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LETTER TO THE EDITOR

Thermodynamic Relationship for Fractionation of Ternary Copolymers

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ABSTRACT

Thermodynamic equations for fractionation of terpolymers were derived, and from them it was obvious that triple or dual cross-fractionation should be carried out to determine the distributions of chemical composition and molecular weight of terpolymers.

Several authors [1-5] have derived thermodynamic equations for binary copolymer solutions by using the Flory-Huggins' lattice model. From the theoretical point of view, it may be merely a simple extension of the theories to derive the thermodynamic equations for ternary copolymer (terpolymer) solutions. From the practical point of view, however, it may be meaningful to obtain those equations and to discuss the fractionation of terpolymers because of their importance in practical use of plastics. In practice, an experimental study of the fractionation of a terpolymer was reported recently [6].

If we assume that 1) the polymer chains are much longer than the average monomer sequence length, 2) only nearest-neighbor

interactions may be taken into account, and 3) solvent molecules and the three species of monomer units have the same volume, we find the mixing free energy of a heterogeneous terpolymer with a single solvent to be

$$\Delta F_M = RT \left[n_1 \ln v_1 + \sum_{X,Y} n_{X,Y} \ln v_{X,Y} + n_1 \sum_{X,Y} v_{X,Y} \chi_{X,Y} \right] \quad (1)$$

$$\chi_{X,Y} = \alpha \chi_A + \beta \chi_B + \gamma \chi_C - \alpha \beta \chi_{AB} - \beta \gamma \chi_{BC} - \gamma \alpha \chi_{AC} \quad (2)$$

where X is the degree of polymerization; $Y = f(\alpha, \beta, \gamma)$ is the chemical composition; α , β , and γ are the mole fractions of A-, B-, and C-monomer units in the terpolymer A-B-C; n_1 and v_1 are the number of molecule and the volume fraction of solvent, respectively [1], and $n_{X,Y}$, $v_{X,Y}$ are the corresponding quantities of a terpolymer (X, Y); $\chi_{X,Y}$, χ_A , χ_B , and χ_C are the interaction parameters of a solvent molecule with a terpolymer of chemical composition Y , A-, B- and C-monomer units, and χ_{AB} , χ_{BC} and χ_{AC} are the parameters characterizing the A-B, B-C and A-C interactions, respectively. Even if assumption 3) fails, as is generally so, Eqs. (1) and (2) may be useful by taking α , β , and γ as volume fractions and X as the volume ratio of polymer and solvent molecules. From Eq. (1), the chemical potential of component (X, Y) is given by

$$\Delta \mu_{X,Y} = RT \left[\ln v_{X,Y} - (X-1) + v_2 \left(1 - \frac{1}{\bar{X}_n} \right) + (1 - v_2) X \chi_{X,Y} - (1 - v_2) v_2 X \bar{\chi}_n \right] \quad (3)$$

where \bar{X}_n is the number average polymerization degree, $v_2 = \sum_{X,Y} v_{X,Y}$, and $\bar{\chi}_n = \sum_{X,Y} n_{X,Y} X \chi_{X,Y} / \sum_{X,Y} n_{X,Y} X$.

Under the condition of phase equilibrium, from Eq. (3) it follows that

$$\begin{aligned}
\ln (v'_{X,Y}/v_{X,Y}) &= X \{ \sigma + (v'_2 - v_2) \chi_Y \} \\
&= X \left[\sigma + (v'_2 - v_2) \{ \alpha(\chi_A - \beta\chi_{AB} - \gamma\chi_{AC}) \right. \\
&\quad \left. + \beta(\chi_B - \gamma\chi_{BC}) + \gamma\chi_C \} \right] \\
&= X \left[\sigma + (v'_2 - v_2) \{ \alpha(\chi_A - \gamma\chi_{AC}) \right. \\
&\quad \left. + \beta(\chi_B - \alpha\chi_{AB} - \gamma\chi_{BC}) + \gamma\chi_C \} \right] \\
&= X \left[\sigma + (v'_2 - v_2) \{ \alpha\chi_A + \beta(\chi_B - \alpha\chi_{AB}) \right. \\
&\quad \left. + \gamma(\chi_C - \beta\chi_{BC} - \alpha\chi_{AC}) \} \right] \tag{4}
\end{aligned}$$

where the prime denotes the precipitation phase and

$$\sigma = v_2(1 - 1/\bar{X}_n) - v'_2(1 - 1/\bar{X}'_n) + (1 - v_2)v_2\bar{X}_n - (1 - v'_2)v'_2\bar{X}'_n$$

