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Statistical-Mechanical Analysis of Thermodynamic Approaches in Theory of Self-Assembling Systems

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Статистико-механічний аналіз термодинамічних підходів у теорії самоасоційованих систем

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Анотація. В роботі досліджено проблеми самоасоціації у водно-міцелярних системах. Сформульовано термодинамічні принципи самоасоціації, отримано розподіли за розмірами асоційованих структур. Дано статистико-механічне обгрунтування термодинамічних підходів у теорії міцелярних систем. Розвинена теорія узагальнена на багатосортний випадок. Досліджено умови утворення агрегатів з частинок одного сорту і умови утворення змішаних міцел.

Statistical-Mechanical Analysis of Thermodynamic Approaches in Theory of Self-Assembling Systems

M.F.Holovko, T.R.Klymko

Abstract. In this work the problems of self-assembly in aqueous-micellar systems are investigated. Thermodynamic principles of self-assembly are formulated and the size distribution of micelles is obtained. The developed theory is generalized for multicomponent case. Conditions of pure and mixed micelles creation are investigated.

Introduction

During the few last year there have been a significant efforts connected with study of assembling problems in water solutions of surfactants. Self-assembling phenomena have a growing interest in such branch of molecular physics. Studies of self-assembling systems are usually carried out by different theoretical and experimental methods. Thermodynamical approach and statistical-mechanical one are supposed to be the main among theoretical methods. Traditionally self-assembling problems are described by using thermodynamical approach and exploring chemical reactions such as

$$A{+}A{=}A_2,$$
$$A_2{+}A{=}A_3,$$
$$\dots\dots\dots\dots$$
$$A_{N-1}{+}A{=}A_N,$$

where N is the number of molecules in molecular aggregate. Such investigations are based on the studying the conditions of chemical equilibrium of molecular groups in assembling system. This is a phenomenologic (thermodynamic) approach in which the sizes of particles and the interactions between them are neglected. Quantitatively the presence of attractive interactions between the molecules leads to formation of bonded states. Macroscopic theory carries only describing character and it doesn't explain the basic causes of self-assembling phenomena. That's why it is necessary to take into consideration the statistical-mechanical approach which is based on consideration of interactions between the molecules.

We consider a three-component system which consist of water-like, oil-like and surfactant-like molecules. Since oil and water do not mix, the addition of a small amount of amphiphile brings them together with formation of complex molecular structures, which range from disordered complexes to regular ordered complexes of molecules. These constructions is defined by the properties of surfactant molecules which could be presented by two types of water-like polar head which prefers water environment and oil-like amphiphile tail which prefers oil.

Note, that the roles of oil and water are reversed in so-called "inverted" micelles. (see Fig. 1)

The ultimate goal of our efforts is to investigate the necessary conditions of formation such systems as micelles. In this work we represent the results obtained by statistical thermodynamic method the case of one-component and two-component system (size distribution, i.e the dependence the concentration of N-mers on number of molecules in aggregates) . Results are generalised for many-component system. Conditions of pure or mixed micelles formation are also determined.

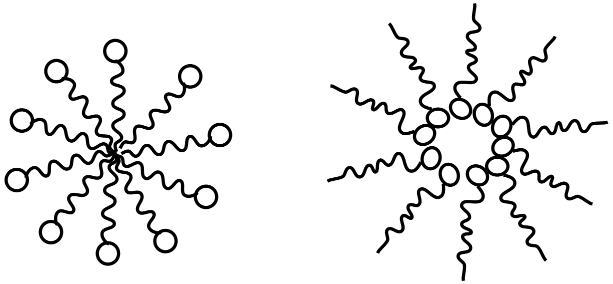


Figure 1. *Direct (on the left) and inverted (on the right) micelles*

1. The Thermodynamic Principles of Self-Assembly

Before the consideration of statistical mechanical treatment of self-assembling problems we briefly review the thermodynamical description of micelle formation. We represents the basic equations of self-association in general terms of thermodynamics.([1])

Equilibrium thermodynamics requires that in a system of molecules which form aggregated structures in solutions the chemical potential of all identical molecules in different aggregates must be the same. This may be expressed as

$$\mu_N = \mu_N^0 + \frac{kT}{N} \ln \frac{X_N}{N} = \text{const} \tag{1.1}$$

where μ_N is the chemical potential of a molecule in aggregate with the aggregation number N, μ_N^0 is the standard part of the chemical potential, X_N is the concentration of molecules in aggregate with number N. According to the mass action law the rate of association is equal to $K_1 X_1^N$ and the rate of dissociation is $\frac{K_N X_N}{N}$. The equilibrium constant $K = \frac{K_1}{K_N} = exp[\frac{-N(\mu_N^0-\mu_1^0}{kT})]$ and

$$X_N = N\left(X_1 e^{\frac{\mu_1^0-\mu_N^0}{kT}}\right)^N \tag{1.2}$$

where μ_1^0 and X_1 corresponds to monomers in solution. Note, that this expression may be rewritten as

