THE PHASE INSTABILITY AND CRITICAL POINT IN A LIQUID MIXTURE OF AN ASSOCIATING AND INERT COMPONENT

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The problem of phase instability in a binary mixture of an associating component with an inert component is analyzed from the standpoint of the theory of association equilibria. It is demonstrated that conditions of the spinodal and critical point for such a binary system are equivalent to those of the spinodal and critical point of a multicomponent mixture consisting of complex species arising by association (including nonassociated molecules).These conditions are formulated so as if species in this mixture did not participate in association and dissociation processes; configurational terms expressing changes in the content of the individual complexes depending on changes in total composition are included implicitly.

The theory of association equilibria appeared to be one of the useful tools of theoretical analysis of the thermodynamic behaviour of mixtures with strong association. Its principle consists in that we assume formation of association complexes consisting of molecules of nominal components of the mixture. First, we write an expression for the Gibbs energy of mixing as a function of concentrations of all existing complexes (including nonassociated molecules). In this way we start from a hypothetical multicomponent mixture of various complex and monomeric species in which so far no association and dissociation processes take place; such a system is further referred to as a nonequilibrating mixture of complexes. Only after that, by minimizing the Gibbs energy, we introduce the condition of an association equilibrium between complexes; by substituting the equilibrium concentrations into the original expression, the Gibbs energy of a real system is obtained. The other thermodynamic quantities are calculated by partial differentiation with respect to temperature, pressure and the number of moles or the concentration of nominal components. In differentiating one should also consider a change in the equilibrium content of the individual complexes, which gives rise to configurational or relaxation terms. In the first derivatives of the Gibbs energy these terms cancel each other, so that similarly to the Gibbs energy of the non-equilibrating mixture of complexes alone, we can take the concentration dependence of the non-equilibrating mixture of complexes, with equilibrium concentrations simply substituted into it[1]. Moreover, the equality between the chemical potential of the nominal component with the chemical potential of its monomeric form proved by Prigogine is valid in this case[2]. For the second and higher derivatives the configurational terms cannot however be eliminated.

If separation into two liquid phases takes place in the association system, the binodal is calculated without difficulties, since it is based on the equality between the chemical potentials of the nominal component. On the other hand, expressions used in the calculation of the spinodal and critical point contain the second or third derivatives with respect to composition, and the calculation procedure may thus be rather difficult. This holds mainly in the case where nonspecific interactions between complexes depend on the degree of association, so that parameters of this interaction are not eliminated in the minimization of the Gibbs energy, and appear in equations of the asociation equilibrium. In this paper we demonstrate, by employing a general thermodynamic procedure, that conditions of the spinodal and critical point for a binary system are changed into conditions for a non-equilibrating mixture of complexes if one component is associated to an arbitrary number of complex species. Conditions of the association equilibrium are then simply substituted into these conditions (configurational terms are already involved in the final expressions).

THEORETICAL

In a binary system (one component of which is denoted with the subscript O and the other with the subscript S) the dependence of the Gibbs energy on the variables of state is expressed as

$$G_v \equiv G_v(\varphi_S, T, P) ; \qquad (1)$$

here, v denotes a quantity related to the unit volume of the system and φ_S is the volume fraction. The corresponding partial derivatives with respect to composition are

$$G_S \equiv (\partial G_v/\partial \varphi_S)_{T,P} , \qquad G_{SS} \equiv (\partial^2 G_v/\partial \varphi_S^2)_{T,P} . \qquad (2)$$

In the theory of association equilibria we introduce a multicomponent (non-equilibrating) mixture of complexes. If the component S forms by association various oligomeric complexes and the component O does not associate, it may be written

$$G_v \equiv G_v(\varphi_1, \varphi_2, \ldots, \varphi_i, \ldots, \varphi_N, T, P) , \qquad (3)$$

where φ_i is the volume fraction of the i-mer complex and N is the number of various complex species (including the monomer). Partial derivatives corresponding to this expression are

$$G_i \equiv (\partial G_v/\partial \varphi_i)_{T,P} , \qquad G_{ij} \equiv (\partial^2 G_v/\partial \varphi_i \partial \varphi_j)_{T,P} . \qquad (4)$$

Differentiation with respect to Eqs (2), (4) must be carried out in expressions (1)

or (3), rearranged so as not to contain explicitly φ_0. Below, the subscripts T, P are omitted.

