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Author(s)	Kurata, Michio
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Thermodynamic Analysis of Polymer-
Mixed Solvent Systems

Part I. Osmotic Pressure and Theta Composition of Solvent

Michio KURATA*

The osmotic equilibrium between polymer-mixed solvent system and dialyzate has been analysed by using the characteristic function $F = A - \sum_{i=0}^{d} n_i \mu_i$ and the volume molality as composition variable. Here A is the Helmholtz free energy, n_i and μ_i are the amount and the chemical potential of diffusible components i $(=0, 1,..., d)$. It is proved that at the theta composition of the dialyzate, the second virial coefficient of the polymer solution vanishes, and simultaneously, the phase separation sets in if the polymer molecular weight is infinitely large. Thus, if the dialysis method is properly applied, the nature of the theta state in mixed solvent systems becomes exactly identical with that in single solvent systems.

INTRODUCTION

The theta temperature of a polymer solution is usually defined as the temperature at which the second virial coefficient vanishes. It can be also obtained by extrapolating the critical solution temperature of the solution to the limit of infinite polymer molecular weight. The two methods should lead to the same result according to the Flory theory of polymer solutions.[1] Furthermore, the theory predicts that the excluded volume effect within each polymer molecule vanishes at the same temperature and that the intrinsic viscosity becomes proportional to the square root of the polymer molecular weight. These predictions have been verified experimentally for a number of polymer-solvent systems, including polyelectrolytes in aqueous salt solutions.

Recently, Benoit has pointed out that in the case of neutral polymers in mixed solvents, the intrinsic viscosity at the theta composition of solvent often deviates from the square-root dependence of molecular weight.[2] Thus, we find it necessary to re-examine the thermodynamic significance of the theta state of mixed solvent systems. This paper describes a brief preliminary account of the study.

COMPOSITION VARIABLES

In thermodynamic analysis of multicomponent systems, the use of appropriate composition variables is essential for developing clear calculations. Thus, we give first a review on the nature of various composition variables.

Consider a multicomponent system which consists of $r+1$ nonreacting components,

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* 倉田道夫 : Laboratory of Polymer Solutions, Institute for Chemical Research, Kyoto University, Kyoto.

and label these components as $i=0, 1,\ldots, r$. We denote the amount of component i by n_i and the total amount of substances by n:

$$n = \sum_{i=0}^{r} n_i \qquad (1)$$

If the system is closed against the environment, the total amount of substances n is constant, and hence it serves as a good measure of the size of the system. Then, the mole fractions defined by

$$x_i = n_i/n \qquad i=1, 2,\ldots r \qquad (2)$$

will form an appropriate set of variables for specifying the composition of the solution. The weight fractions can also be used for the same purpose. However, if the system is open to the environment, n is not kept constant and the mole fractions can no longer be the best composition variables.

Open multicomponent systems may be divided into two types according to whether the pressure remains unspecified or not. In the former case, we can adopt the volume V for defining the size of the system, and conveniently use the volume molality c_i for specifying the composition:

$$c_i = n_i/V \qquad i=1, 2,\ldots r \qquad (3)$$

The volume molality of component 0 can also be defined as $c_0=n_0/V$, but this is merely a dependent variable which satisfies the relationship,

$$\sum_{i=0}^{r} c_i V_i = 1 \qquad (4)$$

Here V_i represents the partial molar volume of component i. The mass concentrations C_i are defined by

$$C_i = n_i M_i/V = c_i M_i \qquad i=1, 2,\ldots r \qquad (5)$$

where M_i is the molar mass of component i, and they can be used instead of c_i.

In order to treat open systems under constant pressure properly, it is better to use the amount of one selected component, say n_0, for defining the system size. Thus, in this case, the molality m_i given by

$$m_i = n_i/n_0 M_0 \qquad i=1, 2,\ldots r \qquad (6)$$

may be a most natural choice of composition variables. n_0 is here assumed to be constant by definition, hence any change of n_i affects m_i directly. This simplifies greatly the treatment of the constant pressure systems.

