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Thermodynamic and Kinetic Theory of Ionic Micellar Systems: 1. Work of Aggregation

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Abstract—The approach to the thermodynamics of molecular aggregates based on the methods of the previously developed nucleation theory is extended to including ionic aggregative systems ~~based on~~ with the choice of the real concentration of monomeric ions of surfactants as a standard concentration of aggregates. Results are also generalized to multicomponent systems and a new expression for the work of aggregation is derived. Three models of ionic aggregates are analyzed, i.e., bare aggregate (containing no counterions), fully dressed aggregate (with maximal number of counterions), and dressed aggregate with arbitrary numbers of counterions. In the consideration of the ionic aggregate as a complex ion that yields simpler ions upon dissociation, the notion of the average activity coefficient of the ionic aggregate is introduced. Characteristics of real dressed ionic aggregates are studied. Restrictions in the use of the model of the dressed ionic aggregate are revealed.

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INTRODUCTION

Despite the differences in the mechanism and driving force of the processes of nucleation and micellization of surfactants, they have close similarities because they are reduced to the aggregation (association, clusterization) of molecules or ions. The nucleation leads to phase transition, i.e., to the formation of macroscopic phase. Micellization is ended with the establishment of an equilibrium distribution of nanosized micelles over aggregation numbers. If we use phase terminology, the micelle can be referred to as "microphase," which has no macroscopic analogs and is not a nucleus of any phase [1]. If we digress from the differences in the final states, as in the cases of nucleation and micellization, the same type of development of the process takes place and is characterized by passage over the energy barrier, which is of special significance for the kinetics of the process. Seemingly, the formulation of the kinetic theory should be of one type; however, historic circumstances arose such that micellization was described based on the law of mass action. Ideas and apparatus of the nucleation theory, which were developed in detail by generations of scientists, have not been used in practical applications for a long time.

In connection with this, we undertook a cycle of studies on the kinetic theory of micellization [2–18] based on the concepts of the nucleation theory. It is natural that we ~~should~~ needed also ~~get acquainted with~~ to analyze the thermodynamic aspect of the problem, particularly ~~with~~ procedures for determining the work of micellization (or, generally speaking, the work of aggregation). Compared to the traditional approach (see, e.g., [1]), the new definition of this work (equivalent to that used in the nucleation theory) appears to be quite unusual because it coincides with the standard work of micellization, when the real concentration of monomeric molecules of surfactants at equilibrium with micelle is used as a standard concentration of micelles (and other molecular aggregates of surfactants in a system). Since the concentration of monomers is a variable parameter, the standard work of micellization (in the general case, the standard work of aggregation) becomes variable. The study of the dependences of the thus defined work of aggregation on the aggregation number and relevant energy barriers for direct and reverse transitions between premicellar and micellar states of aggregates on the concentration of surfactant monomers was an important link for constructing the kinetic theory of micellization in our works.

The aforementioned cycle of studies refers to nonionic surfactants and, now, we have the problem of generalizing all that has been done before to the case of ionic surfactants. In fact, the problem is formulated even more broadly. The point is that, in view of the electroneutrality condition, the number of ions in an aggregative system cannot be smaller than two. However, this means that the transition from nonionic to ionic surfactants also implies ~~that~~ the transition from a single-component (if the type of particles participating in the aggregation is assumed to be the component) to molecular and ionic multicomponent aggregates. The impression of the multicomponent state becomes stronger when the solvation of ions is taken into account. It can be said that the problem of generalizing the ~~available data~~ existing approach to multicomponent systems is posed; moreover, as was already demonstrated in the traditional approach [1], many relations appeared to be applicable

simultaneously to both the aggregates of ionic surfactants and the aggregates of the mixture of nonionic surfactants with the same aggregation numbers. The only difference here is that the overall number of individual types of particles in the case of ions should satisfy the electroneutrality condition and cannot be taken in arbitrary proportion as in the case of nonionic surfactants.

At the same time, there are problems that are specific for ionic surfactants. Among these problems, e.g., is the effect of background electrolytes on the aggregation processes. However, the most significant problem is the binding of counterions with ionic aggregates. Although the notion of term binding is conditional [1], attempts to connect this term with thermodynamics are rather interesting [19–22]. When treating micelles and ionic aggregates as dressed species, i.e., covered by counterions, the possibility arises of using the approximation of an ideal solution that opens the way for simple ~~decisions~~ relations. However, it should be noted that all that has been done so far in this field is not faultless and needs to be corrected.

It is clear from all of the above-said that there is a broad field of activity and real opportunity for further development of the theory of micellization. First of all, it is necessary to broaden available thermodynamic basis and this is precisely the aim of this communication.

~~0.~~ 1. CHOICE OF STANDARD STATE AND WORK OF AGGREGATION IN MULTICOMPONENT SYSTEM

The composition of a complex molecular ionic aggregate composed of arbitrary number of particles of different types, is characterized by the set of aggregation numbers $\{n\} \equiv n_1, n_2, \ldots$ of these particles and total aggregation number $n \equiv \sum_i n_i$. Under isobaric-isothermic conditions, which are typical for laboratory experiments, we will be interested in the changes in the Gibbs energy of solution, ΔG, upon the formation of one additional aggregate $\{n\}$, which is defined as [1]

$$\Delta G = \mu_{\{n\}} - \sum_i n_i \mu_i, \tag{1.1}$$

where $\mu_{\{n\}}$ is the chemical potential of aggregates $\{n\}$ in solution and μ_i is the chemical potential of monomeric particles of the ith type. Strictly speaking, for charged particles, electrochemical potentials containing terms (additional to chemical potentials) of type $ez_k\varphi$ (where e is the elementary positive charge, z_k is the charge number, and φ is the phase electric potential) should appear in expression (1.1). However, these terms are eliminated due to that fact that charges in both terms of the right-hand side of equality (1.1) are ~~identical~~ equal as shown below:

$$z_{\{n\}} = \sum_i n_i z_i. \tag{1.2}$$

This circumstance allowed equality (1.1) to be written in terms of the common chemical potentials for both molecules and ions. Note that, in the published literature on micellization [1], the ΔG value is called the work of micellization (aggregation). The right-hand side of equality (1.1) taken with opposite sign is the chemical affinity for aggregation. At equilibrium, the ΔG value and chemical affinity are nullified; then, from Eq. (1.1), we obtain the known condition of aggregation equilibrium

$$\mu^{(e)}_{\{n\}} = \sum_i n_i \mu_i, \tag{1.3}$$

where superscript (e) denotes the state of aggregation equilibrium at preset chemical potentials of monomers, μ_i.

