

Physical Chemistry of Polymer Solutions

Theoretical Background

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Answer

$A_{2,v}$ is related to $A_{2,o}$ through Eq. (2.18.1)

$$A_{2,v} = A_{2,o} + \left(\frac{V_0}{M^2}\right) \left\{ \left(\frac{RT_0}{\Delta H} - \frac{1}{2}\right) \left(\frac{K_s}{K_c}\right)^2 + \frac{K_s}{K_c} - \frac{1}{2} \right\} \quad (2.18.1)$$

When Eq. (2.20.1) is satisfied, Eq. (2.18.1) is converted to

$$\left(\frac{RT_0}{\Delta H} - \frac{1}{2}\right) \left(\frac{K_s}{K_c}\right)^2 + \frac{K_s}{K_c} - \frac{1}{2} = 0 \quad (2.20.2)$$

From Eq. (2.20.2), we obtain

$$\frac{K_s}{K_c} = \frac{1}{1 + \left(\frac{2RT_0}{\Delta H}\right)^2} \quad (2.20.3)$$

When the ratio K_s/K_c is in agreement with Eq. (2.20.3), Eq. (2.20.1) is realized.

In case where

$$K_s = K_c \quad (2.20.4)$$

is hypothetically valid, Eq. (2.18.1) is simplified into

$$A_{2,v} = A_{2,o} + \left(\frac{V_0}{M^2} \cdot \frac{RT_0}{\Delta H}\right) = A_{2,o} + \frac{K_c}{T_0} \cdot \frac{1}{M^2} \quad (2.20.5)$$

Generally, the relationship

$$K_c \ll T_0 M^2 \quad (2.20.6)$$

holds, then Eq. (2.20.5) is reduced to

$$A_{2,v} \cong A_{2,o} \quad (2.20.1)'$$

* Putting $R(\text{cal/deg-mole}) = 1.987$, $T_0(\text{K}) = 300$, $V_0(\text{ml/mol}) = 1 \times 10^4$, $M = 300$, we obtain $K_c = 1.8 \times 10^3 < T_0 M^2 = 2.7 \times 10^7$.

Chapter 3 Lattice Theory

<<Problem 3-1>> Lattice theory for low molecular weight solution

Suppose a binary mixture consisting of N_A molecules of A and N_B molecules of B on a lattice with a coordination number z (each molecule has z nearest neighbors). Here, the total number of sites N is the sum of N_A and N_B :

$$N = N_A + N_B \quad (3.1.1)$$

We consider only the interactions between the nearest neighbor molecules and denote the interaction (potential) energy for a pair of molecules A-A, B-B and A-B as ϵ_{AA} , ϵ_{BB} and ϵ_{AB} ($=\epsilon_{BA}$), respectively, and the numbers of the three pairs by P_{AA} , P_{BB} and P_{AB} .

(1) Evaluate P_{AA} and P_{BB} when P_{AB} is given by

$$P_{AB} = zX \quad (3.1.2)$$

(2) Evaluate the total lattice energy E (with neglecting non-nearest neighbor interaction)

(3) Show that with a formation of single pair A-B, the increase in the lattice energy is given by

$$\epsilon = \epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \quad (3.1.3)$$

(4) Discuss the sign of ϵ in relation to the solvent nature.

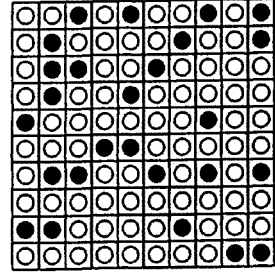


Fig. 3-1 Monomeric solute molecules distributed over a liquid lattice

Answer

(1) The total number of pairs being originated from A is zN_A , which is the summation of two times P_{AA} and P_{AB} , that is,

$$zN_A = 2P_{AA} + P_{AB} = 2P_{AA} + zX \quad (3.1.4)$$

Then we obtain

$$P_{AA} = z(N_A - X) / 2 \quad (3.1.5)$$

Similarly,

$$P_{BB} = z(N_B - X) / 2 \quad (3.1.6)$$

(2) Total lattice energy E is

$$E = P_{AA} \epsilon_{AA} + P_{AB} \epsilon_{AB} + P_{BB} \epsilon_{BB} \quad (3.1.7)$$

From Eqs. (3.1.2), (3.1.5) and (3.1.6), we obtain

$$E = \frac{z}{2} N_A \epsilon_{AA} + \frac{z}{2} N_B \epsilon_{BB} + zX \left(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right) \quad (3.1.8)$$

(3) In Eq. (3.1.8), the first two terms correspond to the interaction energy for pure components before mixing, and the third term to the interaction energy generated by mixing. Then, we have Eq. (3.1.3) for the interaction energy for forming a single pair A-B.

(4) The lattice energy E_0 for N_A molecules of pure A and N_B molecules of pure B before mixing is given by putting $X=0$ in Eq. (3.1.8) as

$$E_0 = \frac{z}{2} N_A \epsilon_{AA} + \frac{z}{2} N_B \epsilon_{BB} \quad (3.1.9)$$

Then the energy of mixing ΔE is given by the difference $E - E_0$:

$$\Delta E = zX \left(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right) = zX \epsilon \quad (3.1.10)$$

The energy increases by mixing when $\epsilon > 0$. In this case, mixing is not favored. When $\epsilon < 0$, mixing is favored. Note that, in practice, the entropy contribution

can never be ignored and we cannot judge the solubility simply from the sign of ϵ .

* **Coordination number z** is defined as the number of the nearest-neighbor lattice points of an arbitrary lattice point. z of a simple cubic lattice, a body-centered cubic lattice and a face-centered cubic lattice are 6, 8 and 12, respectively. A lattice with $z=12$ is called close-packed because no higher value of z is geometrically possible.

* Usefulness of the lattice theory in study of the mixing entropy of polymer solutions were suggested also by Meyer and Mark (K. H. Meyer and H. Mark, *Hochpolymere Chemie*, Bd. 2, p.549 (1940)). (See also N. Saito, *Polymer Physics*, Shoka-Bo, p. 108, 1960)

<<Problem 3-2>> Bragg-Williams approximation

Evaluate P_{AB} in Eq. (3.1.7) in case of random mixing [i.e., the case $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB}$].

Answer

Choose two neighboring sites (i) and (ii) on the lattice. Then the probability of molecule A on (i) is

$$A(i) = \frac{N_A}{N_A + N_B} \quad (3.2.1)$$

and the probability of B on (ii) is

$$B(ii) = \frac{N_B}{N_A + N_B} \quad (3.2.2)$$

Then the probability that a given (i)-(ii) pair is a pair A-B (A(i)B(ii) or A(ii)B(i)) is given by

$$2 \times \frac{N_A}{N_A + N_B} \times \frac{N_B}{N_A + N_B} = 2 \frac{N_A N_B}{(N_A + N_B)^2} \quad (3.2.3)$$

In Eq. (3.2.3), the factor 2 is multiplied in order to take into consideration the two cases: Case 1; A is located on (i) and B is located on (ii) and Case 2; B is on (i) and A is on (ii). P_{AB} is given by the product of the factor of Eq. (3.2.3) with the total number of nearest neighbor pairs in the system $z(N_A + N_B)/2$ as

Answer
 (1) The **partition function** Z is expressed as

$$Z = \omega(N, x) e^{-\Delta E / kT} \quad (3.3.1)$$

Here, $\omega(N, x)$ is the total number of distinguishable ways of arranging $N_A = N(1-x)$ identical molecules of A and $N_B = Nx$ identical molecules of B on the lattice, and thus, the number of combinations of taking $N(1-x)$ lattice sites from total N lattice sites at a time,

$$\omega(N, x) = \frac{N!}{\{N(1-x)\}! \{Nx\}!} \quad (3.3.2)$$

ΔE , the energy of mixing is given by

$$\Delta E = -N(1-x)\chi_A - Nx\chi_B \quad (3.3.3)$$

Substituting Eqs. (3.3.2) and (3.3.3) in (3.3.1), we obtain

$$Z = \frac{N!}{\{N(1-x)\}! \{Nx\}!} \exp \left\{ \frac{N(1-x)\chi_A + Nx\chi_B}{kT} \right\} \quad (3.3.4)$$

(2) Helmholtz free energy F is related to partition function Z through the relation

$$F = -kT \log Z \quad (3.3.5)$$

where k is the **Boltzmann constant**. Substituting Eq. (3.3.4) for Z in Eq. (3.3.5), we obtain the free energy for the binary mixtures of A and B,

$$F = -kT \log Z = -N(1-x)\chi_A - Nx\chi_B + NkT \left\{ (1-x) \log(1-x) + x \log x \right\} \quad (3.3.6)$$

In derivation of Eq. (3.3.6) we utilize **Stirling's approximation**

$$\log N! = N \log N - N \quad (3.3.7)$$

The free energy of the system consisting of pure A and pure B, F_0 , is given by

$$F_0 = -N(1-x)\chi_A - Nx\chi_B \quad (3.3.8)$$

Then the free energy of mixing ΔF_{mix} is obtained as

$$\Delta F_{\text{mix}} = F - F_0 = NkT \left\{ (1-x) \log(1-x) + x \log x \right\} \quad (3.3.9)$$

$$P_{AB} = z \frac{N_A N_B}{N_A + N_B} \quad (3.2.4)$$

Consequently, the parameter X is obtained as

$$X = \frac{N_A N_B}{N_A + N_B} \quad (3.2.5)$$

for random mixing. This assumption is called the **Bragg-Williams approximation**. This is also referred to as the zero-th approximation. Combination of Eqs. (3.1.10) and (3.2.5) leads to

$$\Delta H = \Delta E = \epsilon z X = \epsilon z \frac{N_A N_B}{N_A + N_B} \quad (3.2.6)$$

* Bragg and Williams proposed the above assumption in their study of the arrangement of atoms in an alloy (See W. L. Bragg and E. J. Williams, *Proc. Roy. Soc. A145*, 699 (1934)).

<<Problem 3-3>> Free energy of mixing for random mixing

Consider two kinds of molecules A and B sufficiently similar in size and shape so that they are interchangeable on a lattice. Assume a crystal of the pure substance containing N molecules of A has an energy $-N\chi_A$ when all the molecules are at rest on their lattice points and the zero of energy is defined as that of the molecules at rest at infinite separation. If interactions between pairs of molecules are not nearest neighbors, we may regard $-2\chi_A/z$ as the mutual energy of neighbors both at rest on their lattice points. The mutual energy $-2\chi_B/z$ is similarly defined for the crystal B. If we mix the two substances, there will be contributions to the potential energy of the crystal from AB pairs of neighbors as well as from AA and BB pairs. The mutual energy of a pair of neighbors, one A and the other B, is denoted by $(-\chi_A - \chi_B + w)/z$ and w is called the **interchange energy**. Let's mix $N(1-x)$ molecules of A and Nx molecules of B on the lattice. Derive the expressions for (1) the **partition function** Z , (2) the **change in free energy** ΔF_{mix} by **mixing** (i.e., free energy of mixing), and (3) the **partial molar free energy of mixing for each component** ΔF_{mix}^A and ΔF_{mix}^B , on the assumption of $w=0$ ($\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB}$).

* Since at constant pressure the expression for Gibbs free energy of mixing ΔG_{mix} for the lattice is the same as that for Helmholtz free energy of mixing ΔF_{mix} , Eq. (3.3.9) is identical to Eq. (2.3.1) for ideal solution. Thus, the assumptions that two molecules in the solution are interchangeable and the interchange energy is zero (**random mixing**) are the conditions sufficient for a mixture to be ideal.