$$X_N = N\left(X_1 e^{\alpha}\right)^N e^{-\alpha} \tag{1.3}$$

where α is a positive constant depending on the strength of intermolecular interactions. Note, that this constant α is introduced via relation $\frac{\mu_1^0-\mu_N^0}{kT} = \alpha(1-\frac{1}{N})$ Note, that $\frac{X_N}{N}$ is the mole fraction of the Nth species so that the total concentration C of surfactant is given via relation

$$C = \sum_N X_N \tag{1.4}$$

Aggregates form only when there is the difference in cohesive energies between the molecules in aggregated and dispersed states. If the molecules in different sized aggregates experience the same interactions with their neighbours, the value of μ_N^0 will remains constant in aggregates with different aggregation number. Thus for $\mu_1^0 = \mu_2^0 = \mu_3^0 = \cdots = \mu_N^0$ the concentration of N-mers

$$X_N = N X_1^N \tag{1.5}$$

Since $X_1 < 1$ we must have $X_N \ll X_1$, so that most of molecules will be in the monomer state (with the aggregation number $N = 1$). For sufficiently low concentration of monomers we have that $X_1 > X_2 > X_3 > \cdots$. Thus at low concentrations most of molecules will be in dispersed states. Since X_N never exceed unity it is clear that once monomer concentration approaches $e^{-\alpha}$ it can increase no further as shown in Fig. 2. This monomer concentration is called the critical aggregation concentration or, as a rule, critical micelle concentration (CMC).(see [1]) Thus $X_{1\,cr} = e^{-\alpha}$.

Micelles in equilibrium with each other have a finite distribution on sizes about some mean value. Since at the concentrations greater then CMC we have $X_1 e^{\alpha} \leq 1$, then the Eq. (1.3) shows that $X_N \propto N$ for small N and only for large N the concentration X_N decreases to zero as N approaches infinity. The total concentration of molecules

$$C = \sum_{N=1}^{\infty} X_N = \sum_{N=1}^{\infty} \left(N X_1 e^{\alpha}\right)^N e^{-\alpha} \tag{1.6}$$

or

$$C = \frac{X_1}{\left(1 - X_1 e^{\alpha}\right)^2} \tag{1.7}$$

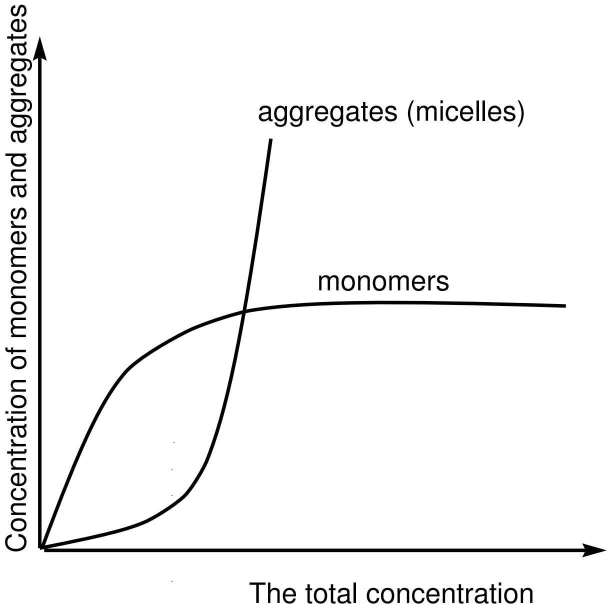


Figure 2. *Monomer and aggregate concentration as a function of total concentration (schematic)*

Thus the concentration of monomers

$$X_1 = \frac{(1 + 2Ce^{\alpha}) - \sqrt{1 + 4Ce^{\alpha}}}{2Ce^{2\alpha}} \tag{1.8}$$

As we shall see at low concentrations (i.e $Ce^{\alpha} \ll 1$) this gives that $X_1 \simeq C$, whereas at high concentrations (i.e $Ce^{\alpha} \gg 1$) the concentration of monomers $X_1 \approx CMC$ as expected. Also above CMC the density distribution of molecules in aggregates of N molecules is given by inserting the above equation into Eq. (1.2), obtaining

$$X_N \approx N[1 - \frac{1}{\sqrt{Ce^{\alpha}}}]^N e^{-\alpha} \approx Ne^{-N/\sqrt{Ce^{\alpha}}} \times e^{-\alpha} \tag{1.9}$$

This function peaks at $\frac{\partial X_N}{\partial N} = 0$ which occurs at $N_{max} = \sqrt{Ce^{\alpha}}$. Finally, the density distribution of aggregates above the CMC is

$$X_N = Ne^{-N/N_{max}} \times e^{-\alpha} \tag{1.10}$$

i.e the concentration of large aggregates decays exponentially with increasing of number N. Thus the distribution on sizes is very broad with the concentration of aggregates first increasing with N for small aggregates and decaying gradually to zero at large N. This distribution is represented graphically. (see Fig. 3)