Association Equilibrium

To describe the association equilibrium between N complex species of the given component, $N - 1$ equations are needed. A set of $N - 1$ processes is contemplated:

$$iS_1 \rightleftharpoons S_i, \qquad i = 2, 3, \ldots N. \tag{A}$$
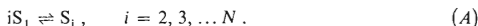
At the given T, P, φ_s the position of the stable association equilibrium in the space of coordinates φ_1, φ_2, ... φ_N is given by the minimum of the Gibbs energy with the binding condition

$$\sum_{i=1}^{N} \varphi_i = \varphi_s. \tag{5}$$

The affinity of the i-th process is defined with respect to Eq. (A) as $(e.g.^3)$

$$A_i \equiv (\partial G_v / \partial \varphi_i)_R, \qquad i = 2, 3 \ldots N, \tag{6}$$

where the index R means the derivative with respect to the reaction coordinate, *i.e.* under conditions

$$\varphi_i + \varphi_1 = \text{const.}, \qquad T, P, \varphi_j = \text{const.}, (j \neq 1). \tag{7}$$

By carrying out this differentiation, we obtain

$$A_i = G_i - G_1. \tag{8}$$

The stable association equilibrium is then determined, on the one hand, by a set of equations

$$A_i = 0, \qquad i = 2, 3, \ldots N, \tag{9}$$

or

$$G_i = G_1, \qquad i = 2, 3, \ldots N, \tag{10}$$

and on the other, by the requirement that the quadratic form

$$\sum_{i,j} B_{ij} \, d\varphi_i \, d\varphi_j,$$

where

$$B_{ij} = (\partial^2 G_v/\partial\varphi_i\partial\varphi_j)_R = G_{ij} - G_{i1} - G_{j1} + G_{11}, \quad i = 2, 3, \dots N \quad (11)$$

ought to be positively definite. The second requirement is satisfied, if all main subdeterminants of the quadratic matrix of the $(N - 1)$-th degree composed of the elements B_{ij} are positive. It must therefore hold that

$$\mathcal{B} = \begin{vmatrix} B_{22}, B_{23}, \dots B_{2N} \\ B_{32}, B_{33}, \dots B_{3N} \\ \dots\dots\dots\dots\dots \\ B_{N2}, B_{N3}, \dots B_{NN} \end{vmatrix} > 0. \quad (12)$$

The determinant may be rearranged using the relationship $\mathcal{B}$ following from Eq. (11),

$$B_{ij} = (A_i)_j - (A_i)_1, \quad (13)$$

where

$$(A_i)_j = (\partial A_i/\partial\varphi_j) = (\partial G_j/\partial\varphi_i)_R, \quad i = 2, 3, \dots, N; \quad j = 1, 2, \dots, N, \quad (14)$$

so that

$$\mathcal{B} = \begin{vmatrix} 1, & 1, & \dots, 1 \\ (A_2)_1, (A_2)_2, \dots, (A_2)_N \\ \dots\dots\dots\dots\dots\dots \\ (A_N)_1, (A_N)_2, \dots, (A_N)_N \end{vmatrix} > 0. \quad (15)$$

The equivalency between Eqs (12) and (15) becomes evident, if in expression (15) the first column is subtracted from all the other columns.

Displacement of the Association Equilibrium

The geometric locus of systems in the association equilibrium is a line the slope of which is given by a set of $N - 1$ derivatives

$$(\partial\varphi_j/\partial\varphi_1)_E, \quad j = 2, 3, \dots, N,$$

where the subscript E denotes the derivative with condition (9) being observed. The line is a special element of a set of lines satisfying the condition

$$A_i = \text{const.}, \quad i = 2, 3, \dots, N. \quad (16)$$

Derivatives corresponding to these lines are denoted as

$$\left(\partial\varphi_j/\partial\varphi_1\right)_A, \qquad j = 2, 3, \ldots, N .$$

Equations needed for the calculation of these derivatives are obtained by differentiating condition (16):

$$\left(A_i\right)_1 + \sum_{j=2}^{N} \left(A_i\right)_j \left(\partial\varphi_j/\partial\varphi_1\right)_A = 0 , \qquad i = 2, 3, \ldots, N . \tag{17}$$

The solution to the set of these equations is

$$\left(\partial\varphi_j/\partial\varphi_1\right)_A = \mathscr{B}_{1j}/\mathscr{B}_{11} , \tag{18}$$

where $\mathscr{B}_{1j}$ is the algebraical complement of the element in the first line and j-th column of the determinant $\mathscr{B}$, which is expressed through equation (15).

