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Thermodynamic and Kinetic Theory of Ionic Micellar Systems: 2. Statistical–Thermodynamic Relations

A. I. Rusanov A. K. Shchekin, and F. M. Kuni

Fock Research Institute of Physics, St. Petersburg State University, ~~Petrodvorets branch,~~
ul. Ul'yanovskaya 1, Petrodvorets, St. Petersburg, 198504 Russia

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Abstract—The role of electrochemical potentials in the grand canonical ensemble of ionic micellar systems is characterized. The notion of relative electrochemical potentials is introduced with allowance for the electroneutrality condition. Fundamental relations and primary statistical-thermodynamic relations are derived for ideal and real ionic micellar systems with participation of electrochemical potentials, in which inaccuracies observed in published literature, are eliminated. A differential equation for the osmotic pressure of ionic aggregated system is obtained. Relations that link ~~nect~~ the work of the aggregation of ionic micelle with chemical and electrochemical potentials and aggregation numbers are established. ~~Single~~ Separate contributions to the work of aggregation are commented on.

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INTRODUCTION

In the first communication of this series [1], we derived expressions for the work of the formation of bare (without counterions) and dressed (covered with bound counterions) ionic aggregates of surfactants in micellar systems. Now, we intend to establish statistical-thermodynamic relations between the work of aggregation and the state parameters of solution. Here, we will deal with the description procedures, particularly with the use of grand canonical ensemble of statistical mechanics in the problems of aggregation in micellar ionic systems. As is known, in the grand canonical ensemble, independent variables are chemical potentials. When passing to ionic systems, electrochemical potentials are substituted for these potentials; however, the problematic character of their independence arises in precisely this case. Previous studies [2–5] of aggregation in micellar solutions of ionic surfactants are worth mentioning. These studies made it possible to clarify the mechanism of the independent variations of electrochemical potentials in the presence of background electrolyte. It was shown [2] that the single variation of the electrochemical potential of one of the ions is ensured by the possible variation in the phase electric potential of solution. At the same time, a number of problems remained intact. Moreover, it can be said that not all of derived relations are correct; thus, this field of the thermodynamic theory of micellization deserves careful inspection. This problem is the focus of this communication.

1. ELECTROCHEMICAL POTENTIALS IN GRAND CANONICAL ENSEMBLE

In thermodynamics, electrochemical potential μ_i^{E} is defined by the same relations as the chemical potential; hence, it is undistinguishable from the latter. A separate term for electrochemical potential was only needed because of its commonly used conventional division into two terms as follows:

$$\mu_i^{\mathrm{E}} = \mu_i + ez_i\varphi, \tag{1.1}$$

where μ_i is the chemical potential of charged particle (ion, ionic aggregate, or colloidal particle) of the ith type in the absence of charge, e is the elementary positive charge, z_i is the charge number of particle, and φ is the electric potential in the point of its localization. For equilibrium homogeneous electrolyte solutions, φ presents internal phase potential (the Galvani potential). Using the expression for chemical potential employed in statistical mechanics, we can write Eq. (1.1) in the form

$$\mu_i^{\mathrm{E}} = g_i^0 + kT\ln(\Lambda_i^3 c_i\gamma_i^0 f_i) + ez_i\varphi, \tag{1.2}$$

where g_i^0 is the Gibbs energy of a single particle of i th type with the quiescent center of mass in a vacuum; k is the Boltzmann's constant; T is the temperature; Λ_i is the average de Broglie wavelength of a particle; c_i is the particle concentration; and γ_i^0 and f_i are activity coefficients, i.e., the zero and concentration coefficients, respectively, the product of which forms the total activity coefficient $\gamma_i \equiv \gamma_i^0 f$). The physical meaning of the activity coefficients is disclosed via a transfer; for an

uncharged particle, $kT\ln\gamma_i^0$ yields the transfer of a particle from a vacuum to a pure solvent and $kT\ln(\gamma_i^0 f_i)$ yields the transfer of a particle from a vacuum to a real solution. However, the last term in Eq. (1.2) is added for a charged particle; this is the work of transferring the particle through the boundary between the considered phase and vacuum, where the drop of electric potential φ exists. The transfer is divided into two stages, i.e., crossing the interface and the rearrangement of the phase structure under the action of a transferred particle; the $ez_i\varphi$ term characterizes the work completed at the first stage, while $kT\ln(\gamma_i^0 f_i)$ depicts the work completed at the second stage, which, in the theory of electrolyte solutions, is called the work of the chemical solvation of ion.