OSMOTIC PRESSURE

The osmotic equilibrium in multicomponent solutions has been studied extensively by Scatchard[3] and by Casassa and Eisenberg.[4] They are able to clarify the thermodynamic meaning of the dialysis method in the study of mixed solvent systems. They developed basic calculations by using the molality as composition variable, and then

rewrite the results by converting the molality into the concentration scale on volume basis. We here show a shortcut for these treatments.

Let there be on one side of a semipermeable membrane a polymer-mixed solvent system consisting of $r+1$ components altogether, of which $d+1$ components permeate the membrane and the remaining s $(=r-d)$ components do not. Following Casassa and Eisenberg, we call the former components the "diffusible" components and the latters the "nondiffusible" components, and the system itself the "inner" solution. On the other side of the membrane is placed an "outer" dialyzate phase containing only $d+1$ diffusible components. If we designate by primes quantities relating the outer solution, the conditions for osmotic equilibrium may be written as

$$\mu_i'(T', p', c_1', \ldots c_d') =$$
$$\mu_i(T, p, c_1, \ldots c_d, c_{d+1}, \ldots c_{d+s}) \qquad i=0, 1, \ldots d \tag{7}$$

$$T' = T \tag{8}$$

$$p - p' = \Pi \tag{9}$$

In ordinary type of osmotic pressure measurements, the outer solution with fixed compositions is maintained at constant temperature and pressure, hence at constant chemical potentials μ_i'. Thus, by the condition (7), the inner solution is also maintained at constant temperature and at constant chemical potentials of the diffusible components. For the sake of brevity, we call this the constant μ_D condition. The pressure change in the inner solution is directly related to the variation of osmotic pressure:

$$d\Pi = (dp)_{T, \mu_D} \tag{10}$$

As is well-known, the characteristic function of a system defined by a given set of variables T, V, and n_i $(i=0, 1, \ldots, d+s)$ is the Helmholtz energy A, for which we have

$$dA = -S dT - p dV + \sum_{i=0}^{d+s} \mu_i dn_i \tag{11}$$

Here S is the entropy of the system. Now, let us define a new function F by

$$F = A - \sum_{i=0}^{d} n_i \mu_i \tag{12}$$

The total differential of F may be given as

$$dF = -S dT - p dV - \sum_{i=0}^{d} n_i d\mu_i + \sum_{i=d+1}^{d+s} \mu_i dn_i \tag{13}$$

This equation indicates that the function F serves as the characteristic function for the system with a given set of variables T, V, $\mu_0, \ldots, \mu_d$, $n_{d+1}, \ldots, n_{d+s}$, hence for the constant μ_D system. From Eq. (13), we obtain

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V, \mu_D, n_S} \tag{14}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,\mu_D,n_S} \tag{15}$$

$$n_i = -\left(\frac{\partial F}{\partial \mu_i}\right)_{T,V,\mu_D,n_S} \qquad i = 0, 1, \dots d \tag{16}$$

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,\mu_D,n_S} \qquad i = d+1, \dots d+s \tag{17}$$

The general form of the Gibbs-Duhem equation for multicomponent systems may be written as

$$-S\,dT + V\,dp - \sum_{i=0}^{d+s} n_i\,d\mu_i = 0 \tag{18}$$

For the present inner solution with fixed T and μ_D, this equation reduces to a simple form

$$V(dp)_{T,\mu_D} - \sum_{i=d+1}^{d+s} n_i(d\mu_i)_{T,\mu_D} = 0 \tag{19}$$

Then, substitution of Eqs. (3) and (10) into Eq. (19) yields

$$d\Pi = \sum_{i=d+1}^{d+s} c_i(d\mu_i)_{T,\mu_D} \tag{20}$$

or

$$\left(\frac{\partial \Pi}{\partial c_j}\right)_{c_k} = \sum_{i=d+1}^{d+s} c_i\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_D,c_k} \tag{21}$$

In terms of the mass concentrations C_i, this equation can be expressed as

$$\left(\frac{\partial \Pi}{\partial C_j}\right)_{C_k} = \sum_{i=d+1}^{d+s} \frac{C_i}{M_i}\left(\frac{\partial \mu_i}{\partial C_j}\right)_{T,\mu_D,C_k} \tag{22}$$