2. Statistical-Mechanical Approach: Basic Equations

2.1. One-component System

The statistical-mechanical approach we begin from consideration of a system of molecules with only strongly attractive interactions. Let we investigate the simplified model in which we assume that all particles interact only with the central particle and do not interact between themselves. We consider a one-component system. The grand partition function of an open system with chemical potential μ and the activity $z = e^{\beta\mu}$ is expressed as (see [2])

$$\Xi(t, V, \mu) = \sum_N z^N \frac{Z_N(T, V)}{N!} \tag{2.1}$$

This partition function is related to the pressure P and to the density ρ by expressions

$$\beta P = \ln \Xi(T, V, \mu) \tag{2.2}$$

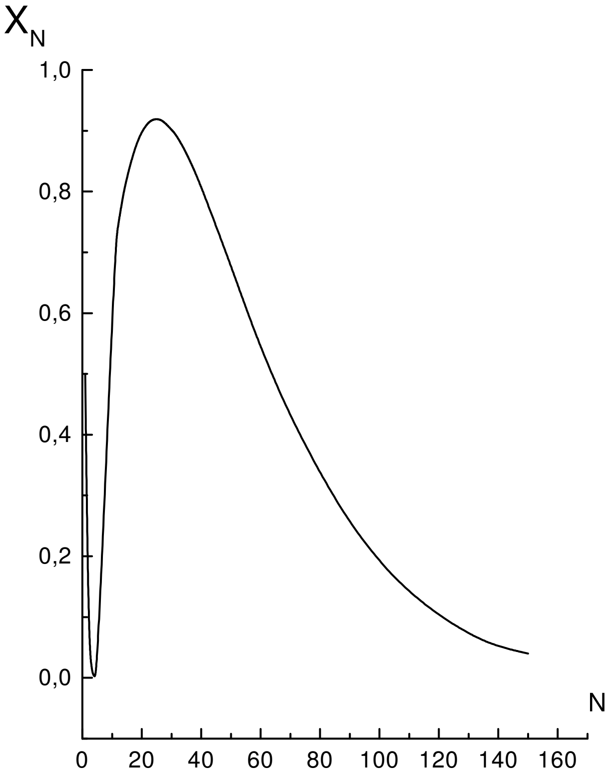


Figure 3. *Distribution of molecule concentration* X_N *as a function of aggregation number* N *in the case of a one-component system. Monomer concentration* $X_1 = 0,5$*, and the value of constant* $\alpha = 1,25$*.*

$$\rho(z) = z\frac{\partial \ln \Xi(T,V,\mu)}{\partial z} = z\frac{\partial \beta P}{\partial z} \tag{2.3}$$

respectivelly. According to microscopic (statistical-mechanical) approach we represent the equation of state via relation (see [2], [3])

$$\beta P = \sum_{N=0}^{\infty} b_N z^N \tag{2.4}$$

and the density

$$\rho = \sum_{N=0}^{\infty} N b_N z^N \tag{2.5}$$

Here b_N is N-th the group coefficients, N is the size of group.

If we take into consideration only such interactions which hold to aggregate formation (our model allow us to suppose that $b_3 = b_2^2, \ldots, b_N = b_2^{N-1}$) then the equation of state is presented as

$$\beta P = \frac{z}{1 - b_2 z} \tag{2.6}$$

and expression for the density, respectively

$$\rho = \frac{z}{(1 - b_2 z)^2} \tag{2.7}$$

The critical activity then

$$z_{cr} = \frac{1}{b_2} \tag{2.8}$$

Members of expansions on activities can be interpreted as concentrations of monomers and multiparticle complexes (see [3]). Because of this interpretation relation between thermodynamic approach and statistical one is carried out. According to this the critical activity

$$z_{cr} = X_{1cr}, \tag{2.9}$$

where X_1 is the concentration of monomers, and $X_{1cr} = z_{cr}$ is the critical micelle concentration. Thus the expression (2.7) for the density is given in the form similar (1.7) where $z = X_1$ and $b_2 = e^{\,\alpha}$.

However, considered description is correct only for the strong attractive interactions which leads for such aggregation. In order to take into account the usual nonassociative interactions we can use the thermodynamic perturbation theory which was developed by Wertheim ([4] - [6]) for the treatment of associative phenomena in associative fluids.

The original theory was developed in finite many-density formalism. In particular in two-density formalism the singlet distribution function $\rho(1)$ is separated into two terms

$$\rho(1) = \rho_0(1) + \rho_1(1)$$

where $\rho_0(1)$ is singlet distribution function for monomer particles and $\rho_1(1)$ is the bounded part of the singlet distribution function.