Since the transferred charged particle only causes the structural rearrangement of the solution in its vicinity and does not involve remote regions, it can be assumed that the whole process takes place at constant values of chemical and electrochemical potentials of solution components. Then, the work of process should be presented as changes in the grand thermodynamic potential Ω, which can be imagined as excess grand thermodynamic potential $\overline{\Omega}_i$ around the i th particle. Unlike the theory of surface and linear phenomena, in this case, we deal with the point excess. Then, for the work of chemical solvation, we can write [6] the following expression:

$$kT\ln\gamma_i = \overline{\Omega}_i \tag{1.3}$$

Adding the electric term to this expression, by analogy with electrochemical potential, we determine the electrochemical work of solvation as follows:

$$kT\ln\gamma_i + ez_i\varphi = \overline{\Omega}_i^{\mathrm{E}}. \tag{1.4}$$

With allowance for Eq. (1.4), we can now represent the expression for electrochemical potential (1.2) as follows (see also formulas (47.5 and (47.6) in [7]):

$$\mu_i^{\mathrm{E}} = g_i^0 + \overline{\Omega}_i^{\mathrm{E}} + kT\ln(\Lambda_i^3 c_i). \tag{1.5}$$

The g_i^0 value in Eq. (1.5) plays the role of a constant and is often omitted in the notation of Eq. (1.5).

The grand thermodynamic potential suggests the consideration of systems with charged particles in a grand canonical ensemble in which electrochemical potentials should play the role of independent variables. However, the concentrations (and, correspondingly, chemical potentials) of charged particles must be related by the electroneutrality condition

$$\sum_i c_i z_i = 0, \tag{1.6}$$

Hence, the question arises as to whether chemical potentials can be independent of one another under these conditions. In order to answer this question, it is sufficient to check whether at least one degree of freedom for a certain chosen electrochemical potential μ_i^{E} remains when the electrochemical potentials of the rest of charged particles are fixed and condition (1.6) is still valid. There is a more general problem in which an answer is obtained for the posed question, i.e., the construction of thermodynamic formalism in terms of electrochemical potentials with allowance for electroneutrality condition (1.6). The traditional approach to electrolyte solutions consists of introducing hypothetical neutral substances and their average activities in view of impossible measurements of activity coefficients for single ions. It should be more realistic to address to ions (particularly, for strong electrolytes) that exist in solution. Moreover, if we could (at least for dilute solutions) calculate activity coefficients for single ions, this approach in the theory is entitled to exist.

As an illustration, let us formulate fundamental equations for the Gibbs energy. Let there be one neutral substance (solvent, index $_0$) and charged particles of arbitrary number of types (index i) in a system. In the absence of electroneutrality, each type of ion can be considered to be a single component and the fundamental differential equation for the Gibbs energy G of the system under consideration is written as

$$dG = -SdT + Vdp + \mu_0 dN_0 + \sum_i \mu_i^{\mathrm{E}} dN_i, \tag{1.7}$$

where S is the entropy, p is the pressure, and N is the number of particles. Now, we introduce electroneutrality condition (1.6), which preliminarily divides this condition by volume V as follows:

$$\sum_i N_i z_i = 0. \tag{1.8}$$

Excluding dN_j, where j is the number of any specified type of charged particles, using Eq. (1.8), we can write Eq. (1.7) in the following form:

$$dG = -SdT + Vdp + \mu_0 dN_0 + \sum_{i\neq j} \mu_{i(j)} dN_i, \tag{1.9}$$

where

$$\mu_{i(j)} \equiv \mu_i^{\mathrm{E}} - \frac{z_i}{z_j}\mu_j^{\mathrm{E}} = \mu_i - \mu_j. \tag{1.10}$$

In comparison with Eq. (1.7), the number of independent variables in the right-hand side of Eq. (1.9) is diminished by unity. It can be seen that electrostatic components of electrochemical potentials in the right-hand side of Eq. (1.10) are mutually eliminated (see Eq. (1.1)), and only the difference of common chemical potentials remains. The $\mu_{i(j)}$ can be called the relative chemical potential of the particles of i th type (counted with the reference to μ_j).

The integration of Eq. (1.9) at a preset physical state yields the fundamental equation for the Gibbs energy

$$G = \mu_0 N_0 + \sum_{i \neq j} \mu_{i(j)} N_i, \quad (1.11)$$

and, comparing Eqs. (1.9) and (1.11), we arrive at the Gibbs–Duhem equation

$$Vdp = SdT + N_0 d\mu_0 + \sum_{i \neq j} N_i d\mu_{i(j)}, \quad (1.12)$$

which is calculated per unit volume by the equation

$$dp = s_v dT + c_0 d\mu_0 + \sum_{i \neq j} c_i d\mu_{i(j)}, \quad (1.13)$$

where s_v is the entropy density. In accordance with Eq. (1.10), if the temperature and all electrochemical potentials except for μ_j^E are fixed, we obtain

$$d\mu_{i(j)} = \frac{z_i}{z_j} d\mu_j^E \quad (1.14)$$

and

$$dp = c_0 d\mu_0 - \frac{d\mu_j^E}{z_j} \sum_{i \neq j} c_i z_i = c_0 d\mu_0 + c_j d\mu_j^E, \quad (1.15)$$

where condition (1.6) is used again. It is interesting to note that the right-hand side of Eq. (1.15) has the same form as in the case of the mutual independence of all electrochemical potentials. Now, if the chemical potential of solvent, μ_0, is fixed, based on Eq. (1.15), we obtain the relation

$$\left(\frac{\partial p}{\partial \mu_j^E}\right)_{T, \mu_0, \mu_{i \neq j}} = c_j, \quad (1.16)$$

which fully corresponds to the grand canonical ensemble. Of course, the pressure can be fixed in Eq. (1.15); in this case, one degree of freedom, which is necessary to vary electrochemical potential μ_j^E, is retained. This case was considered in [2]. However, escape from the grand canonical ensemble is implied in this case, which we obviate not only based on the purity of the method, but also on the necessity to correspond to other relations, which will be derived later. We discuss the general case when the pressure can be varied.