For the system to move at constant T, P along the line of the association equilibrium, we must change the total content of the associating component φ_S. Thus, N derivatives may be defined

$$\varphi_j' = \left(\partial\varphi_j/\partial\varphi_S\right)_E , \qquad j = 1, 2, \ldots, N , \tag{19}$$

which can be calculated by solving a set of N equations

$$\sum_{j=1}^{N} \varphi_j' = 1 , \tag{20a}$$

$$\sum_{j=1}^{N} \left(A_i\right)_j \varphi_j' = 0 , \qquad i = 2, 3, \ldots, N . \tag{20b}$$

The solution is

$$\varphi_j' = \mathscr{B}_{1j}/\mathscr{B} , \qquad j = 1, 2, \ldots, N , \tag{21}$$

as can be ascertained by writing out the equations in detail and comparing them with (15).

The Spinodal

The binary system is known to obey the following conditions: for the stable and metastable phase

$$G_{SS} > 0 \qquad \left[T, P\right] , \tag{22a}$$

on the spinodal

$$G_{SS} = 0 \qquad [T, P], \tag{22b}$$

and for the unstable phase

$$G_{SS} < 0 \qquad [T, P]. \tag{22c}$$

The derivatives G_S, G_{SS} can be expressed by means of G_i and G_{ij}, respectively, while observing the condition that the system moves along the line of the association equilibrium. First, we have

$$G_S = \sum_{j=1}^{N} G_j \varphi'_j ; \tag{23}$$

by substituting terms from the equilibrium condition (10) and equation (20a) into the above expression, we obtain a simple relation

$$G_S = G_1 . \tag{24}$$

Hence, the first derivative G with respect to the volume fraction of the nominal component equals the derivative with respect to the volume fraction of the monomeric species of this component. This result is equivalent to the Prigogine law[2] quoted in the introduction. By differentiating Eq. (24) and substituting from (21), we obtain

$$G_{SS} = \sum_{j=1}^{N} G_{1j} \varphi'_j = (\sum_{j=1}^{N} G_{1j} \mathscr{B}_{1j})/\mathscr{B} = \mathscr{G}/\mathscr{B} . \tag{25}$$

The numerator of the fraction in Eq. (25) may be written as the single determinant $\mathscr{G}$, into which we substitute from the relation

$$(A_i)_j = G_{ij} - G_{1j}, \tag{26}$$

following from Eq. (8). The determinant is then rearranged to

$$\mathscr{G} = \begin{vmatrix} G_{11}, G_{12}, \ldots, G_{1N} \\ G_{21}, G_{22}, \ldots, G_{2N} \\ \ldots\ldots\ldots\ldots\ldots \\ G_{N1}, G_{N2}, \ldots, G_{NN} \end{vmatrix} . \tag{27}$$

According to Eq. (15) for the stable association equilibrium it always holds that $\mathscr{B} > 0$; for this reason, on the left-hand side of conditions (22a, b, c) G_{SS} may be

substituted with $\mathscr{G}$. The equation of the spinodal is, then,

$$\mathscr{G} = 0 , \qquad [T, P] \tag{28}$$

being identical with that of the spinodal in the system of independent components 0, 1, 2, ..., $N^{4.5}$, and thus in the non-equilibrating mixture of complexes. Of all the points of this spinodal, only two points are relevant for the binary system of nominal components O and S, namely, points of intersection with the line of the association equilibrium; they correspond to two points for the given T on the spinodal $T \equiv T(\varphi_s)$ of the real binary system (Fig. 1). If at the given T, P the non-equilibrating mixture of complexes has a spinodal which does not intersect the line of the association equilibrium, the real binary system appears as miscible in all proportions.