If we can assume χ_{AB} , χ_{BC} , and χ_{AC} to be negligible, we can rewrite Eq. (4) as follows:

$$\ln (v'_{X,Y}/v_{X,Y}) = X(\sigma' + K_1\alpha + K_2\beta) \tag{5}$$

where $\sigma' = \sigma + (v'_2 - v_2)\chi_C$, $K_1 = (v'_2 - v_2)(\chi_A - \chi_B)$, and $K_2 = (v'_2 - v_2)(\chi_B - \chi_C)$. From Eq. (5) it is certain, as in the case of binary copolymers [4, 5], that the fractionation of terpolymer is inevitably governed by both molecular weight and chemical composition. For example, in the system of $\chi_A > \chi_C$ and $\chi_B > \chi_C$, the components having higher molecular weight and larger values of α and β (γ is smaller) are first precipitated. Accordingly, the fractions obtained by a simple

fractionation can have neither sharp distributions of chemical composition nor those of molecular weight, except for the case of both $K_1 = 0$ and $K_2 = 0$.

Thus as the dual cross-fractionation is useful for determining the chemical composition distributions of binary copolymers [7-10], the triple cross-fractionation must be used for determining the true distributions of chemical composition and molecular weight of terpolymers. In the triple cross-fractionation, three fractionation systems which have different pairs of signs with respect to K_1 and K_2 must be employed; e.g., ++, +- and --. The sample is first fractionated into primary intermediate fractions in one system, and then every intermediate fraction is fractionated into secondary intermediate fractions in the other system, and finally every secondary intermediate fraction is fractionated in the remaining system.

The triple cross-fractionation may not appear to be practical because of those complicated procedures and, moreover, it may appear very difficult to find three fractionation systems appropriate to triple cross-fractionation. Fortunately, however, chemical compositions of terpolymer polymerized in a batch are usually distributed along a straight line in the triangular diagram of chemical composition. This can be confirmed by plotting the chemical composition distribution of styrene-methyl methacrylate-acrylonitrile terpolymer calculated by Skeist [11] on a triangular diagram. In such cases there is a possibility of determining the true distributions of chemical composition and molecular weight of terpolymers by dual cross-fractionation. As for binary copolymer, we may use two fractionation systems in which the value of χ_Y increases and decreases, respectively, as the composition of the terpolymer is changed along the straight line in a triangular diagram (Fig. 1).

If the parameters characterizing the interactions between two monomer constituents of terpolymer, χ_{AB} , etc., are not negligible in Eq. (4), the value of χ_Y may have a minimum or maximum in the range of $0 < \alpha < 1$, $0 < \beta < 1$, and $0 < \gamma < 1$. Even in such a case the fractionation of terpolymer may be carried out by the same method as stated above if the chemical compositions of the sample is distributed only in a region where the value of χ_Y increases or decreases monotonically.