Referring subscript i in condition (1.6) to any charged kinetic unit of a solution (ion, molecule–ion aggregate, or colloidal particle) and varying the chemical potential (Eq. (1.2)) as a function of the pressure and composition, for all of these kinetic units, except for particles of the chosen jth type, we can write the condition of the fixation of electrochemical potential as follows:

$$d\mu_i^E = v_i dp + kTd\ln c_i + kTd\ln f_i + ez_i d\varphi = 0, \quad (1.17)$$

where v_i is the partial volume of the ith particle. Here, we used the relation

$$\left(\frac{\partial \mu_i^E}{\partial p}\right)_{T, N_0, N_i} = \left(\frac{\partial V}{\partial N_i}\right)_{T, p, N_0, N_{j \neq i}} \equiv v_i.$$

which stems from Eq. (1.7). In view of the low compressibility of the condensed phase (solution), we ignore variations in volume, which means that both the number of particles and their concentrations (and, at the same time, activity coefficients) in the first derivative are constant. Thus, when varying Eq. (1.2), the differentials of concentrations and activity coefficient are written separately, as is shown in Eq. (1.17).

Similarly, for particles of the j th type, we obtain

$$d\mu_j^E = v_j dp + kTd\ln c_j + kTd\ln f_j + ez_j d\varphi. \quad (1.18)$$

Combining Eqs. (1.6) and (1.17), expression (1.18) is transformed into the following form:

$$d\mu_j^E = \frac{1}{c_j z_j}\left(\sum_i c_i z_i v_i dp + kT \sum_i c_i z_i d\ln f_i + 2Ied\varphi\right), \quad (1.19)$$

where the summation is performed over all types of charged particles, including jth particles, and I denotes the ionic strength of solution according to the definition

$$2I \equiv \sum_i c_i z_i^2. \quad (1.20)$$

It follows from Eq. (1.19) that it is necessary to take into account that variables f_i and φ in this equation are the functions of solution composition. Particular emphasis should be placed on potential φ. Theoretically, the effect on the interfacial electric potential can be demonstrated by placing insoluble substances on the solution surface. Then, the φ value can change with the conservation of solution composition and, hence, it ceases to be the state parameter. Although this case is of great practical importance, we exclude it from consideration due to fundamental reasons. The point is that its practical aspect is related primarily to deviations from the equilibrium because of the smallness and slowness of the dissolution of insoluble monolayers. Considering strictly equilibrium systems, we should assume that all substances are soluble (let them be as low as possible) and, based on their concentration in the solution bulk, determine the state of surface layer. In other words, it can be assumed that the surface layer in a really equilibrium system is formed by adsorption. Then, the problem of the independent behavior of the electric potential φ vanishes and this potential, as well as activity coefficients in Eq. (1.19), becomes an unambiguous function of solution composition or, equivalently, of the set of its chemical and electrochemical potentials.

Dividing both sides of Eq. (1.19) by $d\,\mu_j^{\mathrm{E}}$ we arrive at the relation

$$2Ie\left(\frac{\partial\varphi}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_{i\neq j}} = c_j z_j - \sum_i c_i z_i \nu_i \left(\frac{\partial p}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_{i\neq j}} - kT\sum_i c_i z_i \left(\frac{\partial \ln f_i}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_{i\neq j}}. \quad (1.21)$$

Derivatives in Eq. (1.21) are not yet fully determined, since, according to Eq. (1.15), there are two degrees of freedom in a system. Eliminating one of these degrees by fixing μ_0 and taking advantage of relation (1.16), from Eq. (1.21), we obtain the following relation:

$$2Ie\left(\frac{\partial\varphi}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}} = c_j\left[z_j - \sum_i c_i z_i \nu_i - \frac{kT}{c_j}\sum_i c_i z_i \left(\frac{\partial \ln f_i}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_{i\neq j}}\right]. \quad (1.22)$$

Equation (1.22) is the rigorous relation of the theory of nonideal micellar solutions, which can be substantially simplified for ideal solutions. If aggregation takes place at fairly low concentrations of solutes (as in the case of micellization) and the degree of counterion binding is rather high (as in the case of dressed micelles), the effect of activity coefficients in Eq. (1.22) can be ignored and this expression rewritten in the form

$$2Ie\left(\frac{\partial\varphi}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}} = c_j\left[z_j - \sum_i c_i z_i \nu_i\right]. \quad (1.23)$$