According to Werthein diagram analysis ([4])

$$\rho(1) = \rho_0(1) + \rho_0(1) \int g_{00}(12) f_{as}(12) \rho_0(2)\, d(2) \tag{2.10}$$

In homogenous case the total density $\rho(1)$ and the density of monomers $\rho_0(1)$ are related as

$$\rho = \rho_0 + \rho_0^2 \int f_{as}(r) g_{00}(r)\, d(r) \tag{2.11}$$

where $f_{as}(12) = e^{-\beta U(12)} - 1$ is associative Mayer function. and $U(12)$ is the potential of associative interaction between the molecules, $g_{00}(12)$ is nonassociative part of the pair distribution function. Substituting

$$\int f(12) g_{00}(12)\, d(2) = 2K_1$$

leads to the expression for density :

$$\rho = \rho_0 + 2\rho_0^2 K_1 \tag{2.12}$$

In order to generalize this result for self-assembling case we represent (2.10) in the following form:

$$\begin{aligned} \rho(1) = \rho_0(1) &+ \rho_0(1) \textstyle\int g_{00}(12) f(12) \rho_0(2)\, d(2) \\ &+ \rho_0(1) \textstyle\int g_{000}(132) f(123) \rho_0(2) \rho_0(3)\, d(2)\, d(3) + \ldots \end{aligned}$$

For nonassociative part of distribution function we consider the following approximation:

$$g_{000}(123) = g_{00}(12) g_{00}(23),$$

$$g_{\underbrace{00...00}_{N}}(123...N) \;=\; g_{00}(12) g_{00}(23) ... g_{00}(N-1,N)$$

which are exact for one-dimensional systems with short-range interactions ([2]). We also put

$$f(123) = f(12) f(13),$$

$$f(123...N) = f(12)f(23)...f(N-1,N)$$

In result

$$\int\int f(123)g_{00}(123)\,d(2)\,d(3) =$$

$$= \int\int f(12)g_{00}(12)f(23)g_{00}(23)\,d(2)\,d(3) = 3K_2 = 3K_1^2$$

and

$$\underbrace{\int\int...\int}_{N} f(123\ldots N)g_{\underbrace{00...00}_{N}}(123...N)d(2)d(3)...d(N) =$$

$$= \underbrace{\int\int...\int}_{N} f(12)g_{00}(12)f(23)g_{00}(23)...f(N-1,N)\times$$

$$\times g_{00}(N-1,N)d(2)d(3)...d(N) = N\,K_{N-1} = N\,K_1^{N-1}$$

and expression for the density can be presented in the following form:

$$\rho = \rho_0 + 2\rho_0^2 K_1 + 3\rho_0^3 K_1^2 + \ldots \tag{2.13}$$

or this may be formally rewritten the form similar (2.7):

$$\rho = \frac{\rho_0}{(1 - K_1\rho_0)^2} \tag{2.14}$$

Hence, we obtain the same expression for the density as we had earlier. Thus we get an evidence of using z-expansion in our formulated theory. And we took into consideration not only associative interactions ([1]) but also short-range one.

Due to the strong-range character of associative interactions $f_{as}(r)$ has δ-function form:

$$f_{as}(r) = B_2\delta(r - \sigma)$$

where B_2 is the second virial coefficient and σ means the size of the particle. In result:

$$K_1 = \frac{1}{2}\int B_2\,\delta(r\sigma)dr = b_2 g_{00},$$

where $g_{00} = g_{00}(\sigma)$ is the contact value of pair correlation function for the system with non-associative interactions and $B_2 = 2b_2$. ([2])

Then the expression Eq. (2.13) for the density takes the next form:

$$\rho = \rho_0 + 2b_2 g_{00}\rho_0^2 + 3b_2^2 g_{00}^2\rho_0^3 + \ldots, \tag{2.15}$$

As we mentioned above, the members of expansion on activities can be interpreted as concentrations of monomers and multiparticle complexes. Using such concentrations, we may write the expressions for the monomer density as $X_1 = \rho_0$ and for the concentration of N-mers as $X_N = Nb_2^{N-1}g_{00}^{N-1}\rho_0^N$. According to the thermodynamic approach

$$X_N = N(X_1 e^{\alpha})^N e^{-\alpha} = NX_1^N e^{\alpha(N-1)} \tag{2.16}$$

Comparing the last two equations one obtains that

$$g_{00}b_2 = e^{\alpha} \tag{2.17}$$

Thus the last equation carries out the relation between thermodynamic and statistical approaches to the assembling phenomena in the case of one-component systems.

The expression (2.14) for the density in Wertheim perturbation theory corresponds to expression (2.7). It means that we can write appropriate expression for pressure:

$$\beta(P - P_0) = \frac{\rho_0}{1 - b_2 g_{00}\rho_0} \tag{2.18}$$

and P_0 is that part of pressure which corresponds to the system without associative interactions.