If the system is composed of solvent (1), nonsolvent (2), and heterogeneous terpolymer (3), we have the mixing free energy as

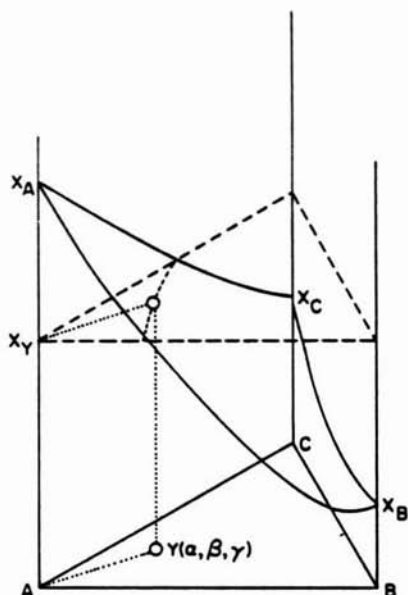


FIG. 1. Interaction parameter χ_{Y} of a solvent with terpolymer of chemical composition Y. Y is plotted in a triangular diagram. χ_{Y} is plotted on a perpendicular axis.

$$\Delta F_M = RT \left[n_1 \ln v_1 + n_2 \ln v_2 + \sum_{X,Y} n_{X,Y} \ln v_{X,Y} + n_1 v_2 \chi_{12} + n_1 \sum_{X,Y} v_{X,Y} \chi_{1Y} + n_2 \sum_{X,Y} v_{X,Y} \chi_{2Y} \right] \quad (6)$$

$$\chi_{1Y} = \alpha \chi_{1A} + \beta \chi_{1B} + \gamma \chi_{1C} - \alpha \beta \chi_{AB} - \beta \gamma \chi_{BC} - \alpha \gamma \chi_{AC} \quad (7)$$

$$\chi_{2Y} = \alpha \chi_{2A} + \beta \chi_{2B} + \gamma \chi_{2C} - \alpha \beta \chi_{AB} - \beta \gamma \chi_{BC} - \alpha \gamma \chi_{AC} \quad (8)$$

where χ_{ij} is the interaction parameter of solvent (i) with segment (j). Then the chemical potential of component (X,Y) becomes

$$\Delta\mu_{X,Y} = RT \left[\ln v_{X,Y} - (X-1) + v_3 X (1 - 1/\bar{X}_n) - v_1 v_2 X \chi_{12} + v_1 X \chi_{1Y} + v_2 X \chi_{2Y} - v_1 v_3 X \bar{\chi}_{1n} - v_2 v_3 X \bar{\chi}_{2n} \right] \quad (9)$$

Under the condition of phase equilibrium we obtain

$$\ln (v'_{X,Y}/v_{X,Y}) = X \{ \sigma^* + (v_1 - v'_1) \chi_{1Y} + (v_2 - v'_2) \chi_{2Y} \} \quad (10)$$

$$\sigma^* = v_3 (1 - 1/\bar{X}_n) - v'_3 (1 - 1/\bar{X}'_n) - (v_1 v_2 - v'_1 v'_2) \chi_{12} - v_1 v_3 \bar{\chi}_{1n} + v'_1 v'_3 \bar{\chi}'_{1n} - v_2 v_3 \bar{\chi}_{2n} + v'_2 v'_3 \bar{\chi}'_{2n} \quad (11)$$

For simplicity, assuming that χ_{AB} , χ_{BC} , and χ_{AC} are negligible, we obtain

$$\ln (v'_{X,Y}/v_{X,Y}) = X (\sigma'' + K_1^* \alpha + K_2^* \beta) \quad (12)$$

where

$$\sigma'' = \sigma^* + (v_1 - v'_1) \chi_{1C} + (v_2 - v'_2) \chi_{2C},$$

$$K_1^* = (v_1 - v'_1) (\chi_{1A} - \chi_{1C}) + (v_2 - v'_2) (\chi_{2A} - \chi_{2C})$$

and

$$K_2^* = (v_1 - v'_1) (\chi_{1B} - \chi_{1C}) + (v_2 - v'_2) (\chi_{2B} - \chi_{2C})$$

Although the contents of K-parameters are more complicated than in the case of a one-solvent system, we can speculate how the fractionation should be carried out from the analogy to the case of a one-solvent system.

Thus, to determine the distributions of chemical composition and molecular weight of terpolymers, dual cross-fractionation may be effective if we can speculate on the distribution of chemical composition of the sample from its polymerization condition. If we cannot do so, triple cross-fractionation should be tried.

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