(3) Partial molar free energy of mixing of the component A is calculated as

$$\Delta F_{\text{mix}}^A = \frac{\partial \Delta F_{\text{mix}}}{\partial N_A} = kT \log \left\{ \frac{x}{1-x} \right\} \quad (3.3.10)$$

Similarly, ΔF_{mix}^B is obtained as

$$\Delta F_{\text{mix}}^B = kT \log \left\{ \frac{1-x}{x} \right\} \quad (3.3.11)$$

<<Problem 3-4>> **Free energy of mixing for athermal solution**

The **partition function Z** for athermal solution is given by

$$Z = \frac{(N_1 + N_2)!}{N_1! N_2!} q_1^{N_1} q_2^{N_2} \exp \left\{ -\frac{z}{2kT} (N_1 \epsilon_{11} + N_2 \epsilon_{22}) \right\} \quad (3.4.1)$$

where we consider the case that N_1 molecules of A and N_2 molecules of B are placed on $N_1 + N_2$ lattice sites with lattice coordination number z (i.e., the number of the nearest neighbors of a site). q_1 and q_2 are the partition functions relating to the molecular motions of molecules A and B, respectively, around a lattice site, and ϵ_{11} and ϵ_{22} , the interaction energy of A-A pair and B-B pair, respectively. On the basis of Eq. (3.4.1), derive (1) **Gibbs free energy**, (2) **chemical potentials of A and B**, μ_1 and μ_2 , and (3) **entropy of mixing** ΔS_{mix} . Here, assume that the total volume of the mixture V can be considered as the summation of the volumes of pure liquid A and pure liquid B, that is,

$$V = N_1 V_1 + N_2 V_2 \quad (3.4.2)$$

where V_1 and V_2 are the volume of a molecule in pure A and B liquids, respectively.

Answer

(1) **Partition function Z** is related to **Helmholtz free energy F** and **Gibbs free energy G** as

$$F = -kT \log Z \quad (3.3.5)$$

$$G = F + PV = -kT \log Z + PV \quad (3.4.3)$$

Substituting Eq. (3.4.1) for Z in Eqs. (3.3.5) and (3.4.3), we obtain

$$\begin{aligned} G = & -kT \left[(N_1 + N_2) \log (N_1 + N_2) - N_1 \log N_1 - N_2 \log N_2 \right. \\ & \left. + N_1 \log q_1 + N_2 \log q_2 - \frac{z}{2kT} (N_1 \epsilon_{11} + N_2 \epsilon_{22}) \right] + P (N_1 V_1 + N_2 V_2) \end{aligned} \quad (3.4.4)$$

In derivation of Eq. (3.4.4), **Stirling's approximation** (Eq.(3.3.7)) is used.

(2) The chemical potential μ_1 is obtained by partially differentiating Eq.

(3.4.4) with respect to $N_1 N_A$ as

$$\begin{aligned} \mu_1 = & \left(\frac{\partial G}{\partial N_1} \right)_{T,P,N_2} N_A \\ = & \left(kT \log \frac{N_1}{N_1 + N_2} - kT \log q_1 + \frac{z}{2} \epsilon_{11} + PV_1 \right) N_A \end{aligned} \quad (3.4.5)$$

Here we denote the chemical potential of pure liquid A at T and P as μ_1^0 :

$$\mu_1^0 = \left(-kT \log q_1 + \frac{z}{2} \epsilon_{11} + PV_1 \right) N_A \quad (3.4.6)$$

Then Eq. (3.4.5) is reduced to

$$\mu_1 = \mu_1^0 + RT \log x_1 \quad (3.4.7)$$

where x_1 is the mole fraction

$$x_1 = \frac{N_1}{(N_1 + N_2)} \quad (3.4.8)$$

3-5). Let's insert each segment of the first polymer molecule and the second, the third,... polymer molecules. After $N' - 1$ polymer molecules have been inserted previously, polymer molecule N' is inserted. The total number of the arrangement of this case is denoted by $v_{N'}$. Then, w is given by the product of v_i for each molecule added consecutively to the lattice divided by $N_i!$ as

$$w = \frac{1}{N_i!} v_1 v_2 v_3 \dots v_{N_i} \tag{3.5.1}$$

Here, note that all N_i polymer molecules are indistinguishable from each other. The way of arrangement of N_0 solvent molecules on the remaining lattice sites $N - nN_i$ ($\neq N_0$) is evidently unity. Next let's evaluate $v_{N'}$ for polymer N' . Let's define the number of ways of arranging the first segment (in this case, the end segment) on the lattice as $v_{N',1}$, and that of the second segment neighbor to the first segment as $v_{N',2}, \dots$, then $v_{N'}$ is given by

$$v_{N'} = (1/\sigma) v_{N',1} v_{N',2} \dots v_{N',n} \tag{3.5.2}$$

Here, σ is two for the case when the head and the tail of a polymer molecule are indistinguishable and one for the case when the head and the tail are different. When we try to insert the first segment of molecule N' into the lattice, $N' - 1$ polymer molecules, that is, $n(N' - 1)$ lattice sites have been arranged previously. Then the first segment can be inserted on the remaining sites $N - (n(N' - 1))$. That is, $v_{N',1}$ coincides with the total number of vacant sites,

$$v_{N',1} = N - n(N' - 1) \tag{3.5.3}$$

The second segment can only be inserted to any of the z neighbors of the site occupied by the first segment of polymer molecule N' . Note that the first and the second segments are directly connected. It can never be considered that all the z neighbors are vacant, because $N' - 1$ polymer molecules have been arranged previously on the lattice. Let's assume that the probability of occupation of a given neighbor site by any segment of 1 $\sim N' - 1$ polymer molecules equals the average probability of occupancy $n(N' - 1)/N$, that is $v_{N',2}$ is given by

$$v_{N',2} = z \left\{ 1 - n(N' - 1)/N \right\} \tag{3.5.4}$$

Similarly, we obtain

$$\mu_2 = \mu_2^0 + RT \log x_2 \tag{3.4.9}$$

(3) The chemical potential μ_i is related to the partial molar entropy S_i by

$$\Delta S_i = S_i - S_i^0 = - \frac{\partial (\mu_i - \mu_i^0)}{\partial T} \tag{3.4.10}$$

Substituting Eqs. (3.4.7) and (3.4.9) in Eq. (3.4.10), we have

$$\Delta S_i = -R \log x_i \quad (i=1,2) \tag{3.4.11}$$

The entropy of mixing is expressed as

$$\Delta S_{\text{mix}} = S - S^0 = \sum N_i (S_i - S_i^0) = \sum N_i \Delta S_i = -k (N_1 \log x_1 + N_2 \log x_2) \tag{3.4.12}$$

<<Problem 3-5>> Flory's theory (I): θ^{th} approximation theory for polymer solution

Calculate the total number of ways w of arranging N_i identical polymer molecules, each of which is composed of n chain segments, and N_0 identical solvent molecules on the lattice consisting of N ($\neq N_0 + nN_i$) sites. Here, assume that a chain segment is equal in size to the solvent and neglect the possible variation of the energy for given ways of arranging the polymers and solvent molecules.

Answer

A segment or a solvent molecule can be located on a site of the lattice (Fig.

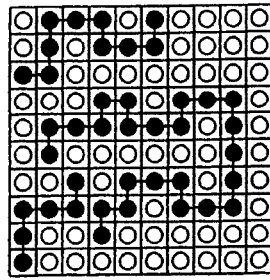


Fig. 3-5 Segments of chain polymer molecules located on a liquid lattice

This assumption is equivalent to assuming that the average concentration of the polymer segments in the site adjacent to the sites unoccupied by the polymeric solute is taken to be equal to the overall average concentration. Similarly, the third segment is located at a site immediately adjacent to the site occupied by the second segment. In this case, one site occupied by the first segment eliminates one of the neighboring sites; one of the neighboring sites of the second segment has been occupied by the first segment, and the third segment can be located on a vacant site among $(z-1)$ sites;

$$v_{N,3} = (z-1) \left\{ 1 - n(N'-1)/N \right\} \quad (3.5.5)$$

All expected numbers $v_{N',4}, v_{N',5}, \dots$ for each successive segment are taken to be equal to $(z-1) \{ 1 - n(N'-1)/N \}$, that is,

$$v_{N,4} = v_{N,5} = \dots = v_{N,n} = (z-1) \left\{ 1 - n(N'-1)/N \right\} \quad (3.5.6)$$

Substituting Eqs.(3.5.3)-(3.5.6) in Eq. (3.5.2) yields

$$v_N = \sigma^{-1} z(z-1)^{n-2} \left\{ N - n(N'-1) \right\}^n N'^{-(n-1)} \quad (3.5.7)$$

Substituting Eq. (3.5.7) for v_N in Eq. (3.5.1), we obtain

$$w = \frac{1}{N_1! \sigma^{N_1}} z^{N_1} (z-1)^{N_1(n-2)} N'^{-(n-1)N_1} \left\{ N(N-n)(N-2n) \dots (N-n(N'-1)) \right\}^n \quad (3.5.8)$$

The term $\{ \}$ in the right-hand side of this equation can be simplified as

$$\begin{aligned} & \left\{ N(N-n)(N-2n) \dots (N-n(N'-1)) \right\} \\ &= \left(\frac{N}{n} \right) \left(\frac{N-1}{n} \right) \left(\frac{N-2}{n} \right) \dots \left(\frac{N-(N'-1)}{n} \right) n^{N_1} \\ &= \frac{(N/n)!}{\left((N-nN_1)/n \right)!} n^{N_1} = \frac{(N/n)!}{(N_0/n)!} \end{aligned} \quad (3.5.9)$$

Then, Eq.(3.5.8) reduces to

$$w = \frac{z^{N_1} (z-1)^{N_1(n-2)}}{N_1! \sigma^{N_1}} N'^{-(n-1)N_1} n^{N_1} \left\{ \frac{(N/n)!}{(N_0/n)!} \right\}^n \quad (3.5.10)$$

* Flory proposed 0th approximation theory in 1941-1942. (See P. J. Flory, *J. Chem. Phys.* 9, 660 (1941); *ibid.* 10, 51 (1942))

<<Problem 3-6>> Flory's theory (II): Entropy of polymer solution

The total number w of ways of arranging N_1 identical polymer molecules and N_0 identical solvent molecules on $N (= N_0 + nN_1)$ lattice sites with the coordination number z is given by Eq.(3.5.10). Derive the entropy of the polymer solution using Boltzmann's principle

$$S = k \log w \quad (3.6.1)$$

where k is the Boltzmann constant.

Answer

Substituting Eq. (3.5.10) for w in Eq. (3.6.1), we obtain

$$S = k \log w = k \log \frac{z^{N_1} (z-1)^{N_1(n-2)}}{\sigma^{N_1}} \left[-k \log N_1! + (n-1)N_1 \log N - nN_1 \log n - n \log (N/n)! + n \log (N_0/n)! \right] \quad (3.6.2)$$

Using Stirling's approximation of Eq.(3.3.7), Eq. (3.6.2) reduces to

$$S = k \log \frac{z^{N_1} (z-1)^{N_1(n-2)}}{\sigma^{N_1}} \left\{ -k \left[N_1 \log N_1 + (n-1)N_1 \log N - nN_1 \log n - N \log \frac{N}{n} + N_0 \log \frac{N_0}{n} + N - (N_1 + N_0) \right] \right\} \quad (3.6.3)$$

Equation (3.6.3) can be rearranged in the form

$$S = k \log \frac{z^{N_1(z-1)^{N_1(n-2)}}}{\sigma^{N_1}} - k \left\{ N_0 \log \frac{N_0}{N_0 + nN_1} + N_1 \log \frac{N_1}{N_0 + nN_1} + (n-1)N_1 \right\} \quad (3.6.4)$$

<<Problem 3-7>> Flory's theory (III): Entropy of mixing for polymer solution

Entropy of mixing ΔS for polymer solutions is defined by

$$\Delta S_{\text{mix}} = S - S^0 \quad (3.7.1)$$

Here, S is the entropy of the mixture and S^0 is the summation of the entropies of pure liquid solvent and the amorphous disorientated polymer solid. ΔS is closely correlated with the configurational entropy of the system. Using Eq.(3.6.4), determine ΔS_{mix} .