Chemical potentials $\mu_{\{n\}}$ and μ_i are given by the following expressions:

$$\mu_{\{n\}} = G^0_{\{n\}} + kT\ln(\Lambda^3_{\{n\}} a_{\{n\}}), \tag{1.4}$$

$$\mu_i = g^0_i + kT\ln(\Lambda^3_i a_{i1}), \tag{1.5}$$

where $G^0_{\{n\}}$ is the Gibbs energy of single aggregate with quiescent center of mass in pure solvent (in the absence of other aggregates), g^0_i is the analogous value for single particle of the ith type, k is Boltzmann's constant, T is the temperature, Λ is the average de Broglie wavelength, and a is the activity (thermodynamic, do not mix it with surface activity). Indices $\{n\}$ and i are referred to aggregates and types of relevant particles, respectively; additional index $_1$ denotes that the particle belongs to the monomeric form of the ith particles. The $\Lambda^{-3}_{\{n\}}$ and Λ^{-3}_i are partition functions of the translational motion of the aggregate and single particle, respectively, as shown below:

$$\Lambda^{-3}_{\{n\}} = \frac{(2\pi m_{\{n\}} kT)^{3/2}}{h^3}, \tag{1.6}$$

$$\Lambda^{-3}_i = \frac{(2\pi m_i kT)^{3/2}}{h^3}, \tag{1.7}$$

where h is the Planck constant and $m_{\{n\}}$ and m_i are masses of the aggregate and single particle, respectively, ~~connected~~ linked by the expression

$$m_{\{n\}} = \sum_i n_i m_i. \tag{1.8}$$

Expressions (1.6)–(1.8) establish the relation between lengths $\Lambda_{\{n\}}$ and Λ_k in the following form:

$$\frac{\Lambda_{\{n\}}}{\Lambda_k} = \left(\frac{m_k}{m_{\{n\}}}\right)^{1/2} = \left(n_k + \frac{1}{m_k}\sum_{i\neq k} n_i m_i\right)^{-1/2}. \tag{1.9}$$

The $kT\ln\Lambda_{\{n\}}^3$ and $kT\ln\Lambda_i^3$ reflect contributions of indicated partition functions to the Gibbs energy.

The standard state of the solute of ith type is chosen in physical chemistry by setting standard activity a_i^s (superscript s denotes ~~magnitudes~~ in the standard states). Correspondingly, according to Eq. (1.5), standard chemical potential μ_i^s of ith particles is written as

$$\mu_i^s = g_i^0 + kT\ln(\Lambda_i^3 a_i^s). \quad (1.10)$$

Standard activity is chosen arbitrarily and does not have to be the same for different types of particles. If we determine the standard activity of each type of monomeric particle as their real activity in solution, expression (1.10) returns to Eq. (1.5); hence, the standard chemical potential of each type of particles will coincide with the real chemical potential

$$\mu_i^s = \mu_i. \quad (1.11)$$

Passing now to the molecular ionic aggregate, we choose its standard activity as follows. Usually, the type of particles with the highest surface activity is present in the mixture of molecules and ions forming solution. These particles initiate the aggregation process and we designate them as $i = 1$. If there are (at least theoretically) a few of these fully identical types of particles, any of them can be chosen as the first type. Now, we can define the standard activity of the aggregate as

$$a_{\{n\}}^s \equiv a_{11}, \quad (1.12)$$

where a_{11} is the real activity of monomeric particles of the first type. Then, in accordance with Eq. (1.4), the expression for the standard chemical potential of aggregate will have the following form:

$$\mu_{\{n\}}^s = G_{\{n\}}^0 + kT\ln(\Lambda_{\{n\}}^3 a_{11}), \quad (1.13)$$

and expression (1.4) can be written as

$$\mu_{\{n\}} = \mu_{\{n\}}^s + kT\ln\frac{a_{\{n\}}}{a_{11}}. \quad (1.14)$$

Note that, generally speaking, this choice of standard activities in a system in the standard state does not satisfy the electroneutrality condition. It is well known that the standard state is arbitrary and hypothetical and cannot be realized in practice. However, it seems that standard states that do not satisfy the electroneutrality condition have not been considered in the literature.

In full analogy with Eq. (1.1), standard change ΔG^s of the Gibbs potential is written in the form

$$\Delta G^s = \mu_{\{n\}}^s - \sum_i n_i \mu_i^s. \quad (1.15)$$

At the standard states of aggregate and monomers chosen above, here and below, we call the ΔG^s value the work of aggregation. Unlike ΔG, the ΔG^s value does not depend on the aggregate concentration and is not nullified at the state of aggregation equilibrium. This makes it possible to express ΔG^s via the activity or concentration of aggregates at aggregation equilibrium. Passing to the dimensionless work of aggregation

$$W_{\{n\}} \equiv \frac{\Delta G^s}{kT}, \quad (1.16)$$

after the substitution of Eq. (1.11) into (1.14) at $\mu_{\{n\}} = \mu_{\{n\}}^{(e)}$ and $a_{\{n\}} = a_{\{n\}}^{(e)}$ in Eq. (1.15) and taking into account Eq. (1.3), we arrive at

$$W_{\{n\}} = -\ln\frac{a_{\{n\}}^{(e)}}{a_{11}} = -\ln\frac{c_{\{n\}}^{(e)} f_{\{n\}}^{(e)}}{c_{11} f_{11}}, \quad (1.17)$$

where c is the concentration and f is the activity coefficient.