2.2. Many-component Systems

The obtained results for a one-component system may be generalized for many-component system. In this case the equation of state is given by the same expression, i.e

$$\beta P = \frac{\hat{z}}{\hat{1} - \hat{b}_2\hat{z}} \tag{2.19}$$

but here $\hat{z}$ is $(n \times n)$-matrix of activities,

$$\hat{z} = \begin{pmatrix} z_{11} & 0 & \ldots & 0 \\ 0 & z_{22} & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & \ldots & z_{nn} \end{pmatrix}$$

$\hat{b}_2$ is $(n \times n)$-matrix of the second virial coefficients,

$$\widehat{b_2} = \begin{pmatrix} b_{11} & b_{12} & \dots & b_{1n} \\ b_{21} & b_{22} & \dots & b_{2n} \\ \dots & \dots & \dots & \dots \\ b_{n1} & b_{n2} & \dots & b_{nn} \end{pmatrix}$$

$\hat{1}$ is unit diagonal $(n \times n)$-matrix, where n is the number of different sorts of molecules in mentioned system. The elements of $\widehat{b_2}$-matrix are defined by the extent of interactions between the molecules of the same or different sorts. To take into account all types of interactions in the case of many-component systems one rewrites the above expression as

$$\beta(P - P_0) = \frac{\hat{\rho}_0}{\hat{1} - \hat{K}_1 \hat{\rho}_0} \tag{2.20}$$

Here $\widehat{K_1^{ij}} = b_2^{ij} g_{00}^{ij}$. Note, that $i = \overline{1,n}$, $j = \overline{1,n}$. It's clear that $\hat{\rho}_0$ is $(n \times n)$-diagonal matrix, elements of which are defined by the concentrations of molecules of each sort,

$$\hat{\rho}_0 = \begin{pmatrix} \rho_0^1 & 0 & \dots & 0 \\ 0 & \rho_0^2 & 0 & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \rho_0^n \end{pmatrix}$$

g_{00}^{ij} is the contact value of pair correlation function of the system with non-associative interaction for the particles of each sort.

We may introduce the last expression for pressure as

$$\beta(P - P_0) = -\sum_{\alpha,\beta} \frac{\partial}{\partial K_{1_{\alpha,\beta}}} \ln\det(\hat{1} - \hat{K}_1 \hat{\rho}_0) \tag{2.21}$$

Here subscripts α and β denotes the sort of particle. According to (2.3), expression for density can be written in the next form:

$$\rho^\alpha = \rho_0^\alpha \frac{\partial}{\partial \rho_0^\alpha} \sum_{\alpha,\beta} \frac{\partial}{\partial K_{1_{\alpha,\beta}}} \ln\det(\delta_{\alpha,\beta} - K_1^{\alpha,\beta} \rho_0^\alpha) \tag{2.22}$$

where ρ^α is the density of molecules of sort α and ρ_0^α is the density of monomers of the same sort.

2.3. Two-component System

To illustrate the developed theory we consider a two-component system and we represent the applying of general equations for many-component system to two-component system. In this case the second virial coefficient is represented as a sum of b_{11}, b_{12} that is equal to b_{21} and b_{22}, i.e

$$b_2 = b_{11} + b_{12} + b_{21} + b_{22} \tag{2.23}$$

Here b_{11} describes the interactions between the molecules of the first sort, b_{22} describes the interaction between the molecules of the second sort and $b_{12} = b_{21}$ describes the interaction between the molecules of different types.

As we mentioned above, the equation of state for many-component systems

$$\beta(P - P_0) = \frac{\hat{\rho}_0}{\hat{1} - \hat{K}_1 \hat{\rho}_0}$$

In the case of two-component system the matrix of concentrations seems as

$$\hat{\rho}_0 = \begin{pmatrix} \rho_0^1 & 0 \\ 0 & \rho_0^2 \end{pmatrix}$$

and the matrix $\widehat{K_1}$, respectively

$$\widehat{K_1} = \begin{pmatrix} b_{11}\, g_{00}^{11} & b_{12}\, g_{00}^{12} \\ b_{21}\, g_{00}^{21} & b_{22}\, g_{00}^{22} \end{pmatrix}$$

and $\hat{1}$ is (2×2)-unit diagonal matrix. Note, that the elements of $\hat{b}_2$-matrix defines the strength of interaction between the particles of different or the same sorts.