It can be easily proven that the sum in the right-hand side of Eq. (1.23) is the small correction to z_j. It is sufficient to remember the thermodynamic relation for partial volumes

$$c_0\nu_0 + \sum_i c_i \nu_i = 1, \quad (1.24)$$

whose physical meaning consists of the fact that the sum of volume fractions of all types of particles is equal to unity. As we consider the dilute solution, it is evident that condition $\sum_i c_i \nu_i \ll 1$ is fulfilled. The sum in Eq. (1.23) is even smaller, since its terms have different signs (in accordance with signs of z_i) and, at a considerable imbalance between the opposite charges in a dressed ionic aggregate, the role of charge numbers cannot be decisive. In view of the fact that $|z_j| \geq 1$, we can now conclude that, in the considered approximation of ideal solution, the sum in Eq. (1.23) can be neglected and we can write

$$2Ie\left(\frac{\partial\varphi}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}} = \frac{c_j z_j}{2Ie}. \quad (1.25)$$

Formula (1.25) is analogous to the result obtained in [2] at constant pressure and variable chemical potential of a solvent. However, in contrast to this result, our formula strictly corresponds to the grand canonical ensemble.

Let us turn now to the general expression for electrochemical potential in the left-hand side of condition (1.17) and divide it by $d\mu_j^{\mathrm{E}}$ at the fixation of all other chemical and electrochemical potentials (including chemical potential of a solvent). In view of condition (1.17), the $d\mu_i^{\mathrm{E}}/d\mu_j^{\mathrm{E}}$ ratio is equal to zero at $i \neq j$ and evidently equal to unity at $i = j$; i.e., it will be set by Kronecker symbol δ_{ij}. Additionally taking into account relation (1.16), we obtain

$$\delta_{ij} = \nu_i c_j + kT\left(\frac{\partial \ln c_i}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}} + kT\left(\frac{\partial \ln f_i}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_{i\neq j}} + ez_i\left(\frac{\partial\varphi}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}}. \quad (1.26)$$

The substitution of Eq. (1.22) into (1.26) with allowance for Eq. (1.20) yields

$$\delta_{ij} = kT\left(\frac{\partial \ln c_i}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}} + \frac{c_j}{2I}\left[z_i z_j + \sum_k c_k z_k \times (z_k\nu_i - z_i\nu_k) + \frac{kT}{c_j}\sum_k c_k z_k\left(z_k\left(\frac{\partial \ln f_i}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_{i\neq j}} - z_i\left(\frac{\partial \ln f_k}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_{i\neq j}}\right)\right]. \quad (1.27)$$

In the approximation of ideal solution, we can ignore terms with activity coefficients and rewrite Eq. (1.27) as follows:

$$\delta_{ij} = kT\left(\frac{\partial \ln c_i}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}} + \frac{c_j z_i z_j}{2I} + \frac{c_j}{2I}\sum_k c_k z_k (z_k\nu_i - z_i\nu_k). \quad (1.28)$$

The last term in the right-hand side of Eq. (1.28) is small compared to the second term in view of inequality $\nu_i \ll z_i z_j / 2I$ due to the smallness of the ionic strength of dilute solution. Neglecting the last term, we arrive at the relation

$$\left(\frac{\partial \ln c_i}{\partial\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}} = \frac{\delta_{ij}}{kT} - \frac{c_j z_i z_j}{2IkT}. \quad (1.29)$$

Since relation (1.29) complies with the approximation of ideal mixture of particles of different types (e.g., the mixture of monomers and the population of ionic aggregates with different sizes), it is interesting to compare this relation with the exact expression for the same derivative in the grand canonical ensemble, which can

be derived from formula (1.5). Differentiating Eq. (1.5) at constant temperature and assuming $f_i \simeq 1$, we have

$$d\mu_j^{\mathrm{E}} = d\overline{\Omega}_i^{\mathrm{E}} + kTd\ln c_i. \quad (1.30)$$

At constant temperature, the fundamental equation for the grand thermodynamic potential of the system considered is written as follows:

$$d\Omega^{\mathrm{E}} = -N_0 d\mu_0 - \sum_j N_j d\mu_j^{\mathrm{E}}, \quad (1.31)$$

where different types of charged particles are assumed to be independent components of a system. With allowance for electroneutrality condition (1.8), the number of independent variables diminishes and Eq. (1.31) takes the form (see Eq. (1.10))

$$d\Omega^{\mathrm{E}} = -N_0 d\mu_0 - \sum_{j\neq i} N_i d\mu_{j(i)}^{\mathrm{E}}. \quad (1.32)$$