Let us now show an important property of all points lying on the spinodal. First, we look for the slope of a line (in an N-dimensional space) which meets $(N-1)$ conditions

$$G_i = \text{const.}, \qquad i = 2, 3, ..., N . \tag{29}$$

The slope is given by a set of $(N-1)$ partial derivatives

$$(\partial \varphi_j / \partial \varphi_1)_G , \qquad j = 2, 3, ..., N ,$$

obtained by solving a system of $(N-1)$ equations

$$G_{i1} + \sum_{j=2}^{N} G_{ij}(\partial \varphi_j / \partial \varphi_1)_G = 0 , \qquad i = 2, 3, ..., N . \tag{30}$$

The solution is

$$(\partial \varphi_j / \partial \varphi_1)_G = \mathscr{G}_{1j}/\mathscr{G}_{11} , \tag{30'}$$

where $\mathscr{G}_{ij}$ is the algebraical complement of the element G_{ij} of the determinant $\mathscr{G}$; *cf.* Eq. (27). If a similar equation for $i = 1$ is added to the set (30),

$$G_{11} + \sum_{j=2}^{N} G_{1j}(\partial \varphi_j / \partial \varphi_1)_G = 0 , \tag{31'}$$

we obtain a set of equations, the determinant of which is given by Eq. (27). The system has a solution only if $\mathscr{G} = 0$, *i.e.* if (28) is fulfilled. The set of conditions $G_i = \text{const.}$ can therefore be fulfilled simultaneously for all the i from 1 to N only on the spinodal.

Under these conditions, the solution can be written in various ways, *e.g.* in the form (31). The set can also be solved so that Eq. (30') is subtracted from all equations

of the subset (30); this yields $(N - 1)$ equations

$$(A_i)_1 + \sum_{j=2}^{N} (A_i)_j \, (\partial \varphi_j / \partial \varphi_1)_G = 0 , \qquad i = 2, 3, \ldots, N . \tag{32}$$

Comparison with the set (17) shows that in each point of the spinodal it holds that

$$(\partial \varphi_j / \partial \varphi_1)_G = (\partial \varphi_j / \partial \varphi_1)_A , \qquad j = 2, 3, \ldots, N . \tag{33}$$

Hence, the condition $G_i = \text{const.}$ for all i is equivalent to the condition $A_i = \text{const.}$ for $i = 2, 3, \ldots, N$.

With respect to Eqs (18) and (31), we also obtain

$$\mathscr{B}_{1j} / \mathscr{B}_{11} = \mathscr{G}_{1j} / \mathscr{G}_{11} \tag{34}$$

and from Eq. (21),

$$\varphi'_j / \varphi'_1 = \mathscr{G}_{1j} / \mathscr{G}_{11} . \tag{35}$$

In those points of the spinodal where the condition of the association equilibrium (9) is simultaneously fulfilled, it holds, moreover, that

$$(\partial \varphi_j / \partial \varphi_1)_G = (\partial \varphi_j / \partial \varphi_1)_E . \tag{36}$$

The equations derived above allow us to infer that in the point in which they cross the spinodal the lines of constant A_i values (and particularly the line of the association equilibrium) have a common tangent with the line satisfying the condition $G_i = \text{const.}$ for $i = 2, 3, \ldots, N$. (It can be demonstrated that the statement is valid also for lines which fulfil the condition of constant G_i for all i with the omission of one arbitrary value of i.)

The Critical Point

In a binary system, conditions

$$G_{SS} = 0 , \qquad G_{SSS} = 0 \tag{37}$$

are valid for the critical point. With respect to the validity of Eqs (25) and (28), the latter condition can be rewritten as

$$\mathscr{G}' \equiv (\partial \mathscr{G} / \partial \varphi_S)_E = 0 . \tag{38}$$

The left-hand side may be rearranged to become

$$(\partial \mathscr{G}/\partial \varphi_s)_E = \sum_{j=1}^{N} (\partial \mathscr{G}/\partial \varphi_j) \, \varphi'_j \,, \tag{39}$$

so that, using Eq. (35), we have for the critical point the condition

$$\mathscr{G}' = 0 \,, \tag{40}$$

where

$$\mathscr{G}' = \sum_{j=1}^{N} \frac{\partial \mathscr{G}}{\partial \varphi_j} \, \mathscr{G}_{1j} = \begin{vmatrix} \dfrac{\partial \mathscr{G}}{\partial \varphi_1}, \dfrac{\partial \mathscr{G}}{\partial \varphi_2}, \ldots, \dfrac{\partial \mathscr{G}}{\partial \varphi_N} \\ G_{21}, \, G_{22}, \, \ldots, \, G_{2N} \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ G_{N1}, \, G_{N2}, \, \ldots, \, G_{NN} \end{vmatrix} \,. \tag{41}$$

But this is the equation of the critical point in a system of independent components 0, 1, 2, ..., N (cf.[4,6]).