We may introducing the equation of state in the case of two component system via relation

$$\beta(P - P_0) = -\sum_{\alpha,\beta=1,2} \frac{\partial}{\partial b_{\alpha,\beta}} \ln\det(\hat{1} - \hat{b}_2 \hat{\rho}_0) \tag{2.24}$$

or

$$\beta(P - P_0) = -\left(\frac{\partial}{\partial b_{11}} + 2\frac{\partial}{\partial b_{12}} + \frac{\partial}{\partial b_{22}} \right) \ln\det(\hat{1} - \hat{b}_2 \hat{\rho}_0)$$

where $K_1^{ij} = b_2^{ij} g_{00}^{ij}$ is again defined as b_2^{ij} Doing some simplifications one obtains the equation of state for two-component system in the next form:

$$\beta(P - P_0) = \frac{\rho_0^1(1 - b_{22} g_{00}^{22} \rho_0^2) + \rho_0^2(1 - b_{11} g_{00}^{11} \rho_0^1) + 2\rho_0^1 \rho_0^2 b_{12} g_{00}^{12}}{1 - b_{11} g_{00}^{11} \rho_0^1 - b_{22} g_{00}^{22} \rho_0^2 + \rho_0^1 \rho_0^2 (b_{11} b_{22} g_{00}^{11} g_{00}^{22} - b_{12}^2 {g_{00}^{12}}^2)}$$

(2.25)

Investigating the dominator of equation of state, i.e investigating the equation

$$1 - b_{11}g_{00}^{11}\rho_0^1 - b_{22}g_{00}^{22}\rho_0^2 + \rho_0^1\rho_0^2(b_{11}b_{22}g_{00}^{11}g_{00}^{22} - b_{12}^2{g_{00}^{12}}^2) = 0$$

one finds the critical activities for particles of each sort. If the concentration of the first-sort molecules is much greater than concentrations of the second-sort molecules or if $b_{22} \longrightarrow 0$ then the critical concentration of the first-sort molecules is given via relation

$$\rho_0^1 cr = \frac{1}{b_{11}g_{00}^{11} + b_{12}^2{g_{00}^{12}}^2\rho_0^2} \qquad (2.26)$$

Analogically if the $b_{11} \longrightarrow 0$ then the critical concentration for the molecules of the second sort is represented in the similar form:

$$\rho_0^2 cr = \frac{1}{b_{22}g_{00}^{22} + b_{12}^2{g_{00}^{12}}^2\rho_0^1} \qquad (2.27)$$

Thus we conclude that the addition of another(i.e the second) component in such system as solution reduces the value of critical micelle concentration. To investigate Eq. (2.3) in detail one introduces new variables $\rho_0 = \rho_0^1 + \rho_0^2$ as the density of monomers and $X = \frac{\rho_0^1}{\rho_0^1+\rho_0^2}$ as the concentration of monomers of the first sort. Thus the dominator of state equation may be represented as

$$\rho^2 X(1-X)(b_{11}b_{22}g_{00}^{11}g_{00}^{22} - b_{12}^2{g_{00}^{12}}^2)$$

$$-\rho(b_{11}g_{00}^{11}X + b_{22}g_{00}^{22}(1-X)) + 1 = 0$$

Solution of the above equation depends on relations between the parameters b_{11}, b_{22} and b_{12}.

Rewriting the Eq. (2.2.3) for two-component case after some transforming and simplifications we have, that the densities of molecules are defined as

$$\rho_1 = \rho_0^1\frac{[1 - \rho_0^2(b_{22}g_{00}^{22} - b_{12}g_{00}^{12})]^2}{[1 - b_{11}g_{00}^{11}\rho_0^1 - b_{22}g_{00}^{22}\rho_0^2 + \rho_0^1\rho_0^2(b_{11}b_{22}g_{00}^{11}g_{00}^{22} - b_{12}g_{00}^{12}]^2}$$

(2.28)

and

$$\rho_2 = \rho_0^2\frac{[1 - \rho_0^1(b_{11}g_{00}^{11} - b_{12}g_{00}^{12})]^2}{[1 - b_{11}g_{00}^{11}\rho_0^1 - b_{22}g_{00}^{22}\rho_0^2 + \rho_0^1\rho_0^2(b_{11}b_{22}g_{00}^{11}g_{00}^{22} - b_{12}g_{00}^{12}]^2}$$

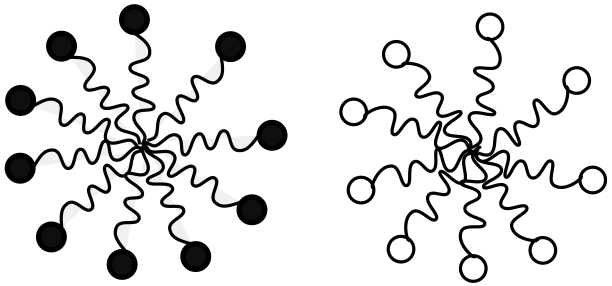
(2.29)

for the molecules of the first sort and the second sort, respectively. We conclude that the results obtained for the two-component system fully agree with the same one for one-component system under the condition that the concentration of one of the sorts approaches to zero.

Neglecting by the interactions between the molecules of different sorts (i.e we suppose that $b_{12} \ll b_{11}$ and $b_{12} \ll b_{22}$) the total concentration of molecules may be represented as a sum of molecules densities:

$$\rho = \frac{\rho_0^1}{(1 - \rho_0^1 b_{11}g_{00}^{11})^2} + \frac{\rho_0^2}{(1 - \rho_0^2 b_{22}g_{00}^{22})^2} \qquad (2.30)$$

Thus we conclude if the interactions between the molecules of different types is too small, that in such system one observes the formation of two types of micelles: one of them consists only of first-sort molecules, the second one consists only of molecules of another type.