It is known that the aggregation in surfactant solutions occurs, not due to the mutual attraction of dissolved particles, but mainly due to the solvophobous effect; i.e., it is explained by the properties of solvent. In this case, the situation is different from nucleation and aggregation can take place at rather low concentrations. Because of this, the combination of aggregates and monomers is often considered to be the ideal mixture. Then, the contribution of aggregates vanishes ($f_{\{n\}} = 1$ and $f_{11} = 1$) and formula (1.17) can be rewritten as

$$c_{\{n\}}^{(e)} = c_{11}\exp(-W_{\{n\}}). \quad (1.18)$$

The same relation was derived previously when considering single-component aggregation [2, 14]. We can see now that this relation is universal and retains its form for ideal systems with any number of different particles. For nonideal systems, according to Eq. (1.17), this relation is replaced for

$$a_{\{n\}}^{(e)} = a_{11}\exp(-W_{\{n\}}). \quad (1.18a)$$

Formula (1.18) is well known in the theory of nucleation. However, the classical theory of nucleation is based on the phase approach, in which the translational motion of nuclei and their multiplicity are not taken into account. Indeed, for macroscopic phases, these factors are redundant; however, for small molecular aggregates, they can be significant, as for single molecules. We demonstrated many times [23–25] that the simplest procedure for solving the problem is to introduce chemical potentials for not only molecules, but also molecular aggregates (unlike the phase approach, this approach is referred to as chemical or quasi-chemical). In doing so (see Eq. (1.4)), we automatically take into account both the motion of molecular aggregates (via the $\Lambda_{\{n\}}^3$ value) and their concentration (via the activity $a_{\{n\}}$). In this work, we follow precisely to this approach. In the classical theory of nucleation, the work refers to the emergence of one quiescent nucleus from monomers in the absence of other nuclei and these

conditions are responsible for ~~their~~ a specific standardization. However, once formula (1.18) was derived, it was demonstrated that the same work could be also used in the strict aggregation theory, provided that the activity of monomers is taken as the standard activity of molecular aggregates. Thus, we achieve the joining of the quasichemical theory of micellization and the phase theory of nucleation that open new opportunities for the theory of micellization.

As was noted above, in Eqs. (1.18) or (1.18a), the work of aggregation, $W_{\{n\}}$, is independent of the concentration of aggregates, but the effect of the concentration of monomers is retained because it is related to the choice of standard states. In order to illustrate this statement, we write the law of mass action, which stems from condition (1.13) in the approximation of an ideal mixture of aggregates and monomers as follows:

$$c_{\{n\}}^{(e)} = K_{\{n\}} \prod_i c_{i1}^{n_i}, \quad (1.19)$$

where $K_{\{n\}}$ is the constant of the law of mass action (determined by the choice of standard concentrations, albeit is independent of real concentrations). Comparing Eqs. (1.18) and (1.19), we derive the following expression for the work of aggregation:

$$W_{\{n\}} = -\ln K_{\{n\}} - (n_1 - 1)\ln c_{11} - \sum_{i \geq 2} n_i \ln c_{i1}. \quad (1.20)$$

If only one type of particle participates in aggregation, the sum in expression (1.20) vanishes and we arrive at the previous result [2, 14]. However, in the general case, expression (1.20) is a new result, which indicates that the work of aggregation, $W_{\{n\}}$, depends on monomer concentrations of all types of particles that participate in aggregation. When choosing the constant in expression (1.19) for a standard concentration, such as 1 M, the c_{i1} values in expression (1.20) represent dimensionless ~~magnitudes~~ quantities that are numerically equal to molarities, while the $-\ln K_{\{n\}}$ term yields the work of aggregation, $W_{\{n\}}^{\mathrm{M}}$, which is known in traditional approach [1]. Then, formula (1.20) acquires the form

$$W_{\{n\}} = W_{\{n\}}^{\mathrm{M}} - (n_1 - 1)\ln c_{11} - \sum_{i \geq 2} n_i \ln c_{i1}, \quad (1.21)$$

Substantial differences between works $W_{\{n\}}^{\mathrm{M}}$ and $W_{\{n\}}$ can follow from this relation; if the first work in the ideal aggregated system is independent of monomer concentrations, then the second work is dependent on concentration. This dependence is more pronounced for micelles, when aggregation numbers are large. For micelles, works $W_{\{n\}}^{\mathrm{M}}$ and $W_{\{n\}}$ can even differ in their signs. The $W_{\{n\}}^{\mathrm{M}}$ work is approximately defined via the critical micellization concentration (CMC) c_{1m} as (formula (19.11) in [1])

$$W_{\{n\}}^{\mathrm{M}} \approx (n-1)\ln c_{1m} + \sum_{i \geq 2} n_i \ln \frac{c_i}{c_1}, \quad (1.22)$$

where n is the total aggregation number and all concentrations have the meaning of overall concentrations (combining monomeric and aggregation forms of substance). The first term in the right-hand side of expression (1.22) is negative and large by the absolute value due to large n and small CMC values (when the CMC is expressed by the molarity). The remaining terms vanish completely when different types of particles are present in equal quantities, e.g., ions of symmetric electrolyte. In other cases, it is necessary to take into account that $n_i < n$ and the ratios of overall concentrations should be very large in order to change the sign of the whole expression. Hence, in practice, the $W_{\{n\}}^{\mathrm{M}}$ work is typically (or more often) negative. Conversely, as was demonstrated in [2], the $W_{\{n\}}$ work in Eq. (1.21) is positive for a system with one type of particle; i.e., with allowance only for the second term in the right-hand side of Eq. (1.21). For low monomer concentrations, additional terms in expression (1.21) will operate in the same direction and only tend to increase the $W_{\{n\}}$ work. The case of high concentrations (e.g., the presence of large excess of background electrolyte) requires separate estimations.