Answer

The entropy for pure liquid solvent is S at $N_1=0$ and the entropy for an absolutely amorphous solid is S at $N_0=0$ in Eq. (3.6.4). Then S^0 is given by

$$S^0 = S(N_1=0) + S(N_0=0) = k \log \frac{z^{N_1(z-1)^{N_1(n-2)}}}{\sigma^{N_1}} + kN_1 \log n - k(n-1)N_1 \quad (3.7.2)$$

Then, ΔS_{mix} is obtained as

$$\Delta S_{\text{mix}} = S - S^0 = -k \left(N_0 \log \frac{N_0}{N_0 + nN_1} + N_1 \log \frac{nN_1}{N_0 + nN_1} \right) \quad (3.7.3)$$

If we define the volume fractions of solvent and polymer, ϕ_0 and ϕ_1 , by

$$\phi_0 = \frac{N_0}{N_0 + nN_1} \quad (3.7.4)$$

$$\phi_1 = \frac{nN_1}{N_0 + nN_1} \quad (3.7.5)$$

Eq.(3.7.3) is rewritten as

$$\Delta S_{\text{mix}} = -k (N_0 \log \phi_0 + N_1 \log \phi_1) \quad (3.7.6)$$

* On the other hand, from Eq. (3.4.12) the entropy of mixing for ideal solution $\Delta S_{\text{mix}}^{\text{id}}$ is

$$\Delta S_{\text{mix}}^{\text{id}} = -k \left(N_0 \log \frac{N_0}{N_0 + N_1} + N_1 \log \frac{N_1}{N_0 + N_1} \right) = -k (N_0 \log x_0 + N_1 \log x_1) \quad (3.7.7)$$

where x_0 and x_1 are the mole fractions of solvent and solute, respectively. By comparing Eq.(3.7.6) with Eq.(3.7.7), it is clear that the entropy of mixing of polymer solutions can be expressed by the volume fraction in place of the mole fraction.

* Eq.(3.7.6) does not contain z . Therefore, Eq.(3.7.6) is expected to be valid, regardless of the lattice model. Figure 3-7 shows the plots of ΔS_{mix} vs. $\log x_1$ for polymer and ideal solutions.

* In deriving Eq.(3.7.2), we used the relationship

$$\lim_{x \rightarrow 0} x \log x = 0 \quad (3.7.8)$$

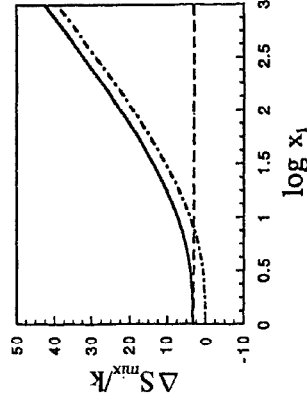


Fig. 3-7 Calculated entropy of mixing for $N_0=9$ and $N_1=1$. Solid, broken and chain lines denote the entropy of mixing for polymer solution (Eq. (3.7.6)), ideal solution (Eq. (3.7.7)) and the difference of them ($\Delta S_{\text{mix}} - \Delta S_{\text{mix}}^{\text{id}}$), respectively.

Proof: On putting $x=1/t$, the left-hand side of Eq. (3.7.8) can be rewritten as

$$\lim_{x \rightarrow 0} x \log x = \lim_{t \rightarrow \infty} -(\log t)/t = -\lim_{t \rightarrow \infty} 1/t = 0$$

<<Problem 3-8>> Flory's theory (IV): Partial molar entropy of mixing of solvent and polymer

Consider a system consisting of N_1 polymer molecules, each occupying n sites, and N_0 solvent molecules, each occupying one site, the total number of sites being $N=nN_1+N_0$. The entropy of mixing of disorientated polymer and solvent is given by

$$\Delta S_{\text{mix}} = -k \left(N_0 \log \phi_0 + N_1 \log \phi_1 \right) \quad (3.7.6)$$

Here, ϕ_0 and ϕ_1 are the volume fractions of solvent and polymer, respectively. Using Eq. (3.7.6), derive the **partial molar entropy of mixing of solvent and polymer**, ΔS_0 and ΔS_1 .

Answer

The partial molar entropies of mixing of the solvent and the polymer are obtained by differentiating the entropy of mixing ΔS_{mix} with respect to the number of moles N_0/N_A of solvent molecules and to the number of moles N_1/N_A of polymer molecules, as given by

$$\Delta S_0 = \frac{\partial \Delta S_{\text{mix}}}{\partial N_0} N_A, \quad \Delta S_1 = \frac{\partial \Delta S_{\text{mix}}}{\partial N_1} N_A \quad (1.2.6)$$

respectively. From Eq. (3.7.6) we obtain

$$\begin{aligned} \frac{\partial \Delta S_{\text{mix}}}{\partial N_0} N_A &= -R \left\{ \log \frac{N_0}{N_0 + nN_1} + \frac{nN_1}{N_0 + nN_1} \cdot \frac{N_1}{N_0 + nN_1} \right\} \\ &= -R \left\{ \log (1 - \phi_1) + \left(1 - \frac{1}{n} \right) \phi_1 \right\} \end{aligned} \quad (3.8.1)$$

$$\begin{aligned} \frac{\partial \Delta S_{\text{mix}}}{\partial N_1} N_A &= -R \left\{ \frac{-nN_0}{N_0 + nN_1} + \log \frac{nN_1}{N_0 + nN_1} + \frac{N_0}{N_0 + nN_1} \right\} \\ &= -R \left\{ (1-n)\phi_0 + \log (1 - \phi_0) \right\} \end{aligned} \quad (3.8.2)$$

Accordingly,

$$\Delta S_0 = -R \left\{ \log (1 - \phi_1) + \left(1 - \frac{1}{n} \right) \phi_1 \right\} \quad (3.8.3)$$

$$\Delta S_1 = -R \left\{ (1-n)\phi_0 + \log (1 - \phi_0) \right\} \quad (3.8.4)$$

Note that Eqs. (3.8.3) and (3.8.4) are valid for the solution of random mixing.

<<Problem 3-9>> Flory's theory (V): van Laar-Scatchard approximation
van Laar and Scatchard showed that the **heat of mixing for regular solution** which consists of N_0 solvent molecules and N_1 solute molecules is given by

$$\Delta H_{\text{mix}} = \varepsilon z N_0 N_1 / (N_0 + N_1) \quad (3.2.6)$$

where ε is the change in energy for formation of an unlike contact pair (0-1 pair) and z is the lattice coordination number. Now consider N_1 polymer molecules, each consisting of n segments as solute, and derive expressions for the heat of mixing ΔH_{mix} and the partial molar heat of dilution of the solvent and of the polymer ΔH_0 and ΔH_1 , respectively.

Answer

Suppose that ΔH_{mix} is proportional to the total contact number between polymer segments and solvent molecules. Eq. (3.2.6) can be rewritten by replacing N_1 with nN_1 in the form

$$\Delta H_{\text{mix}} = \varepsilon z N_0 n N_1 / (N_0 + n N_1) \quad (3.9.1)$$

ΔH_0 and ΔH_1 are defined by (See Eq.(1.2.12))

$$\begin{aligned}\Delta G_{\text{mix}} &= \varepsilon z N_0 n N_1 / (N_0 + n N_1) + kT \left(N_0 \log \phi_0 + N_1 \log \phi_1 \right) \\ &= kT \left(N_0 \log \phi_0 + N_1 \log \phi_1 \right) + \varepsilon z N_0 \phi_1\end{aligned}\quad (3.10.1)$$

<<Problem 3-11>> **Flory's theory (VII): Chemical potential of solvent for non-athermal random mixing polymer solution**

In <<Problem 3-8>> the partial molar entropy of mixing of solvent ΔS_0 was derived in the form

$$\Delta S_0 = -R \left\{ \log \left(1 - \phi_1 \right) + \left(1 - \frac{1}{n} \right) \phi_1 \right\} \quad (3.8.3)$$

In <<Problem 3-9>> the partial molar heat of mixing of solvent ΔH_0 was derived in the form

$$\Delta H_0 = B N_A \phi_1^2 \quad (3.9.4)$$

Derive the expression for the **chemical potential of solvent μ_0** for non-athermal random mixing polymer solutions using these equations.

Answer

At constant temperature and pressure, $\Delta\mu_0$ is related to ΔH_0 and ΔS_0 through the relation

$$\Delta\mu_0 = \Delta H_0 - T\Delta S_0 \quad (3.11.1)$$

Substituting Eqs.(3.8.3) and (3.9.4) in Eq.(3.11.1), we have

$$\begin{aligned}\Delta\mu_0 &= B N_A \phi_1^2 + RT \left\{ \log \left(1 - \phi_1 \right) + \left(1 - \frac{1}{n} \right) \phi_1 \right\} \\ &= RT \left\{ \log \left(1 - \phi_1 \right) + \left(1 - \frac{1}{n} \right) \phi_1 + \frac{B}{kT} \phi_1^2 \right\}\end{aligned}\quad (3.11.2)$$

Using the thermodynamic interaction parameter $\chi \equiv B/kT$, Eq. (3.11.2) is rewritten as

$$\Delta H_0 = N_A \frac{\partial \Delta H}{\partial N_0} \quad (3.9.2)$$

$$\Delta H_1 = N_A \frac{\partial \Delta H}{\partial N_1} \quad (3.9.3)$$

respectively. Combination of Eq.(3.9.1) and Eq.(3.9.2) or Eq.(3.9.3) leads to

$$\Delta H_0 = B N_A \frac{n N_1^2}{\left(N_0 + n N_1 \right)^2} = B N_A \phi_1^2 \quad (3.9.4)$$

$$\Delta H_1 = B N_A \frac{n N_0^2}{\left(N_0 + n N_1 \right)^2} = B N_A n \phi_0^2 \quad (3.9.5)$$

Here $B \equiv \varepsilon z$.

van Laar-Scatchard equation (Eq. (3.2.6)) is derived on the assumption of random mixing. (See J.J. van Laar, *Z. phys. Chem. A* 137, 421 (1928); G.Scatchard, *Chem. Rev.* 8, 321 (1931))

<<Problem 3-10>> **Flory's theory (VI): Gibbs free energy of mixing of polymer solution**

Suppose heat of mixing ΔH and entropy of mixing ΔS are given by the relations

$$\Delta H_{\text{mix}} = \varepsilon z N_0 n N_1 / (N_0 + n N_1) \quad (3.9.1)$$

$$\Delta S_{\text{mix}} = -k \left(N_0 \log \phi_0 + N_1 \log \phi_1 \right) \quad (3.7.6)$$

respectively. Here the volumetric change of mixing ΔV_{mix} is implicitly assumed to be zero. Derive the expression for the free energy of mixing ΔG_{mix} .

Answer

Substituting Eq. (3.9.1) for ΔH_{mix} and Eq. (3.7.6) for ΔS_{mix} in the equation

$$\Delta G_{\text{mix}} = \Delta F_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (2.3.3)'$$

at constant pressure and temperature, we obtain

$$\Delta\mu_0 = RT \left\{ \log(1 - \phi_1) + \left(1 - \frac{1}{n}\right) \phi_1 + \chi\phi_1^2 \right\} \quad (3.11.3)$$

Equations (3.11.2) and (3.11.3) are the most popular equations for describing the chemical potential of polymer solutions.

If $\phi_1 \ll 1$, $\log(1 - \phi_1)$ is expanded in a Taylor series as

$$\log(1 - \phi_1) = -\phi_1 - \frac{\phi_1^2}{2} - \frac{\phi_1^3}{3} + \dots \quad (3.11.4)$$

Then Eq. (3.11.4) can be further rewritten into

$$\Delta\mu_0 = -RT \left\{ \frac{1}{n} \phi_1 + \left(\frac{1}{2} - \frac{B}{kT} \right) \phi_1^2 + \frac{1}{3} \phi_1^3 + \dots \right\} \quad (3.11.5)$$

* χ defined in Eq.(3.11.3) is the parameter for enthalpy of mixing and should be expressed as χ_h . ΔH_0 and χ are related to the Flory enthalpy parameter κ_0 . (See << Problem 4-23>>)

<<Problem 3-12>> **Flory's theory (VIII): Chemical potential of polymer for non-athermal random mixing polymer solution**

The partial molar entropy of mixing of polymer ΔS_1 is expressed by

$$\Delta S_1 = -R \left\{ (1 - n) \phi_0 + \log(1 - \phi_0) \right\} \quad (3.8.4)$$

The partial molar heat of mixing ΔH_1 is given by

$$\Delta H_1 = BN_A n \phi_0^2 \quad (3.9.5)$$

Derive the **chemical potential of polymer** $\Delta\mu_1$ for non-athermal random mixing polymer solutions using these equations.