In this case, as a rule, we have to deal with two different values of critical micelle concentration, which define by relations

$$\rho_{0\,cr}^1 = \frac{1}{b_{11}g_{00}^{11}} \qquad (2.31)$$

and

$$\rho_{0\,cr}^2 = \frac{1}{b_{22}g_{00}^{22}} \qquad (2.32)$$

for the molecules of the first sort and the second one, respectively. One concludes that the distribution on sizes of formed aggregates in such system is analogical to the same one that we have in the case of one-component system because of analogical structure of Eq.(2.30) and Eq.(1.7). (see Fig. 4)

Generally in dependence on relations between the parameters b_{11}, b_{22} and b_{12} in the system three types of different micelles can be formed:

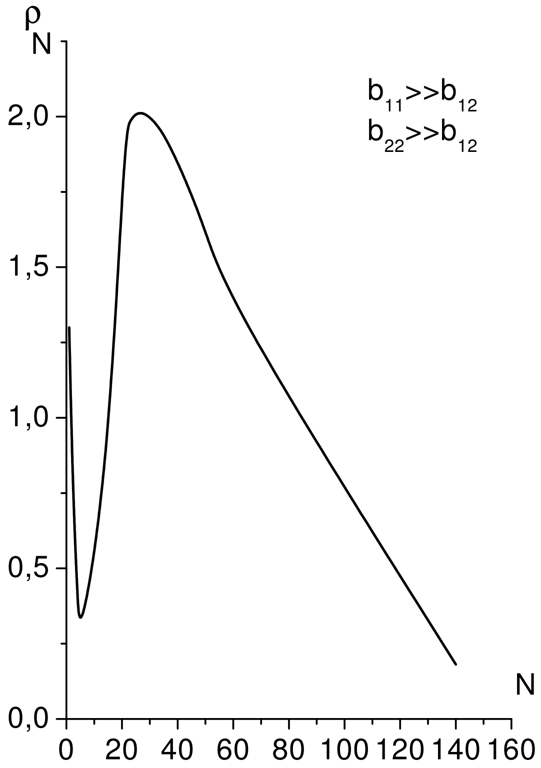


Figure 4. *Distribution on sizes of associated structures in the case of a two-component system at small interaction between the molecules of different types. Monomer concentrations* $\rho_0^1 = 0,5$, $\rho_0^2 = 0,8$ *and the values of parameters are* $b_{11} = 0,22$, $b_{22} = 0,77$, $b_{12} = 0,02$.

(i) micelles consisting only of molecules of the first sort ("pure" micelles);

(ii) micelles consisting only of molecules of the second sort (also "pure" micelles);

(iii) micelles consisting of molecules of the first sort and of the second one as well (mixed micelles). Note, that it is probable the realization of various combinations of above mentioned cases.

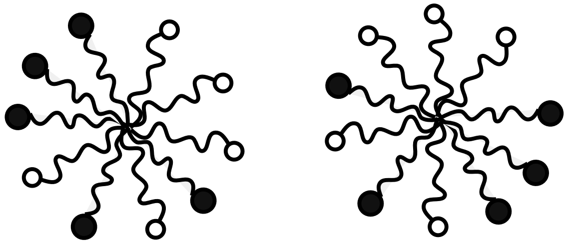
It is possible, that the interactions between the molecules of the different sorts can be much greater than the interactions between identical molecules, i.e $b_{12} \gg b_{11}$, $b_{12} \gg b_{22}$. Then according to Eq. (2.3) and Eq. (2.3) under the mentioned conditions the density of the molecules of the first sort is

$$\rho_1 = \rho_0^1 \frac{(1+\rho_0^2 b_{12} g_{00}^{12})^2}{(1-\rho_0^1 \rho_0^2 b_{12}^2 {g_{00}^{12}}^2)^2} \tag{2.33}$$

and the same one towards the second-sort molecules

$$\rho_2 = \rho_0^2 \frac{(1+\rho_0^1 b_{12} g_{00}^{12})^2}{(1-\rho_0^1 \rho_0^2 b_{12}^2 {g_{00}^{12}}^2)^2} \tag{2.34}$$

The densities of the both-sort molecules depend on the meaning of the coefficient b_{12}. Thus the total concentration C depends only on the value of the coefficient b_{12} which is defined by the interaction between the molecules of different sorts. Finally it means the formation only of mixed micelles because of predominating interaction between the molecules of different sorts.