~~0.~~ 2. MODELS OF IONIC AGGREGATES

The term "bare" micelle is current in the theory of ionic micelles. The term "dressed" micelle appeared later [19], when "dressing" meant the coverage of the surface of primary micelle with counterions. In this section, we will analyze these notions and derive thermodynamic formulas for the work of the formation of bare and dressed aggregates; moreover, unlike the published literature, we distinguish between three, rather than two, types of models of ionic aggregate.

Bare Aggregate

Bare micelle or, in general, bare aggregate is a spontaneously formed, yet densely packed, aggregate of surface-active ions (without counterions). Introducing symbol J_i for surface-active ions, the formation of bare ionic aggregate (denoted by symbol B) can be presented similarly to the chemical reaction

$$\sum_i n_i \mathrm{J}_i \longrightarrow \mathrm{B}. \quad (2.1)$$

In this case, the condition of aggregation equilibrium has the same form as for nonionic surfactants, i.e.,

$$\mu_{\mathrm{B}} = \sum_i n_i \mu_i, \quad (2.2)$$

and the standard work of aggregation is given by the expression

$$\Delta G_B^s = \mu_B^s - \sum_i n_i \mu_i^s. \quad (2.3)$$

In the simplest case of only one type of surface-active ions, in accordance with Eq. (1.5), by choosing standard state (1.11)–(1.13), we arrive at

$$\mu_1^s = \mu_1 = g_1^0 + kT\ln(\Lambda_1^3 a_{11}), \quad (2.4)$$

$$\mu_B^s = G_B^0 + kT\ln(\Lambda_{n_1}^3 a_{11}) = G_B^0 + kT\ln(\Lambda_1^3 a_{11}) - \frac{3}{2}kT\ln n_1, \quad (2.5)$$

where relation $\Lambda_{n_1} = \Lambda_1 n_1^{-1/2}$, which follows from Eq. (1.9) at $\{n\} = n_1$, is taken into account in the second form of notation of Eq. (2.5). Substituting Eqs. (2.4) and (2.5) into (2.3) and using definition $W_B \equiv \Delta G_B^s / kT$ ~~kBT~~ analogous to (1.16), we obtain the following expression for the work of aggregation for bare ionic aggregate:

$$W_B = \frac{G_B^0 - n_1 g_1^0}{kT} - (n_1 - 1)\ln(\Lambda_1^3 a_{11}) - \frac{3}{2}\ln n_1. \quad (2.6)$$

For monomeric ions, $a_{11} \equiv c_{11} f_{11}$, where c_{11} is their real concentration. On the other hand, due to our choice of standard state, $a_{11} = c_B^s f_B^s$, which can be considered to be the equation for calculating standard concentrations and activity coefficients of bare aggregates. It can be said that the role of activity coefficients f_{11} and f_B^s is more significant than in the case of nonionic surfactants. First, the CMC values are one or two orders of magnitude larger for ionic than nonionic surfactants. Second, in ionic systems, we deal with long-range Coulomb forces that increases the deviation of activity coefficients from unity to an even greater extent. In the Debye–Hückel theory, activity coefficients for dilute solutions are given by the expressions (see, e.g., [26])

$$\ln f_i = -\frac{A' z_i^2 I^{1/2}}{1 + B' d_i I^{1/2}} + bI, \quad (2.7)$$

where I is the ionic strength of solution, d is the size of ion, constants A' and B' are tabulated, and b is the constant of salting-out. However, these coefficients are only suitable for symmetric electrolytes with small charge numbers and are quite inapplicable for ionic, as well as, bare aggregates; the square of the charge number of a bare micelle by the absolute value is larger by a factor of n_1^2 (e.g., 10 000) than the charge number of a monomeric ion. Nevertheless, based on Eq. (2.7) and in view of the qualitative estimation, we can state that, at equal concentrations of bare aggregates and monomeric ions, the values of activity coefficients are much larger in the former than the latter case. Thus, under standard conditions, the concentration of bare aggregates should be much lower than that of monomeric ions.

Fully Dressed Aggregate

Fully dressed aggregates are the antipode of bare aggregates. If the bare aggregate does not contain any counterions, a fully dressed aggregate contains the maximum possible amount of counterions, which makes this aggregate electroneutral. This implies that the condition

$$\sum_i n_i z_i = 0. \quad (2.8)$$

is fulfilled. In the simplest case of two types of ions (surface-active and counterions), we have

$$n_1 z_1 + n_2 z_2 = 0, \quad n_1|z_1| = n_2|z_2|, \quad (2.9)$$

where subscript $_2$ refers to counterions. In this case, the degree of counterion binding

$$\beta \equiv \frac{n_2|z_2|}{n_1|z_1|} \quad (2.10)$$

is a constant ($\beta = 1$) and the aggregation number of counterions n_2 can be variable in magnitude due to variations in the basic aggregation number n_1, e.g., due to the salting-out by background electrolyte. The conditions of the system (let say that we deal with large excess of background electrolyte) are such that the aggregate always remains electroneutral and can be considered to be nonelectrolyte.