Answer

At constant temperature and pressure,

$$\Delta\mu_1 = \Delta H_1 - T\Delta S_1 \quad (3.12.1)$$

Then,

$$\Delta\mu_1 = BN_A n \phi_0^2 + RT \left\{ (1 - n) \phi_0 + \log(1 - \phi_0) \right\}$$

$$\begin{aligned} &= RT \left\{ \log(1 - \phi_0) - (n - 1) \phi_0 + \frac{Bn}{kT} \phi_0^2 \right\} \\ &= RT \left\{ -\phi_0 - \frac{\phi_0^2}{2} - \frac{\phi_0^3}{3} - \dots - (n - 1) \phi_0 + \frac{Bn}{kT} \phi_0^2 \right\} \\ &= -RT \left\{ n\phi_0 + \left(\frac{1}{2} - \frac{Bn}{kT} \right) \phi_0^2 + \frac{\phi_0^3}{3} + \dots \right\} \end{aligned} \quad (3.12.2)$$

<<Problem 3-13>> **Flory's theory (IX): Gibbs-Duhem relation for polymer solution**

Verify that $\Delta\mu_0$ in <<Problem 3-11>> and $\Delta\mu_1$ in <<Problem 3-12>> satisfy the **Gibbs-Duhem relation**;

$$\sum N_i d\mu_i = 0 \quad (1.3.1)$$

Answer

The total differentiation of the equations

$$\Delta\mu_0 = RT \left\{ \log(1 - \phi_1) + \left(1 - \frac{1}{n}\right) \phi_1 + \chi\phi_1^2 \right\} \quad (3.11.3)$$

and

$$\Delta\mu_1 = RT \left\{ \log(1 - \phi_0) - (n - 1) \phi_0 + \chi n \phi_0^2 \right\} \quad (3.12.2)$$

is given by

$$d\Delta\mu_0 = RT \left\{ \frac{-d\phi_1}{1 - \phi_1} + \left(1 - \frac{1}{n}\right) d\phi_1 + 2\chi\phi_1 d\phi_1 \right\} \quad (3.13.1)$$

$$d\Delta\mu_1 = RT \left\{ \frac{-d\phi_0}{1 - \phi_0} - (n - 1) d\phi_0 + 2\chi n \phi_0 d\phi_0 \right\} \quad (3.13.2)$$

respectively. Considering

$$\phi_0 + \phi_1 = 1$$

the relationship between the total differential $d\phi_0$ and $d\phi_1$

$$d\phi_0 = -d\phi_1$$

holds. Then Eq. (3.13.2) can be modified into

$$d\Delta\mu_1 = RT \left\{ \frac{d\phi_1}{\phi_1} + (n-1) d\phi_1 - 2\chi n (1-\phi_1) d\phi_1 \right\} \quad (3.13.5)$$

For binary systems, the Gibbs-Duhem relation (Eq. (1.3.1)) can be simplified into

$$N_0 d\Delta\mu_0 + N_1 d\Delta\mu_1 = 0 \quad (3.13.6)$$

Eq. (3.13.6) can be rewritten as

$$\frac{N_0}{N_0 + nN_1} d\Delta\mu_0 + \frac{N_1}{N_0 + nN_1} d\Delta\mu_1 = 0 \quad (3.13.7)$$

Then,

$$(1-\phi_1) d\Delta\mu_0 + \left(\frac{\phi_1}{n} \right) d\Delta\mu_1 = 0 \quad (3.13.8)$$

Substitution of Eq.(3.13.1) for $d\Delta\mu_0$ and Eq. (3.13.5) for $d\Delta\mu_1$ in the left-hand side of Eq. (3.13.8) yields

$$\begin{aligned} & \left(1 - \phi_1 \right) \frac{-d\phi_1}{1 - \phi_1} + \left(1 - \frac{1}{n} \right) (1 - \phi_1) d\phi_1 + 2\chi\phi_1 (1 - \phi_1) d\phi_1 \\ & + \left(\frac{\phi_1}{n} \right) \left(\frac{d\phi_1}{\phi_1} \right) + \left(\frac{\phi_1}{n} \right) (n-1) d\phi_1 - 2\chi n \left(\frac{\phi_1}{n} \right) (1 - \phi_1) d\phi_1 \\ & = d\phi_1 \left\{ -1 + \left(1 - \frac{1}{n} \right) (1 - \phi_1) + 2\chi\phi_1 (1 - \phi_1) + \frac{1}{n} \frac{n-1}{n} \phi_1 - 2\chi\phi_1 (1 - \phi_1) \right\} \end{aligned}$$

$$= d\phi_1 \left(-1 + 1 - \frac{1}{n} - \phi_1 + \frac{\phi_1}{n} + \frac{1}{n} + \phi_1 - \frac{\phi_1}{n} \right) = 0 \quad (3.13.9)$$

<<Problem 3-14>> **Flory's theory (X): Assumptions in Flory's θ^h approximation theory**

Discuss the approximations and assumptions employed in Flory's θ^h approximation theory for polymer solutions in <<Problem 3-5>>.

Answer

Flory's theory of the zeroth approximation^{1,5} assumes:

- (1) There is no volume change on mixing.
- (2) The lattice possesses a definite co-ordination number (i.e., the number of nearest neighbours of each segment per solvent molecule in the solution) z .
- (3) The entropy of mixing ΔS_{mix} can be calculated without reference to the possible energy change caused by the pair formation (i.e., **Bragg-Williams approximation**⁶). In other words, the polymer segments mix with solvent randomly and ΔS_{mix} is the entropy of mixing of athermal solution.
- (4) In the calculation of the total number of configurations w , from which the combinatory entropy of mixing is derived, the possibility that the nearest-neighbour lattice point to the lattice point in question has been already occupied by polymer segment equals the probability of the case where all the polymer segments are uniformly distributed over all the lattice points (i.e., the **average concentration approximation of the chain segment**). This means that the two segments belonging to the same polymer molecule are allowed to occupy the same lattice site. For rearrangement of the expression for w , Stirling's approximation is applicable.

(5) The potential energy of the mixture is the sum of contributions from each pair of the closest neighbouring segments (**van Laar-Scatchard approximation**^{7,8}).

(6) The heat of mixing ΔH_{mix} can be calculated from the average contact numbers where all the segments comprising polymer chains are completely disconnected and randomly mixed with solvents (i.e., the **average concentration approximation**). In this case, the total number of polymer-solvent contact pairs n_c is given by

$$n_c = z\phi_0\phi_1L \quad (\text{Average concentration approximation}) \quad (3.14.1)$$

where L is the total number of lattice sites, ϕ_0 the volume fraction of solvent

and ϕ_1 the volume fraction of polymer. The thermodynamic interaction parameter χ can be purely phenomenologically expressed by⁹

$$\chi = \chi_0(1 + \sum p_i \phi_i)$$

$$\chi_0 = \chi_{00}(1 + k'/n)$$

$$k' = k_0(1 - \theta/T)$$

for monodisperse polymer-single solvent system (Refer to Eqs. (3.16.4), (3.16.11) and (3.16.12)). Here χ_{00} is a parameter independent of ϕ_1 and n , k' and p_i ($i=1 \dots n$), the molecular weight- and concentration-independent coefficients, k_0 the parameter independent of temperature T and the degree of polymerization n , and θ , the Flory temperature. χ_{00} coincides with 0.5 if the second virial coefficient A_2 vanishes at θ .

Generally speaking, the χ -parameter is not the parameter representing polymer-solvent interaction only (typical example is shown in Fig. 3-15), but can be divided semi-empirically into two parts:

$$\chi = \chi_h + \chi_s \quad (3.14.2)$$

Here χ_h is the enthalpy term and χ_s is the entropy term, and both terms may have concentration dependence as expressed by

$$\chi_h = (\Delta H_0 - \Delta H_0^{q,i,d}) / (RT \phi_1^2) = \Delta H_0 / (RT \phi_1^2) = \chi_{h,0} (1 + \sum p_{h,i} \phi_i) \quad (3.14.3)$$

$$\chi_s = -(\Delta S_0 - \Delta S_0^{q,i,d}) / (RT \phi_1^2) = \chi_{s,0} (1 + \sum p_{s,i} \phi_i) \quad (3.14.4)$$

where ΔH_0 is the partial molar heat of dilution of solvent in real solution, $\Delta H_0^{q,i,d}$ is ΔH_0 in quasi-ideal (i.e., random mixing-zero heat of mixing ($n \gg 1$)) solution, ΔS_0 is the partial molar entropy of mixing of solvent in real solution, $\Delta S_0^{q,i,d}$ is ΔS_0 in quasi-ideal solution, and $p_{h,i}$ and $p_{s,i}$ are the concentration dependence parameter of χ_h and χ_s , respectively.

Hypothesis (6) means that in calculation of ΔH the consecutive characteristics of chain segments is neglected. In his theory ΔH is expected to be strictly proportional to $\phi_1(1 - \phi_1)$ and χ -parameter consists of solely the enthalpy term χ_h (See Eq. (3.14.14)) as given by

$$\chi = \chi_0 = \chi_{h,0} \quad (3.14.5)$$

and

$$p_i = p_{h,i} = p_{s,i} = 0 \quad (i=1, \dots, n) \quad (3.14.6)$$

Only in the case where Eq. (3.14.5) holds the χ -parameter is strictly a polymer

-solvent interaction parameter, as first defined by Flory.¹

1. P. J. Flory, *J. Chem. Phys.* **9**, 660 (1941).
2. P. J. Flory, *J. Chem. Phys.* **10**, 51 (1942).
3. P. J. Flory, *J. Chem. Phys.* **12**, 425 (1944).
4. P. J. Flory, *J. Chem. Phys.* **13**, 453 (1945).
5. P. J. Flory, *Principle of Polymer Chemistry*, Cornell Univ. Press, Ithaca, New York, 1953, Chapter XII.
6. W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.* **A145**, 699 (1934).
7. J. J. Van Laar, *Z. phys. Chem.* **A137**, 421 (1928).
8. G. Scatchard, *Chem. Rev.* **8**, 321 (1931).
9. See for example, K. Kamide, *Thermodynamics of Polymer Solutions, Phase Equilibria and Critical Phenomena* (Polymer Science Library 9), Elsevier, 1990.

***Note / Improved zeroth approximation theory (Athermal solution)**

Within the scope of Bragg-Williams approximation and taking into account the succession of segments comprising a polymer molecule and rigorous pattern of arranging segments around a given lattice point Miller¹⁰, Guggenheim¹¹, and Kurata et al.¹² calculated the partial molar entropy of mixing of solvent ΔS_0 as

$$\Delta S_0 / R = -\ln(1 - \phi_1) + \frac{z}{2} \ln\left(1 - \frac{z}{2} \frac{n-1}{n} \phi_1\right) \quad (3.14.7)$$

Eq. (3.14.7) is similar to that derived by Huggins¹³⁻¹⁸, who took into consideration the effect of blocking of sites by other distant segments of the same polymer on the number of sites

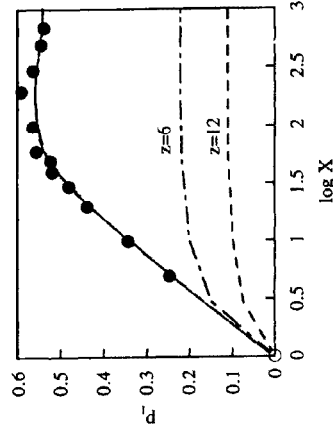


Fig. 3-14.1 Relationship between p_1 and n (full line); broken line: improved zeroth approximation with $z=12$ chain line: improved zeroth approximation with $z=6$

available for the segments of each polymer molecule¹⁰. Eq. (3.14.7) indicates that χ_s is not zero and is given by¹⁹

$$\chi_s = (1-1/n)^2/z + 4(1-1/n)^3 \phi_1^3 / (3z^2) + \dots \quad (3.14.8)$$

$$\chi_{s,0} = (1-1/n)^2/z \quad (3.14.9)$$

$$p_{s,1} = 4(1-1/n)/(3z) \quad (3.14.10)$$

Thus, Miller, Guggenheim, and Kurata et al.'s theories as well as Huggins classical theory predict that χ_s depends on concentration. This suggests that the consecutive properties of polymer chain segments might be one of causes, which lead to $p \neq 0$. Note that $p_{s,1}$ value given by Eq. (3.14.10) is too small to explain the experimentally determined p_1 value for non-polar polymer- non-polar solvent systems (See Fig. 3-14.1). Table 3-14 summarizes ΔS and χ_s proposed by them, including Flory and Fig. 3-14.2 shows a typical example for careful determination of χ_h as a function of concentration.