Passing now to point excesses on one particle of the *i*th type in Eqs. (1.31) and (1.32), we find

$$d\overline{\Omega}_i^{\mathrm{E}} = -\overline{N}_{0(i)} d\mu_0 - \sum_j \overline{N}_{j(i)} d\mu_j^{\mathrm{E}}, \quad (1.33)$$

$$d\overline{\Omega}_i^{\mathrm{E}} = -\overline{N}_{0(i)} d\mu_0 - \sum_{j\neq i} \overline{N}_{j(i)} d\mu_{j(i)}^{\mathrm{E}}, \quad (1.34)$$

where the bar over the symbol denotes the excess and additional subscript *i* indicates the type of particle to which the excess is referred. The excess of solvent, $\overline{N}_{0(i)}$, reflects the solvation of *i*th particle and excess $\overline{N}_{j(i)}$ reflects the distribution of other particles around the first one. Like numbers of particles, their excesses satisfy the electroneutrality condition. This follows from condition (1.8), provided that, in this condition, we pass to the point excesses

$$\sum_j \overline{N}_{j(i)} z_j = -z_i. \quad (1.35)$$

Substituting Eq. (1.34) into Eq. (1.30), we arrive at the expression

$$d\mu_i^{\mathrm{E}} = -\overline{N}_{0(i)} d\mu_0 - \sum_{j\neq i} \overline{N}_{j(i)} d\mu_{j(i)}^{\mathrm{E}} + kTd\ln c_i. \quad (1.36)$$

Combining Eqs. (1.36) and (1.35) (see also definition (1.10)), we obtain

$$\left(\frac{d\ln c_i}{d\mu_i^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{j\neq i}} = \frac{1+\overline{N}_{i(i)}}{kT}, \quad (1.37)$$

$$\left(\frac{d\ln c_i}{d\mu_j^{\mathrm{E}}}\right)_{T,\mu_0,\mu_{i\neq j}} = \frac{\overline{N}_{j(i)}}{kT}, \quad (1.38)$$

$$\left(\frac{d\ln c_i}{d\mu_0}\right)_{T,\mu_j} = \frac{\overline{N}_{0(i)}}{kT}. \quad (1.39)$$

All of these equations can be written in the compact form of one expression as follows:

$$\left(\frac{d\ln c_i}{d\mu_k^{\mathrm{E}}}\right)_{T,\mu_{k\neq i}} = \frac{\delta_{ik}+\overline{N}_{k(i)}}{kT}, \quad (1.40)$$

where *k* is the number of any type of particles (charged or neutral) and δ_{ik} is the Kronecker symbol. Formula (1.40) is rigorous relation of statistical mechanics (in grand canonical ensemble), which is true at any set of particles, including the simultaneous presence of molecular and ionic aggregates of different sizes and any group of neutral substances that form mixed solvent. Note that analogous formulas in [2] only conform to ours at $k = i$.

Relation (1.40) is more general than Eq. (1.29) because it suggests the possibility of differentiation with respect to the chemical potential of a solvent. However, if we only focus on charged particles and assume that $k = j$, comparing Eqs. (1.29) and (1.40), we arrive at the following expression for the excess number of *j*th charged particles type on a particle of *i*th type:

$$\overline{N}_{j(i)} = -\frac{c_j z_i z_j}{2I} \quad (1.41)$$

As can be seen from expression (1.41), the positive excess of counterions and negative excess of co-ions are formed on the particle of *i*th type; moreover, at preset ionic strength of solution, this excess is proportional to the charge number of ions or the concentration and squared charge number, if we deal with the excess of the *i*th type of ions on one of the *i*th particles. Multiplying both sides of Eq. (1.41) by z_j and summing over all *j*, it can easily be proven that formula (1.41) satisfies electroneutrality condition (1.35). Taking into account the definition of ionic strength (1.20), we can also state that the absolute value of point excess $\overline{N}_{i(i)}$ is always smaller than unity. Note that formula (1.41) refers to the dilute solution and, hence, can be derived directly in terms of the Debye–Hückel theory of electrolyte solutions [8]. Moreover, if we deal with ionic aggregates, it is natural that we mean dressed aggregates whose charges are not large enough to prevent the application of the Debye–Hückel theory. Finally, it should be noted that the excess number of counterions and the number of bound counterions are notions that belong to different categories. The second number cannot by judged by the first one and, correspondingly, formula (1.41) does not determine the degree of counterion binding in the ionic aggregate or micelle.

2. OSMOTIC PRESSURE OF AGGREGATION SYSTEM

As is known, the notion of osmotic pressure appears when considering the membrane equilibrium. Let us imagine that the solution in which aggregation processes take place is placed on one side of a membrane

that is only permeable for solvent molecules, while, on the other side, we have pure solvent. The chemical potential of the solvent is a function of only the temperature and pressure and, if they are fixed in solvent (T = const and p_0 = const), the chemical potential of the solvent is also constant. Then, to maintain the membrane equilibrium by variations in the composition of solution, it is necessary to change its pressure p. The difference in pressures p and p_0 determines osmotic pressure Π as follows:

$$\Pi \equiv p - p_0. \tag{2.1}$$

The use of osmotic pressure to describe the system of monomeric ions and monodisperse ionic micelles has already been considered in [5]. However, the result obtained calls for refinement, which precisely is what we are going to do.