However, the situation is typical when it is necessary to consider a fully dressed aggregate to be an electrolyte. In other words, a fully dressed aggregate is only electroneutral in the sense that any electrolyte that dissociates into ions is electroneutral. Furthermore, fully dressed aggregate is often considered to be an imaginary electrolyte (this substance does not exist in reality); however, this by no means restricts the possibility of using a similar image. For this purpose, average activity coefficient can be introduced by analogy, as is done in the theory of electrolyte solutions. Let us first imagine that the solution contains only ion-monomers and no aggregates. The Gibbs energy of unit volume of this solution is given by the expression

$$G = \mu_0 c_0 + \sum_i \mu_i c_{i1}, \quad (2.11)$$

where subscript 0 refers to the solvent. In order to describe the same solution in terms of fully dressed aggregates with the identical sets of aggregation numbers $\{n_i\}$ (these aggregates are denoted by symbol D) in the absence of monomeric ions, then we should write

$$G = \mu_0 c_0 + \mu_D c_D. \quad (2.12)$$

The right-hand sides of Eqs. (2.11) and (2.12) should be identically equal to one another; hence, taking into account the balance of substance,

$$c_D = c_{i1}/n_i, \quad (2.13)$$

we arrive at the identity

$$\mu_D = \sum_i n_i \mu_i. \quad (2.14)$$

Let us underline the fundamental difference between equilibrium condition (1.14) and identity (2.14). The former refers to real equilibrium between the aggregate and monomers and acts as an equation for finding the equilibrium concentration of aggregates. On the contrary, the concentration of aggregates in identity (2.14) is already set by condition (2.13) and the identity (2.14) itself is used to determine (define) the average activity coefficient $f_{D\pm}$. For this purpose, we introduced the averaged chemical potential of ions, $\bar{\mu}$, as follows:

$$\bar{\mu} \equiv n^{-1} \sum_i n_i \mu_i, \quad (2.15)$$

where n is the total aggregation number and the bar over μ denotes averaging. According to Eqs. (1.5) and (1.10), the expression for the chemical potential of the ith particles [cf. Eq. (1.14)] is as follows:

$$\mu_i = \mu_i^s + kT \ln \frac{a_{i1}}{a_i^s}. \quad (2.15a)$$

The expression for the averaged chemical potential is formally written in the same way, i.e.,

$$\overline{\mu} = \bar{\mu}^s + kT \ln \frac{a_{D\pm}}{a_D^s}, \quad (2.15b)$$

where $\bar{\mu}^s$ is the result of the averaging of standard chemical potentials by the same formula (2.15) and $a_{D\pm}$ is the average activity, which can be formally written as the product of certain average concentration $\bar{c}$ and average activity coefficient $f_{D\pm}$ (their meaning is clarified below). If all standard activities are set identically (not necessarily as a constant value, but even, e.g., as the real activity of surface-active ion, a_{11}), then, upon the substitution of Eqs. (2.15a) and Eqs. (2.15b) into Eq. (2.15), all standard ~~magnitudes~~ quantities are eliminated and we arrive at the condition

$$(\bar{c} f_{D\pm})^n \equiv \prod_i (c_{i1} f_i)^{n_i}, \quad (2.16)$$

or, separately for each side of identity (2.16),

$$\bar{c} \equiv \prod_i c_{i1}^{n_i/n}, \quad (2.17)$$

$$f_{D\pm} \equiv \prod_i f_i^{n_i/n}, \quad (2.18)$$

It can be seen that averaging is a geometric mean procedure. Using Eq. (2.13), the geometric mean concentration $\bar{c}$ can easily be expressed via the concentration of aggregates c_D as follows:

$$\bar{c} = c_D \prod_i n_i^{n_i/n}. \quad (2.19)$$

In the theory of simple electrolyte solutions, instead of aggregation numbers, stoichiometric coefficients ν_i appear whose values are equal to only a few unities. Therefore, the concentrations of ions and electrolyte are usually of the same order of magnitude (they coincide for 1 : 1 electrolyte). In our case, aggregation numbers can reach into the hundreds and the numerical coefficient in relation (2.19) is large. This means that $c_D \ll \bar{c}$ and, in this case, standard state ($c_D = c_{11}$) is far from reality, which, incidentally, does not deprive one of the right to use it, since the choice of the standard state is arbitrary.

When, it is assumed (as in the previous section) that the standard activities of monomeric ions coincide with their real values, then, upon the substitution of Eqs. (2.15a) and (2.15b) into Eq. (2.15), all standard chemical potentials are eliminated once again, and all logarithmic terms in the right-hand side of Eq. (2.15) vanish. As a result, we arrive at the simple identity

$$\bar{c} f_{D\pm} \equiv a_D^s, \quad (2.19a)$$

according to which the average activity coefficient is determined by setting the standard activity. In other words, the activity coefficient can acquire any value; however, it is then unreasonable to introduce it. We do not consider this fact to be a disadvantage of our method. Simply put, some notions of the theory of electrolyte solutions require also classical approach to the choice of standard state.

We can assume that a fully dressed aggregate is formed by covering a bare aggregate, by the direct aggregation of ions in solution, or upon the aggregation of the molecules of imaginary neutral electrolyte. The chemical potential of this electrolyte is given by the expression

$$\mu = \mu^* + \nu kT \ln(c f_\pm), \quad (2.20)$$

where μ^* is the temperature-dependent constant, $\nu = \sum_i \nu_i$ s the sum of stoichiometric coefficients (the total number of ions formed upon the dissociation of electrolyte molecule), c is the concentration of electrolyte, and $f_\pm \equiv \prod_i f_i^{\nu_i/\nu}$ is its average activity coefficient. In particular, in the Debye–Hückel theory,

$$\ln f_\pm = -\frac{A'|z_1 z_2| I^{1/2}}{1 + B' d I^{1/2}} + bI \quad (2.21)$$

(see Eq. (2.7) for notations, where d is the averaged value of d_i). The aggregation number n of this imaginary substance in a fully dressed aggregate is calculated as $n = n_i/\nu_i$ (ν_i is the stoichiometric coefficient, i.e., the number of ions of i th type in the electrolyte molecule, and the standard work of aggregation is

$$W_D^s = \mu_D^s - n\mu^s, \tag{2.22}$$

where μ_D^s is the standard part of chemical potential μ_D of a fully dressed aggregate. This form of representation only differs from the case of nonionic surfactants in that imaginary substances are considered to be electrolytes and, in this case, activity coefficients are used. Otherwise, the approach is identical.