10. A. R. Miller, *Proc. Camb. Phil. Soc.* **39**, 54 (1943).
11. E. A. Guggenheim, *Proc. Roy. Soc. A* **183**, 203 (1944).
12. M. Kurata, M. Tamura and T. Waiari, *J. Chem. Phys.* **23**, 991 (1955).
13. M. L. Huggins, *J. Chem. Phys.* **9**, 440 (1941).

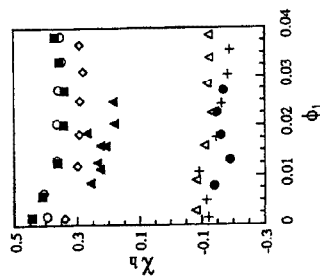


Fig. 3-14.2 χ_h determined from the heat of dilution as a function of volume fraction of polymer ϕ_1 for the systems polystyrene in cyclohexane and polystyrene/cyclohexane. \blacksquare $M_w=6200$, \circ $M_w=10200$, \diamond $M_w=42800$, \blacktriangle $M_w=107000$; polystyrene/benzene \triangle $M_w=6200$, $+$ $M_w=10200$, \bullet $M_w=107000$ (I. Fujihara and R. Fujishiro, unpublished results)

Table 3-14 Entropy of mixing and χ_s proposed theoretically

Researcher	ΔS	χ_s
Flory ⁽¹⁾	$-R[\log(1-\phi_1) + \phi_1]$	0
Huggins ⁽²⁾	$-R \left[\log(1-\phi_1) + \left(1 - \frac{n}{z}\right) \log \left\{ 1 - \frac{z}{2} \log \left(\frac{2\phi_1}{z} \right) \right\} \right]$	$\left(1 - \frac{n}{z}\right) \left(\frac{1-1/n}{z} \right)$
Miller ⁽³⁾	$-R \left[\log(1-\phi_1) - \left(\frac{z}{2} \log \left\{ 1 - \left(\frac{z}{2} \right) \phi_1 \right\} - \left(\frac{1-1/n}{z} \right) \right] \right]$	$\left(1 - \frac{n}{z}\right) \left(\frac{1-1/n}{z} \right)$
Guggenheim ⁽⁴⁾	$-R \left[\log(1-\phi_1) - \left(\frac{z}{2} \log \left\{ 1 - \left(\frac{z}{2} \right) \phi_1 \right\} - \left(\frac{1-1/n}{z} \right) \right] \right]$	$\left(1 - \frac{n}{z}\right) \left(\frac{1-1/n}{z} \right)$

$p_1 = \{n_1(z-2) + 2\}/z$

- 1) P. J. Flory: *J. Chem. Phys.* **9**, 660 (1941); *ibid.* **10**, 51 (1942)
- 2) M. L. Huggins: *J. Phys. Chem.* **46** 151 (1942); *Ann. N.Y. Acad. Sci.* **41**, 1 (1942)
- 3) A. R. Miller: *Proc. Camb. Phil. Soc.* **35**, 109 (1942); *ibid.* **39** 54, 131 (1943)
- 4) E. A. Guggenheim: *Proc. Roy. Soc. A* **183**, 203 (1944)

14. M. L. Huggins, *J. Phys. Chem.* **46**, 151 (1942).
15. M. L. Huggins, *Ann. N.Y. Acad. Sci.* **41**, 1 (1942).
16. M. L. Huggins, *J. Am. Chem. Soc.* **64**, 1712 (1942).
17. M. L. Huggins, *J. Phys. Colloid Chem.* **52**, 248 (1948).
18. M. L. Huggins, *Physical Chemistry of High Polymer*, John Wiley & Sons, Inc., New York, 1958, Chapter 6.
19. K. Kamide and H. Shirataki, *Mem. Fac. Educ., Kumamoto Univ.* **47**, 137 (1998).

***Note 2 First approximation theory (Non-athermal solution)**

For non-athermal solutions ($\Delta H \neq 0$), Bragg-Williams and van Laar-Scatchard approximations (hypotheses (3) and (6), respectively) might seem more or less unrealistic and less appropriate. Then several attempts to improve Flory's zeroth approximation theory were made by calculating the total number of configurations w through the use of quasi-chemical equilibria method, which is equivalent to the mathematical technique originally developed by Bethe²⁰ for treating order-disorder transitions in alloys. This method was occasionally referred to as the Flory-Huggins first approximation theory. The disparity of values of ΔH for polymethylmethacrylate/trichloroethylene²¹ and ΔS for rubber/ethylacetate²², both calculated on the basis of the first approximation theory from their corresponding experimental data is significantly larger than those by the zeroth approximation theory, indicating that the first approximation is less reliable and cannot be recommended to use it for analysis^{23,24}. This might appear to be somewhat surprising to note that allowance for hypotheses (3) and (6) does nothing to improve the agreement with experiments.

20. H. A. Bethe, *Proc. Roy. Soc. A150*, 552 (1935).

21. H. Tompa, *Polymer Solutions*, Butterworth Sci. Pub., 1956, §3.7.

22. C. Booth, G. Gee and G. R. Williams, *J. Polym. Sci.* **23**, 3 (1956).

23. See for example, N. Saito, *Polymer Physics* (revised ed.), Syoka-bo Pubs., Tokyo, 1967, Chapter 4.

***Note 3 Huggins' 'new' theory (1964)**

In his 'new' theory, Huggins²⁴ assumed as basic tenet that the interior segments of a convoluted molecule are partially shielded from contact with interior segments of other polymer molecules and the shielding factor depends on the concentration. He derived theoretical equations for χ_h and χ_s in closed form and as expansions in powers of the concentration, introducing a number of physical quantities, such as molecular surface area, effective surface area, multiple contact factor, shielding factor and empirical constant relating to shielding factor's concentration dependence. All of which cannot be determined by independent absolute method, although he described that these quantities are "observable". He considered that from experimental data of χ and its dependence on concentration and temperature one can evaluate all the parameters introduced. That is, the parameters introduced in his theory are only adjustable parameters to fit the experimental relations between χ , ϕ_1 and T . Note that in mid-1960s the methods based on phase separation and

critical phenomena were not yet established and there was lack of extensive and reliable experimental data to judge theories. Huggins²⁴ described "Testing of the equations presented in the paper, using published experimental data, has been begun. The results will be reported in due course". Unfortunately as far as we know, there is no his succeeding paper.

24. M. L. Huggins, *J. Am. Chem. Soc.* **86**, 3535 (1964).

***Note 4 Validity of hypothesis 6**

The most probable inadequate hypothesis in the Flory theory is that the total number of solvent-polymer contacts is strictly proportional to the product $\phi_0\phi_1$ (hypothesis 6). For example, κ defined by $\Delta H_0/(RT\phi_1^2)$ is expected, if the above hypothesis is accepted, to be constant over wide ranges of T and ϕ_1 , but it was confirmed by numerous experiments that κ directly measured by accurate calorimetry, depends strongly on both T and ϕ_1 .²⁵ Validity of the application of overall average concentration approximation of polymer segment to estimate the heat of mixing has never hitherto been tried to examine thoroughly due to mathematically extreme difficulty, although the first approximation, of course, did also treat this problem in rather rough and insufficient manner.

25. See for example, A. Kagemoto, S. Murakami and R. Fujishiro, *Bull. Chem. Soc. Jpn.* **39**, 15 (1966); I. Fujihara, PhD Dissertation in Osaka City Univ. (1979).

***Note 5 Strictness and adequacy of the model, and mathematical complexity and approximation**

As Flory²⁶ pointed out at Fifteenth Spiers Memorial Lectures in 1970, sponsored by the Royal Society, that "to be effective, any conceptual scheme, or theory of liquids and solutions must entail approximations, either in model or in mathematical technique, even for the simplest of real liquids". Mathematical approximations become more serious in the first approximation theory than in the zeroth approximation theory and this is the reason why introduction of more adequate concepts into the first approximation theory failed, on the contrary, to get rid of the disparity between the theory and actual experiments. This means that even if seemingly more adequate models are used, we cannot always derive accurate theoretical relations between the time-average observable physical quantities like ΔG , ΔS and ΔH , and the structural, molecular and thermodynamic parameters (for example, z , n and the enthalpy change of formation of an unlike contact pair $\Delta\epsilon$) from the models by traditional method of statistical mechanics, because the system in question is too complicated. Since then, serious limit of further evolution of the lattice theory was widely recognized, although it was largely successful in semi-quantitatively accounting for unusual (from the stand point of low molecular weight solutions) behavior of ΔG , observed in polymer solutions, by differences in size and shape of the species that make up the solution, and there has been no generally accepted explanation of physical significance of the concentration- and molecular weight-dependences of χ -parameter, in spite of its experimentally unquestionable existence.

26. P. J. Flory, *Dis. Farad. Soc.* 49, 7 (1970).

*Note 6 **New strategy to give theoretically reasonable explanation to χ -parameter: Computer simulation of lattice model**

Recently Kamide and Shirataki²⁷ examined the validity of average concentration approximation in hypotheses (4) and (6), employed in the Flory-Huggins lattice theory of polymer solution, and investigated the concentration- and molecular weight-dependences of χ (accordingly, the reliability of the expression of χ (Eqs. (3.16.4), (3.16.11) and (3.16.12))) for quasi-strictly regular solution (i.e., random mixing-nonathermal solution²⁸). For this purpose, computer experiments by applying Monte Carlo simulation method to the lattice model, where hypotheses (1), (2) and (5) are strictly adopted, were carried out to calculate the total number of polymer segment-solvent pairs at equilibrium state $n_{c,e}$ as functions of the concentration ϕ_1 and the degree of polymerization n of the polymer solutes. Two types of chain motions (crankshaft motion and then reptation motion) were applied to all the polymer molecules in the lattice simultaneously and this operation (crankshaft-reptation motions) was repeated 1500 times. Any possible multiplicated arrangement of two or more segments belonging to the same or different chain was avoided.

By using Eq. (3.14.3), $n_{c,e}$ is given by

$$n_{c,e}(\phi_0\phi_1L) = C_x (1 + \sum p_i \phi_1) \quad (3.14.11)$$

with

$$C_x \equiv \lim_{\phi_1 \rightarrow 0} n_{c,e} / (\phi_0\phi_1L) = C_0 (1 + k' / n) \quad (3.14.12)$$

$$C_0 = Rb / \Delta\epsilon \quad (3.14.13)$$

When the average concentration approximation (hypothesis (4)) is applied, C_x and p_i are given by

$$C_x = z \quad (3.14.14a)$$

$$p_i = 0 \quad (3.14.14b)$$

Then, from the plots of C_x vs. $1/n$ and the plots of $n_{c,e}/(\phi_0\phi_1L)$ against ϕ_1 the validity of the expression of χ (Eqs. (3.16.4), (3.16.11) and (3.16.12)) could be confirmed by the computer experiments (Figs. 4a, 4b and 5 of reference 28). If Eqs. (3.16.4), (3.16.11) and (3.16.12) is applicable, k' and p_i can be determined from the above plots, respectively. Figure 3-14.1 shows the plots of p_i estimated thus against $\log n$. p_i first increases rapidly with an increase in n , then slowly approaching an asymptotic value (ca. 0.6) at $n \approx 200$. Inspection of the figure shows that successive connection of the polymer segments brings about the concentration dependence of χ -parameter. p_i values of PS in non-polar solvents are close to 2/3 (See <<Problem 3-16-b>>), theoretically predicted at $T = \theta$ for random mixing-non zero heat of mixing solution²⁹ and are little higher than the value (ca. 0.6) obtained in this computer

experiments, but no significantly so.