Now, remembering Eq. (17) for μ_i, we obtain

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,V,\mu_D,n_S} = \frac{\partial^2 F}{\partial n_j \partial n_i} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,V,\mu_D,n_S} \tag{23}$$

which may be rewritten as

$$\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_D,c_k} = \left(\frac{\partial \mu_j}{\partial c_i}\right)_{T,\mu_D,c_k} \tag{24}$$

or

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial C_j}\right)_{T,\mu_D,C_k} = \frac{1}{M_j}\left(\frac{\partial \mu_j}{\partial C_i}\right)_{T,\mu_D,C_k} \tag{25}$$

This symmetry suggests that in dilute solutions under constant T and μ_D, the chemical potential μ_i of nondiffusible solute component i can be expanded in the form

$$\mu_i(T, \mu_D, C_{d+1}, \dots C_{d+s}) = \mu_i^0(T, \mu_D) + RT \ln C_i + RT \ln y_i \tag{26}$$

with

$$\ln y_i = M_i \left\{ \sum_{j=d+1}^{d+s} B_{ij}(T, \mu_D) C_j \right.$$

$$\left. + \frac{1}{2} \sum_{j=d+1}^{d+s} \sum_{k=d+1}^{d+s} B_{ijk}(T, \mu_D) C_j C_k + \cdots \right\} \tag{27}$$

Here R is the gas constant and y_i is the activity coefficient in the C-concentration scale. All the coefficients, B_{ij}, B_{ijk}, and so on, are symmetric with respect to permutation of suffixes.

Substituting Eqs. (26) and (27) into Eq. (22), we obtain

$$\frac{1}{RT}\left(\frac{\partial \Pi}{\partial C_j}\right)_{Ck} = \sum_{i=d+1}^{d+s} \left\{ \frac{\delta_{ij}}{M_i} + B_{ij}C_i + \sum_{k=d+1}^{d+s} B_{ijk}C_iC_k + \cdots \right\} \tag{28}$$

where δ_{ij} represents the Kronecker delta. Then, integration of Eq. (28) leads to

$$\frac{\Pi}{RT} = \sum_{i=d+1}^{d+s} \frac{C_i}{M_i} + \frac{1}{2} \sum_{i=d+1}^{d+s} \sum_{j=d+1}^{d+s} B_{ij}C_iC_j$$

$$+ \frac{1}{3} \sum_{i=d+1}^{d+s} \sum_{j=d+1}^{d+s} \sum_{k=d+1}^{d+s} B_{ijk}C_iC_jC_k + \cdots \tag{29}$$

The total concentration C_s and the number-average molar mass M_n of the solutes may be defined as

$$C_s = \sum_{i=d+1}^{d+s} C_i \tag{30}$$

and

$$M_n = \frac{\Sigma_i n_i M_i}{\Sigma_i n_i} = \frac{C_s}{\Sigma_i(C_i/M_i)} = \frac{1}{\Sigma_i(\xi_i/M_i)} \tag{31}$$

$$\xi_i = C_i/C_s \tag{32}$$

Using these notations, we can rewrite Eq. (29) in the form,

$$\frac{\Pi}{RT} = \frac{C_s}{M_n} + A_2(T, \mu_D)C_s^2 + A_3(T, \mu_D)C_s^3 + \cdots \tag{33}$$

$$A_2(T, \mu_D) = \frac{1}{2} \sum_{i=d+1}^{d+s} \sum_{j=d+1}^{d+s} \xi_i\xi_j B_{ij}(T, \mu_D) \tag{34}$$

$$A_3(T, \mu_D) = \frac{1}{3} \Sigma_i\Sigma_j\Sigma_k \xi_i\xi_j\xi_k B_{ijk}(T, \mu_D) \tag{35}$$

Equation (33) is the virial expansion for the osmotic pressure in the constant μ_D system, and the coefficients A_2 and A_3 may be called the second and the third virial coefficients, respectively. The above equations (33) to (35) are formally identical with the corresponding equations for solutions in single solvent.