According to (2.1), at preset p_0, we have $d\Pi = dp$. Taking into account the constancy of temperature and relevant constancy of the chemical potential of the solvent, we write the Gibbs–Duhem equation (1.13) as follows:

$$d\Pi = \sum_{i \neq j} c_i d\mu_{i(j)}. \tag{2.2}$$

Equation (2.2) is written in terms of relative chemical potentials. Using definition (1.10) and electroneutrality condition (1.6), we can reduce Eq. (2.2) to the traditional form

$$d\Pi = \sum_i c_i d\mu_i, \tag{2.3}$$

where the electroneutrality condition is not manifested in any way. However, this makes it possible to replace all chemical potentials in Eqs. (2.2) and (2.3) with electrochemical potentials when it is necessary to differentiate the osmotic pressure with respect to the electrochemical potential (in this presentation, this is not necessary).

Partial expressions for chemical potentials, which stem from Eqs. (1.17) and (1.18), can also be written, like the Gibbs–Duhem equation, in terms of osmotic pressure at $d\Pi = dp$ as follows:

$$d\mu_i = \mathrm{v}_i d\Pi + kTd\ln c_i + kTd\ln f_i, \tag{2.4}$$

where v_i is the partial volume of one charged ith particle. After substitution of Eq. (2.4) into (2.3), we arrive at the equation

$$\left(1 - \sum_i c_i \mathrm{v}_i\right) d\Pi = kT \sum_i (dc_i + c_i d\ln f_i). \tag{2.5}$$

The sum in coefficient at $d\Pi$ is the volume fraction of all charged particles in solution taken together. Denoting this sum as ϕ, we can write equation (2.5) for osmotic pressure as

$$d\Pi = \frac{kT}{1-\phi} \sum_i (dc_i + c_i d\ln f_i). \tag{2.6}$$

Equation (2.6) is the general thermodynamic relation, which is true for any set of charged particles in solution including ionic aggregates. This equation is also valid for any treatment of aggregates (bare or dressed); the difference will be only in the values of activity coefficients. For dressed aggregates, activity coefficients are closer to unity and the application of the model of ideal solution as approximation is more substantiated. In this model, rejecting the terms with activity coefficients and classifying particles into monomeric ions (additional subscript *1*) and ionic aggregates with sets of aggregation numbers $\{n\} \equiv n_1, n_2, \ldots$, we can write Eq. (2.6) in the following form:

$$d\Pi = \frac{kT}{1-\phi} d\left(\sum_i c_{i1} + \sum_{\{n\}} c_{\{n\}}\right), \tag{2.6a}$$

where the summation is performed over all monomeric forms of free ions and all types of dressed aggregates, including micelles. The integration of Eq. (2.6) with neglect of ϕ and substitution of the sum of aggregate concentrations over aggregation numbers {n} for the concentration of micelles at average aggregation number yields the formula for the osmotic pressure of infinitely dilute micellar solution, which was used by Maeda [5] without generalization to the case of the mixture of aggregates with different sizes, which was done in this work. Note, however, that surfactant molecules are ten times larger than water molecules and, at small molar fraction of surfactant, its volume fraction can be noticeable. This is taken into account in formula (2.6).

3. RELATIONS FOR THE WORK OF AGGREGATION

In previous communication [1], we defined the dimensionless standard work of aggregation (for brevity, called simply the work of aggregation) by the expression

$$W_{\{n\}} \equiv \frac{\mu^{\mathrm{s}}_{\{n\}} - \sum_i n_i \mu^{\mathrm{s}}_i}{kT}, \tag{3.1}$$

where $\mu^{\mathrm{s}}_{\{n\}}$ is the standard chemical potential of molecular ionic aggregate as a whole, n_i is the aggregation number of ith ions, and μ^{s}_i is the standard chemical potential of monomeric particles of ith type; the summation is performed over all types of particles participating in the aggregation. In correspondence with the postulates of the nucleation theory, for ionic aggregate, the standard activity $\mu^{\mathrm{s}}_{\{n\}}$, which comprises $a^{\mathrm{s}}_{\{n\}}$ in Eq. (3.1), is chosen as equal to activity a_1 of surface-active monomers (denoted by subscript *1*) and the standard chemical potentials of monomers are identified with real chemical potentials (see Eq. (1.2) [1]). Strictly speaking, for charged particles, electrochemical poten-

tials containing additional (to chemical potentials) terms of type $ez_k\varphi$ should appear in expression (3.1). However, these terms are eliminated due to the fact that charges for both terms in the right-hand side of Eq. (3.1) are identical as shown below:

$$z_{\{n\}} = \sum_i n_i z_i. \tag{3.2}$$

This circumstance allowed equality (3.1) to be written in terms of ordinary chemical potentials for both uncharged and charged particles.