Dressed Aggregate

The primary event of the formation of bare aggregate is not accompanied by the binding of counterions until the aggregation number and aggregate do not achieve certain threshold when the average Coulomb energy of electrostatic interaction between aggregate and counterion does not exceeds (by the absolute value) kT. Further aggregate growth is accompanied by the binding of counterions. The state of completely formed ionic micelle M is much more similar to a fully dressed micelle than to bare micelle; we refer to it as simply a "dressed micelle." In general, the term "dressed aggregate" is understood as an ionic aggregate $\{n\}$ that contains counterions, but does not necessarily satisfy the electroneutrality condition.

We can imagine several schemes of aggregation. The first (classical) scheme is written as

$$\sum_i n_i J_i + \sum_k n_k J_k \longrightarrow \{n\}, \tag{2.23}$$

where the first sum refers to surface-active ions and the second sum refers to counterions. Scheme (2.23) can be divided into two parts, i.e., the formation of a bare aggregate according to scheme (2.1) and its further coating by the following scheme:

$$B + \sum_k n_k J_k \longrightarrow \{n\}. \tag{2.24}$$

Corresponding change in the Gibbs energy of solution can be presented as

$$\begin{aligned}\Delta G_{\{n\}} &= \mu_{\{n\}} - \sum_i n_i\mu_i - \sum_k n_k\mu_k \\ &= \Delta G_B + \Delta G_{B\{n\}},\end{aligned} \tag{2.25}$$

where $\Delta G_{B\{n\}}$ is the work of coating a bare aggregate to a certain state $\{n\}$, which is intermediate between states B and D as follows:

$$\Delta G_{B\{n\}} = \mu_{\{n\}} - \mu_B - \sum_k n_k\mu_k. \tag{2.26}$$

Value (2.26), taken with the opposite sign, is the chemical affinity for the coating. At equilibrium, when real bare and dressed aggregates are present on the distribution curve, this value is nullified and we arrive at the condition

$$\mu_{\{n\}} = \mu_B + \sum_k n_k\mu_k, \tag{2.27}$$

which is the constituent part of the aggregation equilibrium condition. However, the standard work of coating

$$\Delta G_{B\{n\}}^s = \mu_{\{n\}}^s - \mu_B^s - \sum_k n_k\mu_k^s \tag{2.28}$$

is not nullified, even at equilibrium state, and is a constituent of the standard work of aggregation. In accordance with Eqs. (1.15) and (2.25), the latter is given by the expression

$$\begin{aligned}\Delta G_{\{n\}}^s &= \mu_{\{n\}}^s - \sum_i n_i\mu_i^s - \sum_k n_k\mu_k^s \\ &= \Delta G_B^s + \Delta G_{B\{n\}}^s.\end{aligned} \tag{2.29}$$

In a specific case of one type of surface-active ions and one type of counterions, expression (2.29), with allowance for definition (2.10), can be written as

$$\begin{aligned}\Delta G_{\{n\}}^s &= \mu_{\{n\}}^s - n_1\mu_1^s - n_2\mu_2^s \\ &= \mu_{\{n\}}^s - n_1\left(\mu_1^s + \beta\frac{|z_1|}{|z_2|}\mu_2^s\right).\end{aligned} \tag{2.30}$$

On the other hand, the formation of a real ionic aggregate can also be considered to be a process of the dissociation (partial undressing) of a fully dressed aggregate

$$D = \{n\} + \sum_k \tilde{n}_k J_k. \tag{2.31}$$

Here, $\tilde{n}_k$ are additional aggregation numbers of counterions that satisfy the condition

$$\sum_k (n_k + \tilde{n}_k)|z_k| = \sum_i n_i|z_i|. \tag{2.32}$$

For system with two types of ions, condition (2.32) has the following form:

$$(n_2 + \tilde{n}_2)|z_2| = n_1|z_1|, \tag{2.33}$$

moreover, $\tilde{n}_2 < n_1$ (and even $\tilde{n}_2 \ll n_1$). The work of process (2.31) is

$$\Delta G_{D\{n\}} = \mu_{\{n\}} + \sum_k \tilde{n}_k\mu_k - \mu_D. \tag{2.34}$$

This scheme is based on fully dressed aggregate. However, this aggregate should first be created (maybe from neutral substances, as was mentioned above) so that

$$\begin{aligned}\Delta G_{\{n\}} &= \Delta G_{\mathrm{D}} + \Delta G_{\mathrm{D}\{n\}} \\ &= \Delta G_{\mathrm{B}} + \Delta G_{\mathrm{BD}} + \Delta G_{\mathrm{D}\{n\}},\end{aligned} \tag{2.35}$$

where ΔG_{BD} is the work of the full coating of bare aggregate. It is very likely that this scheme is more ponderous and we adhere to the first scheme.

In the theoretical consideration, it is necessary to distinguish between a dressed ionic aggregate as an actually existing particle (kinetic unit) and a dressed ionic aggregate as the virtual image for describing the bare aggregate. Both cases are analyzed separately. For clarity, we assume that only two types of ions are present in solution, including surface-active ions (as agreed, we attribute number *1* to these ions) and counterions (number *2*).

Let us first consider the case of a real dressed ionic aggregate, which can be present in solution together with bare aggregate. Their equilibrium proportion is determined by condition (2.27), which is now simplified to the following form:

$$\mu_{\{n\}} = \mu_{\mathrm{B}} + n_2\mu_2. \tag{2.36}$$

The work of the formation of bare aggregate B was already calculated (see Eq. (2.6)] and, hence, we need to find only the standard work of coating, which, in accordance with Eq. (2.28), has the form

$$\Delta G^{\mathrm{s}}_{\mathrm{B}\{n\}} = \mu^{\mathrm{s}}_{\{n\}} - \mu^{\mathrm{s}}_{\mathrm{B}} - n_2\mu^{\mathrm{s}}_2. \tag{2.37}$$

