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Apparent Second Virial Coefficient Γ for Ternary Solutions of Two Polymers in a Solvent

ZHEN TONG

Research Institute of Materials Science, South China University of Technology, Guangzhou 510641, China

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Introduction

Several years ago, Einaga et al.[1] found that the thermodynamic behavior of quasibinary solutions consisting of two narrow-distribution polystyrene samples in cyclohexane can be described almost quantitatively and consistently with the apparent second virial coefficient Γ. The separation factor measured on cyclohexane solutions containing as many as four narrow-distribution polystyrene samples and an observed phase diagram showing three-phase separation have been predicted well with the same Γ function.[2,3] In the above approach, van't Hoff solution was chosen as a thermodynamic reference[1,4] and Γ is defined to absorb all the deviations of a given solution from the reference. As pointed out by Fujita and Einaga[4] and by Vink,[5] this reference is more useful than the Flory–Huggins athermal solution for exploring thermodynamic phenomena of polymer solutions in the region where phase separation occurs. Since in the latter the combinatorial entropy of mixing is overestimated,[6] it is thus very hard to determine the interaction function χ with a sufficient accuracy. The success cited above gives a high credit to the accuracy of the Γ expression estimated from experiments.

In this paper, the concept of the apparent second virial coefficient is extended to the ternary solution containing two heterogeneous polymers and a pure solvent. The similar procedure used by Einaga et al.[7] in the derivation of the χ expression for the ternary system is adopted here.

Results and Discussion

Γ Expression. In the formulation for our system, we assign components 0–2, respectively, to the solvent and two monodisperse polymers. The composition variables used here are the same as those in refs 1 and 2, i.e., the volume fraction ϕ_i of component i (i = 1 and 2) in the solution or the total volume fraction ϕ of the polymers 1 and 2 in the solution and the volume fraction ξ_1 of polymer 1 in the polymer mixture.

In the van't Hoff solution formed by these three components, the chemical potential of the solvent μ_0^{v} is given over the entire range of ϕ by

$$\mu_0^{\mathrm{v}} = \mu_0^{\circ} - RT\phi/P_{\mathrm{n}} \qquad (1)$$

where μ_0° is the chemical potential of the pure solvent, RT has the usual meaning, and P_{n} is the number-average relative chain length of the polymer mixture defined by

$$P_{\mathrm{n}}^{-1} = \xi_1 P_1^{-1} + \xi_2 P_2^{-1} \qquad (2)$$

with P_i the chain length of polymer i relative to the solvent molar volume V_0, and $\xi_2 = 1 - \xi_1$. The chemical potential of the solvent μ_0 in our ternary system is then expressed by

$$\mu_0 = \mu_0^{\circ} - RT\phi/P_{\mathrm{n}} - RT\Gamma\phi^2 \qquad (3)$$

This equation shows the definition of the apparaent second virial coefficient Γ, which lumps all the deviations in μ_0 of a given solution from the reference. Therefore, Γ should be treated as a function of composition, T, and pressure p, evaluated through any measurements of $\mu_0 - \mu_0^{\circ}$.

Owing to the assumption that the partial molar volume of each component is independent of composition and p, the osmotic pressure Π^* of the ternary solution at fixed T and μ_0 can be expressed in powers of ϕ_i as[8]

$$V_0\Pi^*/RT = P_{\mathrm{n}}^{-1}\phi + (1/2)\sum_{i,j=1}^{2} D_{ij}\phi_i\phi_j + (1/3)\sum_{i,j,k=1}^{2} D_{ijk}\phi_i\phi_j\phi_k + \ldots \qquad (4)$$

where D_{ij}, D_{ijk}, etc., associated with the irreducible cluster integrals,[9] are invariant with the exchange of subscripts. Substituting eq 3 into eq 4 through the relation

$$\Pi^* = -(\mu_0 - \mu_0^{\circ})/V_0 \qquad (5)$$

we obtain

$$\Gamma = \phi^{-2}[(1/2)\sum_{i,j=1}^{2} D_{ij}\phi_i\phi_j + (1/3)\sum_{i,j,k=1}^{2} D_{ijk}\phi_i\phi_j\phi_k + \ldots] \qquad (6)$$

which may be rewritten as follows:

$$\begin{aligned}\Gamma = {} & \xi_1^2(D_{11}/2 + D_{111}\phi_1/3 + D_{1111}\phi_1^2/4 + \ldots) + \\ & \xi_2^2(D_{22}/2 + D_{222}\phi_2/3 + D_{2222}\phi_2^2/4 + \ldots) + \\ & 2\xi_1\xi_2[D_{12}/2 + (D_{112}\phi_1 + D_{122}\phi_2)/2 + (D_{1112}\phi_1^2 + \\ & D_{1222}\phi_2^2 + 3D_{1122}\phi_1\phi_2/2)/2 + \ldots] \end{aligned} \qquad (7)$$

When $\xi_1 = 1$, this equation reduces to the first row, corresponding to the Γ for the binary solution of polymer 1 and solvent 0, thus denoted by $\Gamma_{11}(\phi_1)$. The same can be said for the case of $\xi_2 = 1$, denoting Γ by $\Gamma_{22}(\phi_2)$. The third term in eq 7 depends simultaneously on ϕ_1 and ϕ_2 and can be taken as the contribution from all types of interactions for polymers 1 and 2 in the ternary solution. Hence, this term may be denoted by $2\xi_1\xi_2\Gamma_{12}(\phi_1,\phi_2)$. Therefore

$$\Gamma = \xi_1^2\Gamma_{11}(\phi_1) + \xi_2^2\Gamma_{22}(\phi_2) + 2\xi_1\xi_2\Gamma_{12}(\phi_1,\phi_2) \qquad (8)$$

which is the general expression of Γ derived from the present ternary system.