In accordance with what has been said above, standard chemical potentials $\mu^s_{\{n\}}$ and μ^s_i are given by the expressions

$$\mu^s_{\{n\}} = G^0_{\{n\}} + kT\ln\Lambda^3_{\{n\}} + kT\ln a_1, \tag{3.3}$$

$$\mu^s_i = g^0_i + kT\ln\Lambda^3_i + kT\ln a_i, \tag{3.4}$$

where $G^0_{\{n\}}$ – is the Gibbs energy of a single aggregate with a quiescent center of mass in pure solvent (in the absence of other aggregates) and a is the activity; subscripts $\{n\}$ and i denote aggregates and all types of particles in solution, respectively.

Combining Eqs. (3.1), (3.3), and (3.4), we derive the following equation:

$$dW_{\{n\}} = d\left(\frac{G^0_{\{n\}} - \sum_i n_i g^0_i}{kT}\right) + d\ln\frac{\Lambda^3_{\{n\}}}{\prod_i \Lambda_i^{3n_i}} + d\ln a_1 - \sum_i n_i d\ln a_i, \tag{3.5}$$

where the sum and product are taken over all types of particles, including type *1*. The following important relation is derived from Eq. (3.5):

$$\frac{\partial W_{\{n\}}}{\partial \ln a_i} = \delta_{i1} - n_i, \tag{3.6}$$

which can be considered to be the thermodynamic definition of aggregation numbers in polydisperse micellar systems. It is natural that the differentiation in Eq. (3.6) is performed at fixed temperatures and chemical potentials of remaining components with respect to activities only of the types of particles that participate in the aggregation process. Moreover, if we deal with a charged particle, its activity depends on the charge and ionic strength of the solution in spite of the absence of phase potential φ in expression (3.8). At the same time, it reasonable to put the question of the analogous relation when using electrochemical potentials of charged particles in the grand canonical ensemble as variables. Let us attempt to consider this possibility.

We return to expression (3.2) and substitute electrochemical potentials in this equation for chemical potentials. After this, we differentiate the whole expression with respect to the electrochemical potential of one of the types of charged particles, μ^E_k, which participates in the aggregation, at constant temperature and other electrochemical potentials as follows:

$$kT\frac{\partial W_{\{n\}}}{\partial \mu^E_k} = \frac{\partial \mu^{Es}_{\{n\}}}{\partial \mu^E_k} - n_k = kT\frac{\partial \ln a_1}{\partial \mu^E_K} + ez_{\{n\}}\frac{\partial \varphi}{\partial \mu^E_k} - n_k, \tag{3.7}$$

where Eq. (3.3) was used. From Eq. (3.4), we obtain

$$kTd\ln a_1 = d\mu^E_1 - ezd\varphi. \tag{3.8}$$

Substituting Eq. (3.8) into (3.7) and taking into account evident equality $d\mu^E_1/d\mu^E_k = \delta_{k1}$, we arrive at the general relation

$$kT\frac{\partial W_{\{n\}}}{\partial \mu^E_k} = \delta_{k1} - n_k + e(z_{\{n\}} - z_1)\frac{\partial \varphi}{\partial \mu^E_k}. \tag{3.9}$$

For the last derivative in Eq. (3.9), we have expression (1.25); however, it refers to an ideal solution such that, beginning at this moment, our speculations lose their generality. Now we can say that, in view of expression (1.25) for an ideal solution, Eq. (3.9) takes the form

$$kT\frac{\partial W_{\{n\}}}{\partial \mu^E_k} = \delta_{k1} - n_k + \frac{c_k z_k (z_{\{n\}} - z_1)}{2I}. \tag{3.10}$$

Note that the contribution to ionic strength I is made by all charged particles of a system, but not only by particles directly involved in the aggregation. Therefore, in the presence of background electrolytes in solution, the denominator in the right-hand side of Eq. (3.10) can be much greater than the numerator. Then, the whole fraction can be ignored and we can rewrite Eq. (3.10) in the shorter form

$$kT\frac{\partial W_{\{n\}}}{\partial \mu^E_k} = \delta_{k1} - n_k. \tag{3.11}$$

As an example, we dwell on the simplest case when aggregates are formed by only two types of ions (we denote their concentrations of monomeric forms as additional subscript *1*), i.e., surface-active ions that initiate the aggregation (first subscript *1*) and counterions (first subscript *2*). Then, for the population of formed ionic aggregates, we have condition $\{n\} = n_1, n_2$, where aggregation numbers n_1 and n_2 can take any possible value. In addition, it is assumed that there are co-ions in the solution (subscript *3*) due to the presence of background electrolyte, the second ion of which coincides

with the counterion. In this case, it follows from Eq. (3.10) that

$$kT\frac{\partial W_{\{n\}}}{\partial \mu_1^{\mathrm{E}}} = 1 - n_1 + \frac{c_{11}z_1(z_{\{n\}} - z_1)}{2I}, \quad (3.12)$$

$$kT\frac{\partial W_{\{n\}}}{\partial \mu_2^{\mathrm{E}}} = -n_2 + \frac{c_{21}z_2(z_{\{n\}} - z_1)}{2I}, \quad (3.13)$$

where

$$2I = c_{11}z_1^2 + c_{21}z_2^2 + \sum_{\{n\}} c_{\{n\}}z_{\{n\}}^2 + c_3z_3^2, \quad (3.14)$$