Computer experiments on random mixing-nonathermal polymer solutions indicated that the average concentration approximation hypothesis cannot be approved even if random mixing is assumed and Eqs. (3.16.4), (3.16.11) and (3.16.12) appears to be of correct form to represent χ -parameter. In other words, this hypothesis employed in Flory-Huggins theory can never be accepted even in the quasi-regular solutions and the concentration- and molecular weight-dependences of the χ -parameter, observed in actual experiments, can be explained reasonably, if the consecutive characteristics of linear chain molecules is strictly considered.

27. K. Kamide and H. Shirataki, *Mem. Fac. Educ., Kumamoto Univ.* 47, 137 (1998).

28. K. Kamide, *Mem. Fac. Educ., Kumamoto Univ.*, 46, 213 (1997).

29. K. Kamide, S. Matsuda and M. Saito, *Polym. J.* 17, 1013 (1985).

<<Problem 3-15>> Thermodynamic interaction parameter χ

The thermodynamic interaction parameter χ in the Flory-Huggins theory [see Eq. (3.11.3)] can be experimentally evaluated by the following methods.

(1) Determination of the activity of solvent a_0 by vapor pressure depression,

$$P_0 = a_0 P_0^0 \quad (2.10.3)$$

or membrane osmometry,

$$\Pi = - \frac{RT}{V_0} \log a_0 \quad (2.10.4)$$

(2) Substitution of a_0 , determined by the above methods into the equation:

$$\log a_0 = \log \left(1 - \phi_1 \right) + \left(1 - \frac{1}{n} \right) \phi_1 + \chi \phi_1^2 \quad (3.15.1)$$

Originally, χ was assumed to be independent of polymer concentration ϕ_1 . Figure 3-15 shows the plots of χ , experimentally determined, against ϕ_1 for polystyrene-cyclohexane. The figure shows a significant ϕ_1 dependence of χ . In this sense, χ should be considered to be an empirical parameter, defined by the equation:

$$\Delta\mu_0 = RT \left\{ \log \left(1 - \phi_1 \right) + \left(1 - \frac{1}{n} \right) \phi_1 + \chi \phi_1^2 \right\} \quad (3.11.3)$$

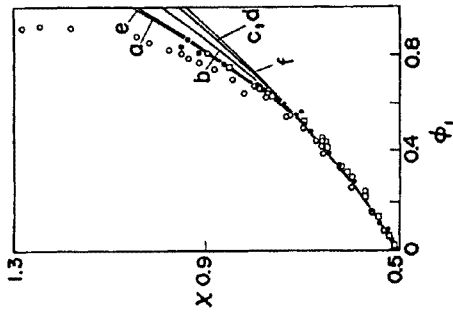


Fig. 3-15 Concentration dependence of χ parameter for polystyrene in cyclohexane. (O) osmotic pressure isothermal distillation by Krigbaum and Geymer¹, (●) vapor pressure by Krigbaum and Geymer¹, (□) ultracentrifuge by Scholte². Lines a to f are calculated using p_1 and p_2 in the equation $\chi = \chi_0(1 + p_1\phi_1 + p_2\phi_1^2)$, obtained by experiment, (a) Krigbaum and Geymer¹; (b) Scholte²; (c) Koningsveld et al.³; (d) Koningsveld et al.⁴; (e) Kuwahara et al.⁵; (f) Kamide et al.⁶. This expression for χ yields a better fit compared with Eq. (3.16.1). (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* **16**, 839 (1984))

1. W.R.Krigbaum and D.O.Geymer, *J. Am. Chem. Soc.* **81**, 1859 (1959)
2. Th.G.Scholte, *Eur. Polym. J.* **6**, 1063 (1970); *J. Polym. Sci., Polym. Phys. Ed.* **9**, 1553 (1971)
3. R.Koningsveld, L.A.Kleinijens and A.R.Shultz, *J. Polym. Sci., Polym. Phys. Ed.* **8**, 1261 (1970)
4. R.Koningsveld and L.A.Kleinijens, *Macromolecules* **4**, 637 (1971)
5. N.Kuwahara, M.Nakata and M.Kaneko, *Polymer* **14**, 415 (1973)
6. K. Kamide, S.Matsuda, T.Dobashi and M.Kaneko, *Polym. J.* **16**, 839 (1984)

Derive the expression for $\Delta\mu_1$ in the case where χ depends on concentration using the Gibbs-Duhem relation of Eq.(1.3.1).

Answer

The number of molecules i , N_i , is related to the mole fraction x_i through the equation

$$x_i = \frac{N_i}{\sum_i N_i} \quad (3.15.2)$$

Then, Eq. (1.3.1) can be rewritten as

$$\sum_i x_i \left(\frac{\partial \mu_i}{\partial x_j} \right)_{T,P,x_k} = 0 \quad (3.15.3)$$

The suffix denotes that the differentiation with respect to x_j is carried out at constant T, P and the composition except j th component.

For binary polymer solutions, the mole fraction of polymer x_1 is related to the volume fraction of polymer ϕ_1 as

$$x_1 = \frac{(\phi_1 / n)}{(1 - \phi_1) + (\phi_1 / n)} \quad (3.15.4)$$

where n is the number of segments constituting a polymer molecule.

From Eq. (3.15.4), $(1 - 1/x_1)$ is written as

$$(1 - 1/x_1) = -(1 - \phi_1) / (\phi_1 / n) \quad (3.15.5)$$

Equation (3.15.3) can be expressed in the form

$$\left\{ (1 - x_1) \frac{\partial \mu_0}{\partial \phi_1} + x_1 \frac{\partial \mu_1}{\partial \phi_1} \right\} \frac{d\phi_1}{dx_1} = 0 \quad (3.15.6)$$

and then we have

$$\frac{\partial \mu_1}{\partial \phi_1} = \left(1 - \frac{1}{x_1} \right) \frac{\partial \mu_0}{\partial \phi_1} \quad (3.15.7)$$

Differentiation of Eq.(3.11.3) with respect to ϕ_1 leads to

$$\frac{\partial \mu_0}{\partial \phi_1} = \frac{\partial \Delta\psi_0}{\partial \phi_1} = RT \left\{ -\frac{1}{1 - \phi_1} + \left(1 - \frac{1}{n} \right) + \frac{\partial}{\partial \phi_1} (\chi \phi_1^2) \right\} \quad (3.15.8)$$

Substitution of Eq.(3.15.5) for $(1-1/x_1)$ and Eq.(3.15.8) for $\partial\mu_0/\partial\phi_1$, both in Eq.(3.15.7) gives

$$\begin{aligned} \frac{\partial\mu_1}{\partial\phi_1} &= RT \left\{ \frac{1}{\phi_1} + (n-1) + n \left(1 - \frac{1}{\phi_1} \right) \frac{\partial}{\partial\phi_1} (\chi\phi_1^2) \right\} \\ &= RT \left[\frac{1}{\phi_1} + (n-1) - n \frac{\partial}{\partial\phi_1} \left\{ \chi\phi_1 (1-\phi_1) \right\} - n\chi \right] \end{aligned} \quad (3.15.9)$$

Then,

$$\begin{aligned} \Delta\mu_1 &\equiv \mu_1 - \mu_1^0 = RT \int_{\phi_1}^1 \left[\frac{1}{\phi_1} + (n-1) - n \frac{\partial}{\partial\phi_1} \left\{ \chi\phi_1 (1-\phi_1) \right\} - n\chi \right] d\phi_1 \\ &= RT \left\{ \log \phi_1 - (n-1)(1-\phi_1) - \chi n \phi_1 (1-\phi_1) + n \int_{\phi_1}^1 \chi d\phi_1 \right\} \end{aligned} \quad (3.15.10)$$

If χ in Eq. (3.15.10) is constant, the last term in $\{ \}$ is reduced to

$$n \int_{\phi_1}^1 \chi d\phi_1 = n\chi(1-\phi_1) \quad (3.15.11)$$

and we have

$$\Delta\mu_1 = RT \left\{ \log \phi_1 - (n-1)(1-\phi_1) + \chi n (1-\phi_1)^2 \right\} \quad (3.12.2)$$

Equation (3.12.2) was derived for the case where χ does not depend on polymer concentration.

<<Problem 3-16-a>> **Concentration dependence of χ**

When χ is linearly proportional to ϕ_1 in the form

$$\chi = \chi_0 (1 + p_1\phi_1) \quad (3.16.1)$$

show that $\Delta\mu_1$ is given by the expression

$$\Delta\mu_1 = RT \left\{ \log \phi_1 - (n-1)(1-\phi_1) + \chi_0 n (1-\phi_1)^2 + \chi_0 n p_1 \left(\frac{1}{2} - \frac{3}{2}\phi_1^2 + \phi_1^3 \right) \right\} \quad (3.16.2)$$

Answer

$\Delta\mu_1$ is generally expressed as

$$\Delta\mu_1 = RT \left\{ \log \phi_1 - (n-1)(1-\phi_1) - \chi n \phi_1 (1-\phi_1) + n \int_{\phi_1}^1 \chi d\phi_1 \right\} \quad (3.15.10)$$

Combination of Eq.(3.16.1) with Eq.(3.15.10) leads to

$$\begin{aligned} \Delta\mu_1 &= RT \left\{ \log \phi_1 - (n-1)(1-\phi_1) - \chi_0 n (1+p_1\phi_1) n \phi_1 (1-\phi_1) + n \int_{\phi_1}^1 \chi_0 (1+p_1\phi_1) d\phi_1 \right\} \\ &= RT \left\{ \log \phi_1 - (n-1)(1-\phi_1) - \chi_0 n \phi_1 (1-\phi_1) - \chi_0 n p_1 \phi_1^2 (1-\phi_1) \right. \\ &\quad \left. + \chi_0 n (1-\phi_1) + \chi_0 n p_1 \left(\frac{1}{2} - \frac{\phi_1^2}{2} \right) \right\} \end{aligned} \quad (3.16.3)$$

Rearrangement of Eq. (3.16.3) gives Eq. (3.16.2).

<<Problem 3-16-b>> **Virial coefficient at θ point**

If higher order terms of the concentration dependence of χ is required, Eq.(3.16.1) is replaced by the equation

$$\chi = \chi_0 (1 + p_1\phi_1 + p_2\phi_1^2 + \dots + p_n\phi_1^n) \quad (3.16.4)$$

the condition that all the virial coefficients are concurrently zero at θ point is given by

$$\chi_0 = \frac{1}{2} \quad (3.16.5)$$

$$P_1 = \frac{2}{3}, \quad P_2 = \frac{2}{4}, \quad P_3 = \frac{2}{5}, \quad \dots, \quad P_n = \frac{2}{n+2} \quad (3.16.6)$$

Derive Eqs. (3.16.5) and (3.16.6).

Answer

If χ depends on volume fraction as Eq. (3.16.4), the chemical potential of the solvent $\Delta\mu_0$ can be given by

$$\Delta\mu_0 = RT \left\{ \ln \left(1 - \phi_1 \right) + \left(1 - \frac{1}{n_n} \right) \phi_1 + \chi_0 \left(1 + \sum_{i=1}^n p_i \phi_i \right) \phi_1^2 \right\} \quad (3.16.7)$$

where n_n is the number-average chain length. $\Delta\mu_0$ in Eq. (3.16.7) can be rewritten by expanding the term $\ln(1-\phi_1)$ in a Taylor expansion form, and by expressing ϕ_1 by the weight concentration C , as

$$\Delta\mu_0 = -RTCv^0 \left\{ \frac{1}{M_1} + \frac{v}{V^0} \left(\frac{1}{2} - \chi_0 \right) C + \sum_{i=1}^n \frac{v^{i+2}}{V^0} \left(\frac{1}{i+2} - \chi_0 p_i \right) C^{i+1} \right\} \quad (3.16.8)$$

Here, v is the polymer specific volume, and M_n the number-average molecular weight. Osmotic pressure Π is given in a virial expansion form as

$$\Pi = -\frac{\Delta\mu_0}{V^0} = RTC \left(\frac{1}{M_n} + A_2 C + A_3 C^2 + \dots \right) \quad (2.8.10)$$

For the case in question, the virial coefficients A_2, A_3, \dots are given with using Eq. (3.16.8) as

$$A_2 = \frac{v^2}{V^0} \left(\frac{1}{2} - \chi_0 \right) \quad (3.16.9)$$

and

$$A_{i+2} = \frac{v^{i+2}}{V^0} \left(\frac{1}{i+2} - \chi_0 p_i \right) \quad (i = 1, 2, \dots, n) \quad (3.16.10)$$

If we assume that $A_2 = A_3 = A_4 = \dots = 0$, we obtain Eqs. (3.16.5) and (3.16.6). Eq. (3.16.6) is only applicable to the systems of non-polar polymer in non-polar solvent.