Some explanations are helpful in understanding eq 8. In contrast to the interaction parameters of the Scott[10]–Tompa[11] type, the solvent 0 does not explicitly appear in the Γ expression. This is originated from eq 4, the virial expansion of osmotic pressure. As shown by eqs 7 and 8, Γ_{ij} is directly related to the coefficients D_{ij}, D_{ijk}, etc. Since these coefficients represent the interaction between the solute molecules in a given solvent, the present Γ_{ij} is a measure of the interaction between polymer components i and j in the solvent.

Chemical Potential of Polymers. The Gibbs–Duhem relation for the ternary system gives[8]

$$\sum_{i=0}^{2}(\phi_i/V_i)(\partial\mu_i/\partial\phi_k) = 0 \qquad (k = 1 \text{ and } 2) \qquad (9)$$

where μ_i and V_i are the chemical potential and molar volume of component i, respectively. After altering the composition variables into ϕ and ξ_1, we derive

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$$(1-\phi)(\partial\mu_0/\partial\phi) + (\phi\xi_1/P_1)(\partial\mu_1/\partial\phi) + [\phi(1-\xi_1)/P_2](\partial\mu_2/\partial\phi) = 0 \quad (10)$$

$$(1-\phi)(\partial\mu_0/\partial\xi_1) + (\phi\xi_1/P_1)(\partial\mu_1/\partial\xi_1) + [\phi(1-\xi_1)/P_2](\partial\mu_2/\partial\xi_1) = 0 \quad (11)$$

The integrated equation of eq 10 is differentiated with respect to ξ_1 and substituted into eq 11, yielding

$$(\mu_i/RT) = \ln\phi - 1 + (1-\phi)P_i/P_n + (1-\phi)\phi P_i\Gamma + P_i\int_0^{\phi}[\Gamma + (1-\xi_i)(\partial\Gamma/\partial\xi_i)]\,du + P_i[C + (1-\xi_i)(\partial C/\partial\xi_i)] \quad (i = 1 \text{ and } 2) \quad (12)$$

where C is the integral constant depending on ξ_1, T, and p. By defining the reference chemical potential μ_i^{∞} as

$$\mu_i^{\infty} = \lim_{\phi\to 0}(\mu_i - RT\ln\phi_i) \quad (13)$$

the C can be solved from eq 12

$$C = (\xi_1/P_1)(\mu_1^{\infty}/RT + \ln\xi_1) + [(1-\xi_1)/P_2][\mu_2^{\infty}/RT + \ln(1-\xi_1)] \quad (14)$$

Substitution of C into eq 12 leads to

$$(\mu_i - \mu_i^{\infty})/RT = \ln(\phi\xi_i) - \phi_i P_i/P_n + (1-\phi)\phi P_i\Gamma + P_i\int_0^{\phi}[\Gamma + (1-\xi_i)(\partial\Gamma/\partial\xi_i)]\,du \quad (i = 1 \text{ and } 2) \quad (15)$$

Inserting eq 8 into eqs 3 and 15, we obtain the final expressions for μ_0, μ_1, and μ_2 in terms of Γ_{ij}. These expressions will be used in forthcoming papers to analyze the light scattering data and to calculate the composition of two conjugate separated phases.

Comparison of Γ_{ij} with χ_{ij}. Einaga et al.[7] proposed that for the ternary solution the interaction function χ defined by

$$(\mu_0 - \mu_0^{\circ})/RT = \ln(1-\phi) + (1 - 1/P_n)\phi + \chi\phi^2 \quad (16)$$

be expressed as

$$\chi = \xi_1^2\chi_{11}(\phi_1) + \xi_2^2\chi_{22}(\phi_2) + 2\xi_1\xi_2\chi_{12}(\phi_1,\phi_2) \quad (17)$$

where

$$\chi_{ii}(\phi_i) = E_{ii} + E_{iii}\phi_i + E_{iiii}\phi_i^2 + \ldots \quad (18)$$

$$\chi_{12}(\phi_1,\phi_2) = E_{12} + (3/2)(E_{112}\phi_1 + E_{122}\phi_2) + 2E_{1112}\phi_1^2 + 3E_{1122}\phi_1\phi_2 + 2E_{1222}\phi_2^2 + \ldots \quad (19)$$

with

$$E_{ij} = (1/2)(1 - D_{ij}),\quad E_{ijk} = (1/3)(1 - D_{ijk}),\quad \ldots \quad (20)$$

It is found by comparison of eq 3 with eq 16 that

$$\Gamma = -\chi - [\ln(1-\phi) + \phi]/\phi^2 \quad (21)$$

Since the magnitude of Γ is expected to be small in poor solvent systems, this relation indicates that χ for such a system contains a large contribution mainly for compensating the entropy introduced by the term of $-[\ln(1-\phi) + \phi]/\phi^2$, which often has the order of unity. This implies that the use of χ is not always advantageous in studying polymer solutions in which phase separation occurs.

In order to relate Γ_{ij} to χ_{ij}, eq 20 is inserted into eqs 18 and 19, the series of ϕ_i in these equations are written in the form of $\ln(1-\phi_i)$, and resulting equations are introduced into eq 7. Finally, by comparing with eq 8, we arrive at

$$\Gamma_{ii}(\phi_i) = -\chi_{ii} - [\ln(1-\phi_i) + \phi_i]/\phi_i^2 \quad (22)$$

$$\Gamma_{12}(\phi_1,\phi_2) = -\chi_{12} - [\ln(1-\phi) - \ln(1-\phi_1) - \ln(1-\phi_2)]/2\phi_1\phi_2 \quad (23)$$

Therefore, the same comments as that for the χ function mentioned above can be said to the χ_{ii} and χ_{12}.

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