THETA COMPOSITION OF MIXED SOLVENT

As is seen from Eq. (34), the second virial coefficient in the present system depends

on the temperature and the chemical potentials μ_D. Therefore, it is possible to adjust A_2 to zero by changing μ_D. This can be done by adjusting the composition C'_i ($i = 1, ..., d$) of the outer dialyzate phase to appropriate values. We call this state of the dialyzate the "theta composition" of the mixed solvent. Thus, it is important to note that the theta state in mixed solvent systems can never be attained by resolving a given solute into a solvent with a fixed composition. The solvent composition should be defined in the outer dialyzate phase.

Now, let us turn to discussion on the phase diagram in mixed solvent systems. To do this, we consider a simplest example, *i.e.*, a ternary solution consisting of two diffusible components ($i = 0, 1$) and one nondiffusible component ($i = 2$). Under fixed values of T and μ_D, the condition for stable equilibrium is given by

$$(\delta^2 F)_{T,V,\mu_0,\mu_1,n_2} > 0 \tag{36}$$

Then, standard arguments show that the critical solution point is determined by two simultaneous equations,

$$\left(\frac{\partial \mu_2}{\partial C_2}\right)_{T,\mu_0,\mu_1} = 0 \tag{37}$$

$$\left(\frac{\partial^2 \mu_2}{\partial C_2^2}\right)_{T,\mu_0,\mu_1,} = 0 \tag{38}$$

Substitution of these equations into Eq. (22) yields

$$\frac{d\Pi}{dC_2} = 0 \tag{39}$$

$$\frac{d^2\Pi}{dC_2^2} = 0 \tag{40}$$

Now, substituting Eq. (33) into these equations, and neglecting higher terms, we obtain

$$\frac{1}{M_2} + \{2A_2(T, \mu_{Dc}) + 3A_3(T, \mu_{Dc})C_{2c}\}C_{2c} = 0 \tag{41}$$

$$2A_2(T, \mu_{Dc}) + 6A_3(T, \mu_{Dc})C_{2c} = 0 \tag{42}$$

where the suffix c denotes the critical solution point. Equations (41) and (42) give the solution

$$A_2(T, \mu_{Dc})C_{2c} = -\frac{1}{M_2} \tag{43}$$

$$A_3(T, \mu_{Dc})C_{2c}^2 = \frac{1}{3M_2} \tag{44}$$

These equations indicate that at the critical solution point, $A_2(T, \mu_{Dc})$ should be negative, while $A_3(T, \mu_{Dc})$ should be positive. Of course, the latter argument can not be decisive because of the neglect of contributions from higher virial coefficients.

Finally, let us assume that

$$A_3(T, \mu_{Dc}) \propto M_2^{-a} \tag{45}$$

Then, Eqs. (43) and (44) yield

$$C_{2c} \propto M_2^{-(1-a)/2} \tag{46}$$

$$A_2(T, \mu_{Dc}) \propto M_2^{-(1+a)/2} \tag{47}$$

The exponent a is zero in the Flory-Huggins theory. Therefore, we may safely assume that $-1 < a < 1$ for flexible chain polymers. Then, if the symbol θ is used for the critical solution point in the limit of $M_2 \to \infty$, we obtain

$$C_{2\theta} = 0 \text{ and } A_2(T, \mu_{D\theta}) = 0 \tag{48}$$

The two definitions of the theta point, one from A_2 and the other from the critical solution point, give the same result provided that the dialysis method is properly applied to the mixed solvent system under consideration. The significance of the dialysis method has been well recognized among researchers of polyelectrolyte solutions, but often overlooked by researchers of neutral polymer solutions.

Finally, we record the conditions for the critical solution point in multicomponent systems under constant T and μ_D:

$$\left(\frac{\partial \mu_{d+1}}{\partial C_{d+1}} \right)_{T, \mu_0, \cdots \mu_d, \mu_{d+2}, \cdots \mu_{d+s}} = 0 \tag{49}$$

$$\left(\frac{\partial^2 \mu_{d+1}}{\partial C_{d+1}^2} \right)_{T, \mu_0, \cdots \mu_d, \mu_{d+2}, \cdots \mu_{d+s}} = 0 \tag{50}$$

The derivation of these equations may be found in literatures.[5]

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