When choosing the standard activity according to Eq. (1.12), the standard chemical potential of a dressed aggregate is given by expression (1.13), which, with allowance for the equality (see Eq. (1.9))

$$\begin{aligned}\Lambda_{\{n\}} &= \Lambda_1\left(n_1 + \frac{m_2}{m_1}n_2\right)^{-1/2} = \Lambda_1 n_1^{-1/2}\left(1 + \frac{m_2 n_2}{m_1 n_1}\right)^{-1/2} \\ &= \Lambda_{n_1}\left(1 + \frac{m_2 n_2}{m_1 n_1}\right)^{-1/2}\end{aligned} \tag{2.38}$$

acquires the form

$$\begin{aligned}\mu^{\mathrm{s}}_{\{n\}} &= G^0_{\{n\}} + kT\ln(\Lambda_1^3 a_{11}) \\ &- \frac{3}{2}kT\ln\left[n_1\left(1 + \frac{m_2 n_2}{m_1 n_1}\right)\right].\end{aligned} \tag{2.39}$$

Standard chemical potential of a bare aggregate is presented by relation (2.5), while the standard chemical potential of monomeric ions, according to Eq. (1.11), coincide with their total values and are given by formula (1.5). In particular, for counterions, with allowance for Eq. (1.7), we have

$$\begin{aligned}\mu_2 &= \mu^{\mathrm{s}}_2 = g^0_2 + kT\ln(\Lambda_2^3 a_{21}) \\ &= g^0_2 + kT\ln(\Lambda_1^3 a_{21}) - \frac{3}{2}kT\ln\frac{m_2}{m_1}.\end{aligned} \tag{2.40}$$

Combining Eqs. (2.5), (2.39), (2.40), and (2.37), we obtain

$$\mu^{\mathrm{s}}_{\{n\}} - \mu^{\mathrm{s}}_{\mathrm{B}} = G^0_{\{n\}} - G^0_{\mathrm{B}} - \frac{3}{2}kT\ln\left(1 + \frac{m_2 n_2}{m_1 n_1}\right), \tag{2.41}$$

$$\begin{aligned}\Delta G^{\mathrm{s}}_{\mathrm{B}\{n\}} &= G^0_{\{n\}} - G^0_{\mathrm{B}} - \frac{3}{2}kT\ln\left(1 + \frac{m_2 n_2}{m_1 n_1}\right) \\ &- n_2\left[g^0_2 + kT\ln(\Lambda_1^3 a_{21}) - \frac{3}{2}kT\ln\frac{m_2}{m_1}\right].\end{aligned} \tag{2.42}$$

In view of Eq. (2.42), the standard work of coating in the dimensionless form is written as

$$\begin{aligned}W_{\mathrm{B}\{n\}} &\equiv \frac{\Delta G^{\mathrm{s}}_{\mathrm{B}\{n\}}}{kT} = \frac{G^0_{\{n\}} - G^0_{\mathrm{B}} - n_2 g^0_2}{kT} \\ &- \frac{3}{2}\ln\left(1 + \frac{m_2 n_2}{m_1 n_1}\right) - n_2\left[\ln(\Lambda_1^3 a_{21}) - \frac{3}{2}\ln\frac{m_2}{m_1}\right].\end{aligned} \tag{2.43}$$

As can be expected, it can be seen from Eq. (2.43) that the standard work of coating is negative ($G^0_{\mathrm{B}} > G^0_{\{n\}}$, all other terms are also negative). Furthermore, the work depends on the degree of counterion binding, not only explicitly, but also via the difference $(G^0_{\{n\}} - G^0_{\mathrm{B}})$ that rises in the absolute value with an increase in n_2. Here, all terms also change in one direction. The negative work of the coating increases in absolute value with an increase in n_2, but the decrease in the sign is taken into account.

As for the total work of aggregation, in agreement with Eq. (2.29), it can be derived by the addition of Eqs. (2.6) and (2.43) that

$$\begin{aligned}W_{\{n\}} &= \frac{G^0_{\{n\}} - n_1 g^0_1 - n_2 g^0_2}{kT} - (n_1 - 1)\ln(\Lambda_1^3 a_{11}) \\ &- \frac{3}{2}\ln\left(n_1 + \frac{m_2}{m_1}n_2\right) - n_2\left[\ln(\Lambda_1^3 a_{21}) - \frac{3}{2}\ln\frac{m_2}{m_1}\right].\end{aligned} \tag{2.44}$$

For the ideal mixture of monomers and aggregates, activities are replaced by concentrations and expression (2.44) is rewritten as

$$\begin{aligned}W_{\{n\}} &= \frac{G^0_{\{n\}} - n_1 g^0_1 - n_2 g^0_2}{kT} - (n_1 - 1)\ln(\Lambda_1^3 c_{11}) \\ &- \frac{3}{2}\ln\left(n_1 + \frac{m_2}{m_1}n_2\right) - n_2\left[\ln(\Lambda_1^3 c_{21}) - \frac{3}{2}\ln\frac{m_2}{m_1}\right].\end{aligned} \tag{2.45}$$

Let us now pass to the treatment of a virtual dressed ionic aggregate as the procedure for describing bare aggregate. Let bare aggregates B with aggregation number n_1 and concentration c_B, monomeric surface-active ions with concentration c_{11}, and counterions with concentration c_{21} be actually present in a solution. The Gibbs energy per unit volume of this solution is (subscript 0 refers to the inert solvent)

$$G = \mu_0 c_0 + \mu_B c_B + \mu_1 c_{11} + \mu_2 c_{21}. \quad (2.49)$$

The same solution can be described in terms of a dressed aggregate with arbitrary aggregation number n_2 of counterions, which can be varied within the $1 < n_2 < n_1|z_1| / |z_2|$ range (the upper boundary is determined by condition (2.9) for fully dressed aggregate). Moreover, we can set any distribution of these dressed aggregates and describe the system in terms of this distribution. Naturally, we choose the simplest variant, in which all bare aggregates are replaced by imaginary, identically dressed aggregates with the same aggregation number n_2. In the process of coating, the concentration of aggregates remains unchanged and, instead of Eq. (2.46), we have