For a system of non-equilibrating components, Eqs (40), (41) may be derived from the requirement that at an infinitesimal deviation from the critical point along the spinodal none of G_i values is changed; in other words, that in the critical point the spinodal has a common tangent, e.g., with the line given by Eqs (29). A consequence following for the associating system from Eq. (33) is that in the critical point the spinodal has a common tangent also with line of constant A_i values. Of course, the critical point of a mixture of non-equilibrating complexes corresponds to the critical point of the real binary system only at such a temperature at which in the same point the condition of the association equilibrium is also valid. In such a case the spinodal in the critical point has a common tangent with the line of association equilibrium (Fig. 1).

We can also show that the critical point thus specified represents an extreme (maximum as a rule) on the spinodal of the binary system $T \equiv T(\varphi_s)$. The differential equation of this spinodal can be written as

$$\frac{\partial \mathscr{G}}{\partial T} \, \mathrm{d}T + \sum_{j=1}^{N} \frac{\partial \mathscr{G}}{\partial \varphi_j} \, (\mathrm{d}\varphi_j)_E = 0 \,. \tag{42}$$

If now we introduce the condition $\partial T/\partial \varphi_s = 0$, we obtain

$$\sum_{j=1}^{N} (\partial \mathscr{G}/\partial \varphi_j) \, \varphi'_j = 0 \,. \tag{43}$$

However with respect to Eqs (38) and (39) we can see that Eq. (43) passes into the condition of the critical point (40).

Applications

For the purpose of illustration, a binary mixture was chosen in which the Gibbs energy of mixing of association complexes is controlled by the Flory–Huggins equation with the interaction parameter χ independent of the degree of association.

For the Gibbs energy it holds in this case

$$G_v/RT = \varphi_0 \ln \varphi_0 + (1/r) \sum_{i=1}^{N} (\varphi_i/i) \left[(\Delta G_i^0/RT) + \ln \varphi_i \right] + \chi \varphi_0 \sum_{i=1}^{N} \varphi_i , \quad (44)$$

where $r = V_S/V_0$ is the ratio of molar volumes of the components, ΔG_i^0 is the standard Gibbs energy of the process (A) and χ is the parameter of the nonspecific interaction between nominal components (pure monomeric species was chosen as the standard state of the associating component). Using Eq. (10), we can derive the condition of
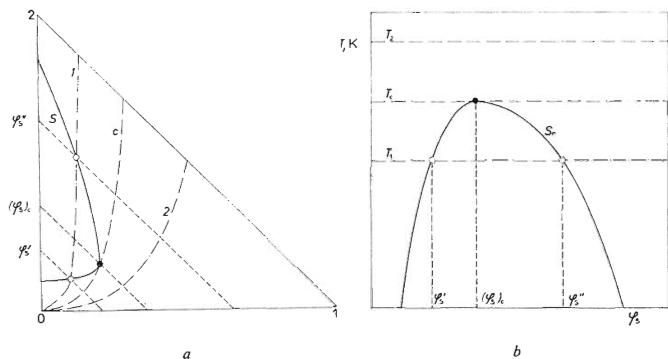

Fig. 1

The Relationship Between (a) Phase Diagram of a Non-Equilibrating Mixture of Complexes and (b) Phase Diagram of a Real Binary Mixture (schematic view)

Components 0,1,2-solvent, monomer, dimer respectively. Lines: S spinodal (for clarity's sake temperature—independent), 1, 2, c lines of the association equilibrium at temperatures T_1, T_2 and at the critical temperature T_c. φ_s', φ_s'' volume fraction of real spinodal phases at T_1, $(\varphi_s)_c$ volume fraction at the critical point. S_r spinodal of the real system.

the association equilibrium

$$\varphi_i = K_i \varphi_1^i, \qquad i = 2, 3, \ldots, N, \qquad (45)$$

$$K_i = \exp\left[-(i - 1 + \Delta G_i^0/RT)\right]. \qquad (45')$$

Equations needed for the spinodal and critical point of the mixture of non-equilibrating complex species have already been derived for the purposes of analysis of phase separation in solutions of a polydisperse polymer[7,8]. The equations of the spinodal may be rewritten in the form

$$\varphi_0^{-1} + \left(r \sum_{i=1}^{N} i\varphi_i\right)^{-1} = 2\chi \qquad (46)$$

and the additional condition of the critical point is

$$\varphi_0^2 = r\left(\sum_{i=1}^{N} i\varphi_i\right)^3 / \left(\sum_{i=1}^{N} i^2 \varphi_i\right), \qquad (47)$$

