the plane (vertical mirror), which is perpendicular to the χ_{13} - χ_{23} plane and whose interception with the χ_{13} - χ_{23} plane gives $\chi_{13} = \chi_{23}$ line. Shadowed boomerang-shape area in the figure is the area, in which two Flory solvent mixtures exist. The χ_{13} - χ_{23} relations belonging to the range of $\chi_{13} > 0.5$ and $\chi_{23} > 0.5$ lie apparently in this area, which expands with an increase in χ_{12} . In addition to this, in the case of $\chi_{12} = 1.9$, two wedge shape regions each giving two Flory solvent compositions, are formed even when $\chi_{13} < 0.5$ and $\chi_{23} < 0.5$, and in the case of $\chi_{12} = 2.0$, the total area of $\chi_{13} < 0.5$ and $\chi_{23} < 0.5$ gives two Flory solvents compositions.

Figure 6 shows the region giving two Flory solvents compositions in χ_{12} - χ_{13} - χ_{23} space. In the figure, the region is shadowed and has a mirror symmetry with respect to the $\chi_{13} = \chi_{23}$ plane, as requested by eq 6. As well as the

Figure 6. The region giving two Flory solvent compositions in χ_{12} - χ_{13} - χ_{23} space.

region of $\chi_{13} > 0.5$ and $\chi_{23} > 0.5$, relating to co-solvency, the region of $\chi_{13} < 0.5$ and $\chi_{23} < 0.5$, relating to co-nonsolvency increases its area remarkably with increasing χ_{12} .¹⁴

In summary, 1) Flory solvent composition can be theoretically calculated regardless of the polymolecularity of the polymer sample for any polymer-solvent 1-solvent 2 system, if χ_{12} , χ_{13} , and χ_{23} and known in advance for the system. 2) Two Flory solvent compositions exist for specific combination of solvents 1 and 2 (*i.e.*, for specific values of χ_{12} , χ_{13} , and χ_{23}). This prediction has not yet been experimentally confirmed. 3) When $\chi_{12} > 1.5$ (*i.e.*, when the thermodynamic property of two solvents are greatly different), mixing of two good solvents is theoretically expected to give a Flory solvent. This prediction has also not yet been experimentally ascertained.

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