$$G = \mu_0 c_0 + \mu_{\{n\}} c_B + \mu_1 c_{11} + \mu_2 c'_{21}, \quad (2.50)$$

where the prime denotes variations in the counterion concentration related to the balance of the number of counterions in the unit volume

$$c_{21} = c'_{21} + c_B n_2. \quad (2.51)$$

Because imaginary manipulations cannot affect the Gibbs energy of a real system, the right-hand sides of Eqs. (2.46) and (2.47) should be identical. If we also take into account Eq. (2.48), we arrive at the identity

$$\mu_{\{n\}} \equiv \mu_B + n_2 \mu_2, \quad (2.52)$$

which coincides in form with equilibrium condition (2.36). However, these relations have different meanings. Condition (2.36) establishes the ratio between the counterions of bare and dressed ionic aggregates. As was demonstrated, the work of the coating of bare aggregates is negative and, hence, the concentration of bare aggregates should be lower (it should be much lower at proper coating) than the concentration of dressed aggregates. On the contrary, in Eq. (2.49), these concentrations are assumed to be identical and we deal with the construction of thermodynamic formalism that satisfies this condition. Let us see how this can be done.

In the theory of electrolyte solutions, the notion of the average activity coefficient is introduced for electroneutral substances capable of dissociating into ions. In full analogy with this statement, we considered fully dressed ionic aggregates that really possess electroneutrality. Now, it must be determined how this procedure can be applied, not to electrolyte, but rather to types of complex ions capable of dissociating into simpler ions. In our case, the complex ion is dressed ionic aggregate $\{n\}$ and simpler ions are bare ionic aggregate B and counterions J_2. In the right-hand side of Eq. (2.49), the total number of simple ions is equal to $n_2 + 1$, and we can introduce the notion of the average chemical potential of ions $\bar{\mu}$ as follows:

$$\bar{\mu} \equiv \frac{\mu_B + n_2 \mu_2}{n_2 + 1}, \quad (2.53)$$

as well as by writing Eq. (2.49) in the form

$$\mu_{\{n\}} \equiv (n_2 + 1)\bar{\mu}. \quad (2.54)$$

Condition (2.50) is introduced for all concentrations, including standard concentration. Hence, we can write

$$\bar{\mu}^s \equiv \frac{\mu_B^s + n_2 \mu_2^s}{n_2 + 1}. \quad (2.55)$$

Now, subtracting Eq. (2.52) from Eq. (2.50), similarly to Eq. (2.16), we find

$$\bar{c}\bar{f}_{\{n\}} \equiv (c_B c_{21}^{n_2} f_B f_2^{n_2})^{1/(n_2+1)}, \quad (2.56)$$

or, postulating single identities for concentrations and activity coefficients,

$$\bar{c} \equiv (c_B c_{21}^{n_2})^{1/(n_2+1)}, \quad (2.57)$$

and

$$\bar{f}_{\{n\}} \equiv (f_B f_2^{n_2})^{1/(n_2+1)}. \quad (2.58)$$

The $\bar{f}_{\{n\}}$ parameter in identity (2.55) can be referred to as the average activity coefficient of ionic aggregate $\{n\}$ as a complex ion.

In view of Eq. (2.48), the relation between concentrations $\bar{c}$ and c_B is now more complex than in the traditional theory of electrolyte solutions. However, it can be accepted that free surface-active ions and the relevant portion of counterions form the electrolyte described in terms of its own (geometrically) average concentrations and activity coefficient. Then, the c'_{21} value in Eq. (2.48) can only be understood as the uncompensated part of free counterions; its role depends on the degree of counterion binding in ionic aggregate $\{n\}$. If this role is great (this is the typical case), then relations $c_{21} \gg c'_{21}$ and $n_2 \gg 1$ (since $n_1 \gg 1$) can be set and we can take advantage of the approximation of electroneutral aggregate $c_{21} \approx c_B n_2$. Then, definition (2.54) yields

$$\bar{c} \approx c_B n_2^{\frac{n_2}{n_2+1}} \approx c_B n_2. \quad (2.59)$$

In the general case, introducing a certain, fairly large (as can be seen from example with (2.56)) identity and assuming that

$$\bar{c} = c_B Q, \quad (2.60)$$

we can write expression (2.51) in the form

$$\mu_{\{n\}} \equiv \mu^{s}_{\{n\}} + (n_2 + 1)kT\ln(c_B Q \bar{f}_{\{n\}}), \qquad (2.61)$$

where factor $(n_2 + 1)$ plays the role of ideal osmotic coefficient. All of the nonideality refers to the average activity coefficient $\bar{f}_{\{n\}}$, moreover, its role becomes greater when the value of multiplier Q is large. Eq. (2.58) yields

$$\ln \bar{f}_{\{n\}} \equiv \frac{1}{n_2 + 1}\ln f_B + \frac{n_2}{n_2 + 1}\ln f_2. \qquad (2.62)$$

Substituting the imaginary Debye–Hückel formula (2.7) into this identity (without assuming strictness), we can see that, although the division by $(n_2 + 1)$ diminishes the role of the charge of bare aggregate in multiplier z_B^2, it still remains very large because, first, charge number z_B is proportional to n_1 and $n_1 > n_2 + 1$ and, second, the charge number is squared. Moreover, the large charge of a bare aggregate (if its value is close to that of micelle) also tends to greatly increase the ionic strength, which in turn affects the activity coefficient. Thus, we arrive at the conclusion that the use of the image of a dressed ionic aggregate for describing a bare aggregate cannot approach the system to an ideal state, although this procedure is used in the published literature [19, 20]. A rather different situation is observed for a real dressed ionic aggregate whose real charge is rather low. The approximation of an ideal solution is quite acceptable in this case; however, we should deprive ourselves of identity (2.40) and pass to equilibrium condition (2.36), in which concentrations of bare and dressed aggregates are different. In the next communication, we demonstrate how to correctly approach the construction of the theory of ionic micellar systems.

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