where

$$\varphi_0 = 1 - \sum_{i=1}^{N} \varphi_i. \qquad (48)$$

We assume below that the number of various types of complexes, N, is very high and the equilibrium constants K_i are controlled by a simple relation[1,9]

$$K_i = iK^{i-1}. \qquad (49)$$

In this we have for the sums in Eqs $(46)-(48)$

$$\sum_{i=1}^{N} i^m \varphi_i = \sum_{i=1}^{N} i^{m+1} K^{i-1} \varphi_1^i, \qquad m = 0, 1, 2, \ldots. \qquad (50)$$

If we start from the sum

$$\Gamma = \sum_{i=1}^{N} \varphi_i/i = \sum_{i=1}^{N} K^{i-1} \varphi_1^i, \qquad (51)$$

which in the limit for $N \to \infty$ gives

$$\Gamma = \varphi_1/(1 - K\varphi_1), \qquad (52)$$

the sums may be calculated by differentiation

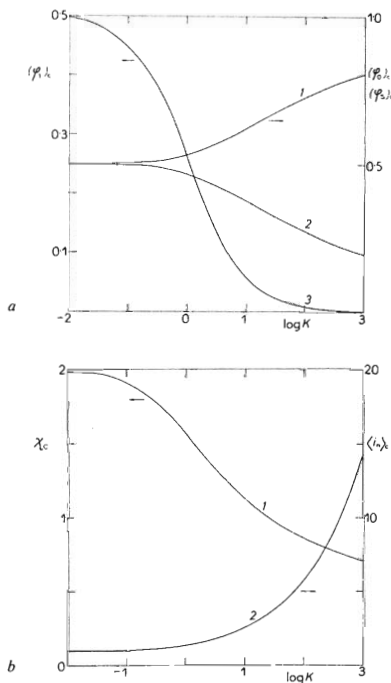$$\sum_{i=1}^{N} i^m \varphi_i = \partial^{m+1} \Gamma / (\partial \ln \varphi_1)^{m+1} . \tag{53}$$

Fig. 2

The Dependence of Critical Quantities on the Association Constant K According to Eqs (53)—(55) for $r = 1$ (index c denotes critical values)

a) 1, 2 volume fractions of nominal components $(\varphi_0)_c$, $(\varphi_s)_c$. 3 volume fraction of the monomeric species $(\varphi_1)_c$ b) 1 interaction parameter χ_c. 2 number average of the degree of association $\langle i_n \rangle_c$.

If expressions thus calculated are substituted into Eqs $(46)-(48)$, we obtain for the spinodal

$$\frac{1}{\varphi_0} + \frac{(1 - K\varphi_1)^3}{r\varphi_1(1 + K\varphi_1)} = 2\chi , \qquad (54)$$

and for the critical point

$$\varphi_0^2 = \frac{r\varphi_1^2(1 + K\varphi_1)^3}{(1 + 4K\varphi_1 + K^2\varphi_1^2)(1 - K\varphi_1)^5} , \qquad (55)$$

where

$$\varphi_0 = 1 - \varphi_1(1 - K\varphi_1)^{-2} . \qquad (56)$$

The dependence of critical quantities on the constant K calculated from the derived equations is shown in Figs 2a, b.

It is obvious that for $K = 0$ the critical quantities assume values characteristic of the binary mixture which obeys the classical Flory–Huggins equation:

$$\chi = \tfrac{1}{2}(1 + r^{-1/2})^2 , \qquad (57)$$

$$\varphi_s = 1/(r^{1/2} + 1) . \qquad (58)$$

On the other hand, in the limit for $K \to \infty$, where complexes with very high i are formed, $\chi \to 1/2$, $\varphi_s \to 0$ as for a polymer with very high molecular mass.

CONCLUSION

The use of Eqs (28), (40) may considerably facilitate the calculation of the spinodal and critical point. In the application just described, the advantage consisted in that Eqs (46), (47) have already been published[7],[8]; their derivation for an associating system is very easy also by employing another procedure than starting with Eqs (28),(40); e.g., we may use a procedure described in ref.[10]. The latter equations are very useful, however, if the interaction parameter χ is different for different complex species; the equilibrium condition is then much more complicated than Eq. (45). Application of the equations derived by us to a case where the nonspecific interaction depends on the degree of association is examined in a forthcoming paper.

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