* p_1 for atactic polystyrene (PS) in cyclohexane (CH) system was determined to be 0.630 by osmotic pressure (34°C)¹, 0.534 by ultracentrifuge (34°C)², 0.610 by solution critical point (SCP) (34°C)³, 0.622 by SCP(34°C)⁴, 0.607 by threshold cloud point⁵, 0.642 by SCP⁶, and 0.600 by cloud point curve combined with relationship between the relative amount of polymer partitioned in a polymer-rich phase and the phase separation temperature⁷. The results indicate that no significant difference in p_1 exists among various methods and p_1 values for atactic PS-CH system are averaged to 0.619 ± 0.023 , except for the ultracentrifuge data². The best and most widely used method for estimating p_1 and p_2 is SCP method. p_1 values for atactic PS in various non-polar or less polar solvents, whose upper or lower critical solution points (UCSP or LCSP) data in literature were analyzed systematically by Kamide et al.⁶ according to Kamide-Matsuda method⁸ (See <<Problem 4-23-b>>), are 0.618 (methyl ethyl ketone, LCSP), 0.615 (cyclopentane, UCSP), 0.631 (cyclopentane, LCSP), 0.642 (cyclohexane, UCSP), 0.638 (cyclohexane, LCSP), 0.602 (methylcyclohexane, UCSP), 0.649 (methylcyclohexane, LCSP), 0.673 (isopropylacetate, UCSP), 0.839 (isopropylacetate, LCSP), 0.643 (n-propylacetate, UCSP), 0.797 (n-propylacetate, LCSP), 0.650 (dimethoxy methane, LCSP), and 0.630 (trans-decalin, UCSP). p_1 values are averaged to 0.663 for all the above systems or 0.636 except two LCSP of PS in iso- and n-propylacetates. It can therefore be concluded that p_1 values of PS in non-polar solvents are close to $2/3$, Eq. (3.16.6), and are slightly higher than the value (ca. 0.6) obtained in a computer experiment, but no significantly so. At the risk of oversimplifying, we could say p_1 will increase with decrease in z . Then, p_1 value estimated here for $z=12$ is not the maximum value theoretically attainable. The correct value of z should be, if possible, determined by other absolute method.

1. W. R. Krigbaum and D. O. Geymer, *J. Am. Chem. Soc.* **81**, 1859 (1959).
2. Th. G. Scholte, *J. Polym. Sci. A-2*, **8**, 841 (1970).
3. R. Koningsveld, L. A. Kleijnens and A. R. Shultz, *J. Polym. Sci. A-2*, **8**, 1261 (1970).
4. R. Koningsveld and L. A. Kleijnens, *Macromolecules* **5**, 637 (1971).
5. N. Kuwahara, M. Nakata and M. Kaneko, *Polym. J.* **20**, 231 (1988).
6. K. Kamide, S. Matsuda and M. Saito, *Polym. J.* **17**, 1013 (1985).
7. K. Kamide, *Mem. Fac. Educ. Kumamoto Univ.* **44**, 199 (1995).
8. K. Kamide and S. Matsuda, *Polym. J.* **16**, 825 (1984).

<<Problem 3-16-c>> **Determination of χ from cloud-point curve**

The parameter χ can be expressed in a power series of concentration as Eq. (3.16.4). The molecular weight dependence of χ is phenomenologically given by

$$\chi_0 = \chi_{00} (1 + k' / n_n) \tag{3.16.11}$$

The temperature dependence of k' and χ_{00} can be empirically expressed as

$$k' = k_0 (1 - \theta / T) \tag{3.16.12}$$

and

$$\chi_{00} = a + b / T \tag{3.16.13}$$

where k_0 , a and b are the constants independent of temperature and θ , the Flory temperature. Describe methods for determining the parameters a , b and p_j ($j=1, \dots, n$) from the cloud-point curve and an empirical relationship between temperature and relative amount of polymers partitioned in polymer-rich phase with the corresponding theoretical ones.

Answer

Parameters a , b , p_j ($j=1, \dots, n$) can be determined when the cloud point temperature $T_{cp,c}$, experimentally determined, coincides with that calculated by a computer simulation for phase equilibrium due to Eqs.(3.16.4) and (3.16.11)-(3.16.13), $T_{cp,c}$.

- (1) Determine the relationships between ρ_p (ρ_p is the weight fraction of the polymer partitioned into the polymer-rich phase to the polymer dissolved in the initial solution) and the temperature T from the two-phase equilibrium experiments.
- (2) Carry out a computer simulation assuming arbitrarily chosen values of p_j ($j=1, \dots, n$) to obtain the relationship between χ_{00} and $1/T$ by using ρ_p vs. T relationship obtained in step (1) and χ_{00} vs. ρ_p relations obtained in step (2) and a and b determined as the intercept and slope of χ_{00} vs. T plot, respectively.
- (4) Calculate CPC ($T_{cp,c}$ vs. ϕ_1 relationship) using a and b obtained in step (3)
- (5) Compute $\delta \equiv \sum_N (T_{cp,c} - T_{cp,c}^j)^2 / N$ (N is the total number of the solutions, for which the cloud point was determined) and determine a set of p_j ($j=1, \dots, n$) to minimize δ (where $N \gg n$).
- (6) Repeat steps 2-5 and evaluate a , b and p_j where δ is below the permissible limit. See <<Problem 4-21.>> for the details of the simulation.

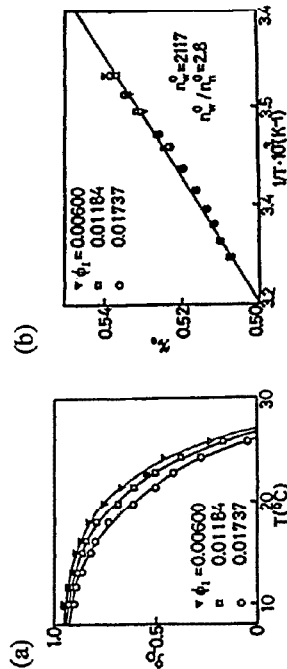


Fig. 3-16-c.1 (a) Experimental relationship between ρ_p and T and (b) temperature dependence of χ_0 in Eq. (3.16.4) for polystyrene ($n_w^0=2117$, $n_w^0/n_n^0=2.8$) in cyclohexane. The polymer volume fractions of the starting solution ϕ_1^0 are 0.6×10^{-2} (∇), 1.184×10^{-2} (\square) and 1.737×10^{-2} (\circ), respectively. Full line in (b) is the theoretical curve calculated by assuming $p_1=0.62$, $p_2=0.20$ and $k_0=0$. (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* 16, 839 (1984))

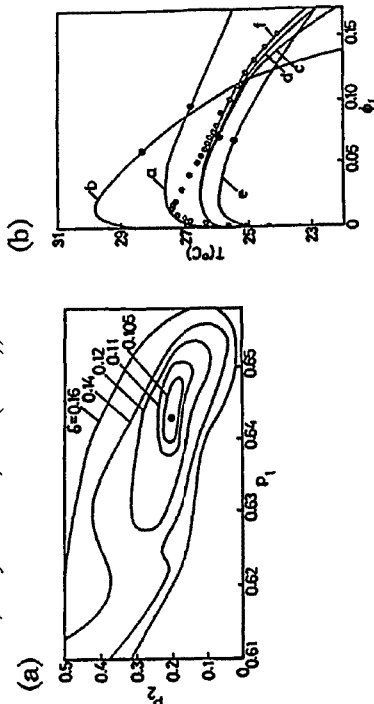


Fig. 3-16-c.2 (a) Relationship among p_1 , p_2 and δ for polystyrene/cyclohexane system: numbers denote δ and the full line is the contour line of the same δ . (b) Cloud point curves for polystyrene/cyclohexane system; full line shows the theoretical curve calculated using the values of a , b , p_1 and p_2 summarized in Table 3-16-c. Lines a-f have the same meaning as those in Fig. 3-15. Unfilled circles are experimental data points. (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* 16, 839 (1984))

Table 3-16-c.1 Parameters a' , b' , p_1 and p_2 in Eq.(3.16.14) for polystyrene-cyclohexane system ($T=299K$)

Author(s)	a'	b'	p_1	p_2
Krigbaum, Geymer(1959)	0.2496	76.67	0.630 ₄	0.480 ₈
Scholte(1970)	0.2631	74.31	0.534 ₄	0.430 ₄
Koningsveld et al. (1970)	0.2035	90.50	0.610 ₆	0.920 ₇
Koningsveld et al. (1971)	0.2211	85.313	0.622 ₂	0.289 ₁
Kuwahara et al. (1973)	0.2798	67.50	0.607 ₃	0.512 ₁
Kamide et al.(1984)	-0.0242 ₄	158.79	0.643	0.200
Kamide et al.(1995)	0.23	82.89	0.600	0.460

1)W.R.Krigbaum and D.O.Geymer, *J.Am.Chem.Soc.* **81**, 1859 (1959).

2)G.Scholte, *J. Polym.Sci. A-2*, **8**, 841 (1970).

3)R.Koningsveld, L.A.Kleitjens and A.R.Shultz, *J. Polym.Sci. A-2*, **8**, 1261 (1970).

4)R.Koningsveld and L.A.Kleitjens, *Macromolecules* **4**, 637 (1971).

5)N.Kuwahara, M.Nakata and M.Kaneko, *Polymer* **14**, 415 (1973).

6)K.Kamide, S.Matsuda, T.Dobashi and M.Kaneko, *Polym. J.* **16**, 839 (1984).

7)K.Kamide, S.Matsuda and H.Shirataki, *Mem. Fac. Education, Kumamoto Univ.* **44**, 199,

(1995); They recalculated based on the data of ref. 6). (See K.Kamide, *Thermodynamics of Polymer Solutions: Phase Equilibria and Critical Phenomena*, Elsevier, 1990)

Table 3-16-c.2 Some characteristics of three typical solutions

Solutions	Characteristics	Equation
ideal	random mixing (solute=solvent in size) zero heat of mixing	(3.2.6) (3.8.3-4)
quasi-ideal	'random' mixing (solute>solvent in size) zero heat of mixing	excess function (3.2.6)
real	non-'random' mixing (solute>>solvent in size) non- zero heat of mixing	pseudo-excess function (3.16.1-2)

*Fig. 3-16-c.1 (a) shows the relationship between p_1 and p_2 , obtained by an actual phase separation experiment for the system polystyrene(PS) in cyclohexane(CH). The relationship can be roughly approximated by a part of a circular arc with p_1 approaching zero most appropriate set of p_1 and p_2 , giving the minimum $\delta(-0.1)$, could be determined as $p_1=0.643$ and $p_2=0.200$. These values are very close to the corresponding values evaluated from the critical point data (See K. Kamide and S. Matsuda, *Polym. J.* **16**, 807 (1984)). The cloud point curve, calculated with using these values of a' , b' , p_1 and p_2 can express accurately the experimental data except for the threshold point region ($\phi_1=0.07$). The concentration dependence of the parameter χ , evaluated for PS/CH system by many investigators, is plotted in Fig. 3-15. In the figure, the curves have been calculated from the p_1 and p_2 values evaluated from the critical points. The experimental data points can be reasonably represented by Eqs. (3.16.11), (3.16.12) and (3.16.4) for $n=2$, in which terms higher than ϕ_1^2 are neglected. That is, in the ϕ_1 range of 0-0.15, both p_2 and p_1 are necessary to represent the concentration dependence of χ and in a comparatively dilute range, there is no sharp distinction in χ between the investigators.