The most interesting situation occurs in symmetrical case, when concentrations (or critical activities) of the both-sort molecules are the same, i.e when $\rho_0^1 = \rho_0^2$ and introduces as ρ_0, and the total densities $\rho_1 = \rho_2 = \rho$. Then the densities ρ_1 and ρ_2 are

$$\rho = \rho_0 \frac{(1+\rho_0 b_{12} g_{00}^{12})^2}{(1-\rho_0^2 b_{12}^2 {g_{00}^{12}}^2)^2} \tag{2.35}$$

or

$$\rho = \frac{\rho_0}{(1-\rho_0 b_{12} g_{00}^{12})^2} \tag{2.36}$$

Thus we assume that in this case critical micelle concentration depends on the extent of interaction between the molecules of different types and is defined as $\rho_0 = 1/b_{12}g_{00}^{12}$. The structure of the Eq. (2.36) is fully analogical to the same one as we have above (see Eq. (2.30)). This means the identity of size distributions in these two cases, but note that given results is justify only for symmetrical case when $\rho_0^1/\rho_0^2 = 1$. In more general case when $\rho_0^1/\rho_0^2 \neq 1$, the dominator of Eq. (2.33) and Eq. (2.34) seems as

$$(1-\rho_0^1\rho_0^2 b_{12}^2 g_{00}^{12^2})^2 = (1-\sqrt{\rho_0^1\rho_0^2}\, b_{12} g_{00}^{12})^2 (1+\sqrt{\rho_0^1\rho_0^2}\, b_{12} g_{00}^{12})^2$$

and the total density of molecules can be represented as

$$\rho = \rho_1 + \rho_2 = \tag{2.37}$$

$$\frac{\rho_0^1(1+\rho_0^2 b_{12} g_{00}^{12})^2 + \rho_0^2(1+\rho_0^1 b_{12} g_{00}^{12})^2}{(1-\rho_0^1\rho_0^2 b_{12}^2 g_{00}^{12^2})^2}$$

We can see that the total density depends on the value of the coefficients b_{12}.

The example of distribution on sizes in the case of two-component system with predominating association between surfactant molecules of different types is presented on Fig.5

Note, that all given distributions differ one from another by the value of their parameters b_{11}, b_{22} and b_{12}. Obtained result is represented graphically.

3. Concluding Remarks

In this paper the view of the thermodynamic (phenomenological) and microscopic (statistical-mechanical) approaches in the theory of self-assembling systems is presented. Thermodynamic principles of self-assembly are formulated and the statistical-mechanical arguing of the thermodynamic approach is carried out. Developed theory is generalized on the case of many-component systems.

Using the multi-density formalism of Wertheim theory in statistical thermodynamics of associated system we developed existing theory for self-assembling case. Comparing the expressions for concentration in thermodynamic approach and in statistical-mechanical formalism we

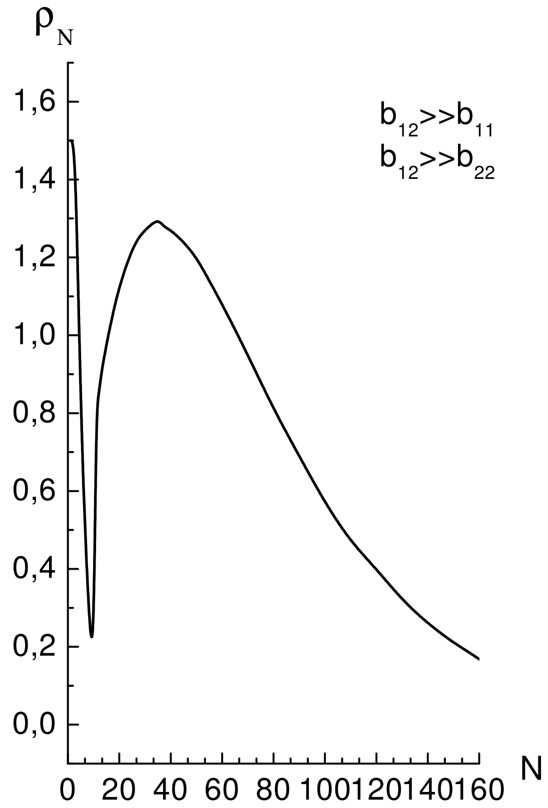


Figure 5. *Distribution on sizes of associated structures in the case of a two-component system at the predominating interaction between the molecules of different types. Monomer concentrations* $\rho_0^1 = 0,8,\quad \rho_0^2 = 0,7$ *and the values of parameters are* $b_{11} = 0,008,\ \ b_{22} = 0,031,\ b_{12} = 0,5$.

obtain relation between thermodynamic and statistical-mechanical description of a system.

Investigating the problems of self-assembly in water-micellar system we conclude that the necessary conditions for the formation of such molecular aggregates as micelles is the achievement of critical micelle concentration. Dependence of critical micelle concentration on the thermodynamic and microscopic parameters is also obtained. Conditions of formation of pure and mixed micelles are investigated too. It is shown that structure of formed molecular aggregates in the case of a many-component system defines by the extent of interactions between the molecules of different types.

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