Table 3-16-c.1 shows the parameters determined for the system polystyrene in cyclohexane and Table 3-16-c.2 summarizes some characteristics of three typical solutions.

<<Problem 3-17>> Chemical potential of polymer in multicomponent polymer solution

Generalize Eq.(3.16.2) to the case where the polymer solute has a molecular weight distribution.

Answer

The chemical potential of n th polymer component $\Delta\mu_n$ in multicomponent polymer solutions with constant χ can be expressed as

$$\Delta\mu_n = RT \left\{ \log \phi_n - (n-1) + \phi_1^n \left(1 - \frac{1}{n_n} \right) + \chi n (1 - \phi_1)^2 \right\} \quad (3.17.1)$$

Here, n_n is the number-average chain length (average number of segments in a polymer). Then, Eq.(3.16.2) can be generalized to this case as

$$\Delta\mu_n = RT \left\{ \log \phi_n - (n-1) + \phi_n n \left(1 - \frac{1}{n} \right) + \chi_0 n (1 - \phi_1)^2 + \chi_0 P_1 n \left(\frac{1}{2} - \frac{3}{2} \phi_1^2 + \phi_1^3 \right) \right\} \quad (3.17.2)$$

Eqs. (3.16.2) and (3.17.2) are practical equations to describe the thermodynamic properties of multicomponent polymer solutions. Eq. (3.17.2) was derived by Huggins-Okamoto (See M. L. Huggins and H. Okamoto, *Polymer Fractionation* (Ed. by M. J. R. Cantow), Chapter 4, Academic Press, 1967) and Kamide-Sugamiya (See K. Kamide and K. Sugamiya, *Makromol. Chem.* **139**, 197 (1970))

<<Problem 3-18>> **Huggins' free energy correction parameter g**
An alternative expression for free energy of mixing is

$$\frac{\Delta G_{\text{mix}}}{NRT} = (1 - \phi_1) \log(1 - \phi_1) + \sum \phi_1 x_i^{-1} \log \phi_i + g(1 - \phi_1) \phi_1 \quad (3.18.1)$$

Here, g is the Huggins free energy correction parameter and $\sum \phi_i = \phi_1$ is the total polymer volume fraction. Verify the relationship between g and χ , given by

$$\chi = g - (1 - \phi_1) \frac{\partial g}{\partial \phi_1} \quad (3.18.2)$$

Answer

Differentiation of Eq.(3.18.1) with respect to solvent mole (N_0) and solute mole (N_1) yields

$$\Delta\mu_0 / RT = \log(1 - \phi_1) + \left(1 - \frac{1}{n} \right) \phi_1 + \left\{ g(1 - \phi_1) \frac{\partial g}{\partial \phi_1} \right\} \phi_1^2 \quad (3.18.3)$$

$$\Delta\mu_1 / RT = \log \phi_1 + 1 - n \phi_1 / n_n - n_1 (1 - \phi_1) + \left\{ g + \phi_1 \frac{\partial g}{\partial \phi_1} \right\} n_1 (1 - \phi_1)^2 \quad (3.18.4)$$

On the other hand, referring to Eq.(3.11.2), $\Delta\mu_0$ is expressed as

$$\Delta\mu_0 / RT = \log(1 - \phi_1) + \left(1 - \frac{1}{n_n} \right) \phi_1 + \chi \phi_1^2 \quad (3.18.5)$$

Comparison of Eq.(3.18.3) and Eq.(3.18.5) leads to Eq.(3.18.2).

<<Problem 3-19>> **Gibbs free energy of mixing for ternary system**

Consider a solution of single-component polymer dissolved in a binary solvent mixture. Derive expressions for ΔG_{mix} , μ_0 , μ_1 and μ_2 , by generalizing the Flory-Huggins theory for binary solutions.

Answer

The entropy change by mixing three amorphous solute ΔS^* is given by

$$\Delta S_{\text{mix}}^* = -k \left(N_0 \log \phi_0 + N_1 \log \phi_1 + N_2 \log \phi_2 \right) \quad (3.19.1)$$

Here, N_0 , N_1 and N_2 are the numbers of molecules of components 0, 1 and 2, respectively, and ϕ_0 , ϕ_1 and ϕ_2 are their volume fractions. The heat of dilution can be written, with reference to Eq. (3.9.1), as

$$\begin{aligned} \Delta H_{\text{mix}} &= z \sum_{i < j} n_i n_j \epsilon_{ij} \\ &= kT \sum_{i < j} N_i N_j \chi_{ij} \\ &= kT \left(N_0 \phi_1 \chi_{01} + N_0 \phi_2 \chi_{02} + N_1 \phi_2 \chi_{12} \right) \end{aligned} \quad (3.19.2)$$

with

$$\chi_{ij} = \frac{z n_i \epsilon_{ij}}{kT}$$

ΔG_{mix} is given by the combination of Eqs. (3.19.1) and (3.19.2) as

$$\begin{aligned} \Delta G_{\text{mix}} &= \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}^* \\ &= kT \left(N_0 \log \phi_0 + N_1 \log \phi_1 + N_2 \log \phi_2 + \chi_{01} N_0 \phi_1 + \chi_{02} N_0 \phi_2 + \chi_{12} N_1 \phi_2 \right) \end{aligned} \quad (3.19.3)$$

The chemical potentials are defined by

$$\begin{aligned}\mu_0 - \mu_0^0 &= \Delta\mu_0 = \left(\frac{\partial \Delta G}{\partial N_0} \right)_{N_j, T, P} N_A \\ \mu_1 - \mu_1^0 &= \Delta\mu_1 = \left(\frac{\partial \Delta G}{\partial N_1} \right)_{N_j, T, P} N_A \\ \mu_2 - \mu_2^0 &= \Delta\mu_2 = \left(\frac{\partial \Delta G}{\partial N_2} \right)_{N_j, T, P} N_A\end{aligned}\quad (3.19.4)$$

The subscript N_j means that the amounts N_j of all the components other than component j (0 or 1 or 2) are held fixed. The volume fractions of solvent 1, solvent 2 and solute 3 are expressed as

$$\begin{aligned}\phi_0 &= \frac{n_0 N_0}{n_0 N_0 + n_1 N_1 + n_2 N_2} \\ \phi_1 &= \frac{n_1 N_1}{n_0 N_0 + n_1 N_1 + n_2 N_2} \\ \phi_2 &= \frac{n_2 N_2}{n_0 N_0 + n_1 N_1 + n_2 N_2}\end{aligned}\quad (3.19.5)$$

Here, n_0 , n_1 and n_2 are the degree of polymerization. Differentiation of Eq. (3.19.5) with respect to N_0 yields

$$\begin{aligned}\frac{\partial \phi_0}{\partial N_0} &= \frac{n_0 (n_0 N_0 + n_1 N_1 + n_2 N_2) - (n_0 N_0) n_0}{(n_0 N_0 + n_1 N_1 + n_2 N_2)^2} \\ &= \frac{n_0}{(n_0 N_0 + n_1 N_1 + n_2 N_2)} (1 - \phi_0) \\ \frac{\partial \phi_1}{\partial N_0} &= \frac{n_0}{-n_1 N_1 n_0} = -\phi_1 \frac{n_0}{n_0 N_0 + n_1 N_1 + n_2 N_2} \\ \frac{\partial \phi_2}{\partial N_0} &= -\phi_2 \frac{n_0}{n_0 N_0 + n_1 N_1 + n_2 N_2}\end{aligned}\quad (3.19.6)$$

From Eqs. (3.19.3) and (3.19.4), we obtain

$$\begin{aligned}\Delta\mu_0 &= \left(\frac{\partial \Delta G}{\partial N_0} \right)_{N_j, T, P} N_A \\ &= RT \left(\log \phi_0 + \frac{1}{N_0} \frac{\partial \phi_0}{\partial N_0} + N_1 \frac{1}{\phi_1} \frac{\partial \phi_1}{\partial N_0} + N_2 \frac{1}{\phi_2} \frac{\partial \phi_2}{\partial N_0} \right) \\ &\quad + \chi_{01} \phi_1 + \chi_{01} N_0 \frac{\partial \phi_1}{\partial N_0} + \chi_{02} \phi_2 + \chi_{02} N_0 \frac{\partial \phi_2}{\partial N_0} + \chi_{12} N_1 \frac{\partial \phi_2}{\partial N_0} \\ &= RT \left\{ \log \phi_0 + \frac{n_0 N_0 (n_0 N_0 + n_1 N_1 + n_2 N_2)}{n_0 N_0 (n_0 N_0 + n_1 N_1 + n_2 N_2)} (1 - \phi_0) \right. \\ &\quad + \frac{N_1 (n_0 N_0 + n_1 N_1 + n_2 N_2)}{n_1 N_1} (-\phi_1) \frac{n_0}{n_0 N_0 + n_1 N_1 + n_2 N_2} \\ &\quad + \frac{N_2 (n_0 N_0 + n_1 N_1 + n_2 N_2)}{n_2 N_2} (-\phi_2) \frac{n_0}{n_0 N_0 + n_1 N_1 + n_2 N_2} + \chi_{01} \phi_1 + \chi_{01} (-\phi_1) \phi_0 \\ &\quad \left. + \chi_{02} \phi_2 + \chi_{02} (-\phi_2) \phi_0 + \chi_{12} (-\phi_2) \frac{n_0 N_1}{n_0 N_0 + n_1 N_1 + n_2 N_2} \right\} \\ &= RT \left\{ \log \phi_0 + (1 - \phi_0) - \left(\frac{n_0}{n_1} \right) \phi_1 - \left(\frac{n_0}{n_2} \right) \phi_2 \right. \\ &\quad \left. + \chi_{01} (\phi_1 - \phi_0 \phi_1) + \chi_{02} (\phi_2 - \phi_0 \phi_2) - \chi_{12} \phi_2 \left(\frac{n_0}{n_1} \right) \phi_1 \right\}\end{aligned}$$

$$\begin{aligned}
&= RT \left\{ \log \phi_0 + (1 - \phi_0) - \left(\frac{n_0}{n_1} \right) \phi_1 - \left(\frac{n_0}{n_2} \right) \phi_2 + (\chi_{01} \phi_1 + \chi_{02} \phi_2) (\phi_1 + \phi_2) \right. \\
&\quad \left. - \chi_{12} \left(\frac{n_0}{n_1} \right) \phi_1 \phi_2 \right\} \tag{3.19.7}
\end{aligned}$$

Similarly, we have

$$\begin{aligned}
\Delta\mu_1 = RT \left\{ \log \phi_1 + (1 - \phi_1) - \left(\frac{n_1}{n_0} \right) \phi_0 - \left(\frac{n_1}{n_2} \right) \phi_2 \right. \\
\left. + (\chi_{10} \phi_0 + \chi_{12} \phi_2) (\phi_0 + \phi_2) - \chi_{02} \left(\frac{n_1}{n_2} \right) \phi_0 \phi_2 \right\} \tag{3.19.8}
\end{aligned}$$

$$\begin{aligned}
\Delta\mu_2 = RT \left\{ \log \phi_2 + (1 - \phi_2) - \left(\frac{n_2}{n_0} \right) \phi_0 - \left(\frac{n_2}{n_1} \right) \phi_1 \right. \\
\left. + (\chi_{21} \phi_1 + \chi_{20} \phi_0) (\phi_1 + \phi_0) - \chi_{01} \left(\frac{n_2}{n_0} \right) \phi_0 \phi_1 \right\} \tag{3.19.9}
\end{aligned}$$

The following relationship holds between χ_{ji} and χ_{ij} :

$$\chi_{ji} = \chi_{ij} \left(\frac{n_j}{n_i} \right) \tag{3.19.10}$$

For ternary systems, Eq. (3.19.10) reads

$$\begin{aligned}
\chi_{12} &= \chi_{21} \left(\frac{n_1}{n_2} \right) \\
\chi_{13} &= \chi_{31} \left(\frac{n_1}{n_3} \right) \\
\chi_{23} &= \chi_{32} \left(\frac{n_2}{n_3} \right) \tag{3.19.11}
\end{aligned}$$

Therefore, three among six χ_{ij} are independent variables.