The summation is performed over all types of aggregates. An increase in the concentration of background electrolyte leads to an increase in c_{21} and c_3; moreover, the degree of counterion binding rises and $z_{\{n\}}$ diminishes. Both factors make the last term in Eq. (3.12) small compared to preceding terms and results in the truncated relation

$$kT\frac{\partial W_{\{n\}}}{\partial \mu_1^{\mathrm{E}}} = 1 - n_1, \quad (3.15)$$

which defines the aggregation number. The situation becomes more complicated with relation (3.13) where high c_{21} concentration is also present in the numerator. In this case, the disregard for the fraction may be justified only by the smallness of the charge number $z_{\{n\}}$ of aggregate (at large n_2). However, if the charge of aggregate is small, this implies that the degree of binding of counterions is close to unity and, hence, the problem of finding their aggregation numbers is solved by itself. Note that this circumstance casts no doubt on relation (3.11), where the presence of foreign background electrolyte, whose ions do not participate in aggregation, was suggested.

4. CONTRIBUTIONS TO THE WORK OF IONIC AGGREGATE FORMATION

According to [9–11], let us present the formation work $W_{\{n\}}$ of the aggregate of normal micelle type (with hydrocarbon core) as the sum of four contributions

$$W_{\{n\}} = W_{\{n\}}^{\mathrm{h}} + W_{\{n\}}^{\mathrm{surf}} + W_{\{n\}}^{\mathrm{conc}} + W_q^{\mathrm{el}}. \quad (4.1)$$

Here, $W_{\{n\}}^{\mathrm{h}}$ is the hydrophobic contribution responsible for the transfer work of hydrocarbon tail of surface-active ions from the solution to the aggregate core at a pressure equals the pressure of solution; $W_{\{n\}}^{\mathrm{surf}}$ is the surface contribution that accounts for the surface tension γ_0 of the aggregate core and the fact that the part of core is covered by head ionic groups and adsorbed counterions; $W_{\{n\}}^{\mathrm{conc}}$ is the concentration contribution due to the difference in concentrations of hydrocarbon tails in the aggregate core and in the surrounding solution; and W_q^{el} is the electric contribution responsible for the work of aggregate charging at preset aggregation numbers and chemical potentials of surface-active ions, counterions, and co-ions.

In the droplet model of a spherical single-component ionic aggregate ($\{n\} = n$), we have the following expressions for the first three terms in Eq. (4.1) [9–11]:

$$W_n^{\mathrm{h}} = -nBn_{\mathrm{C}}, \quad (4.2)$$

$$W_n^{\mathrm{surf}} = \frac{(4\pi)^{1/3}\gamma_0[3\mathrm{v}(n_{\mathrm{C}}+1)]^{2/3}}{kT}n^{2/3} - \frac{(4\pi)^{1/3}(3\mathrm{v})^{2/3}\gamma_0}{kT}n, \quad (4.3)$$

$$W_n^{\mathrm{conc}} = -n\ln(c_1/c^{\alpha}), \quad (4.4)$$

where B is the positive dimensionless magnitude equals to approximately 1.4 at 20°C, n_{C} is the number of carbon atoms in the hydrocarbon chain of surfactant molecule, γ_0 is the surface tension of the hydrocarbon core of aggregate, v is the characteristic volume of methylene group, c_1 is the volume concentration of surfactant monomers in solution, and $c^{\alpha} \approx \frac{1}{\mathrm{v}(n_{\mathrm{C}}+1)}$ is the concentration of hydrocarbon tails in the aggregate core. Note that the ratio between radius r of the aggregate core and aggregation number n has the following form:

$$r = \left[\frac{3\mathrm{v}(n_{\mathrm{C}}+1)}{4\pi}\right]^{1/3} n^{1/3}. \quad (4.5)$$

Under assumption that $n_1 \gg n_2$, formulas (4.2)–(4.5) are directly expanded to spherical ionic aggregate, provided that n 1 is substituted for n_1 and at the understanding that the c_1 value is assumed to be the volume concentration of monomeric surface-active ions in solution. This substantially simplifies the finding of the formation work for spherical ionic aggregate in the droplet model.

Basic difference in the formation work for molecular and ionic aggregates consists of electric contribution W_q^{el}. In the case of ionic surfactant, the electric contribution was calculated as the energy of the spherical capacitor formed by the electric dipoles of the hydrophilic moieties of surfactant molecule [9–11]. In the case of ionic aggregate, the electric contribution can be calculated by the Derjaguin formula [2, 5, 12–14] as follows:

$$w_q^{\mathrm{el}} = \int_0^q \varphi_s(q')dq', \quad (4.6)$$

where $\varphi_s(q')$ is the electric potential on the surface of bare ionic aggregate carrying charge q' (the whole work $W_{\{n\}}$ in Eq. (4.1) refers to the bare ionic aggregate). A

few analytical expressions of the $\varphi_s(q')$ dependence was proposed in the published literature; they are based on the approximate solution of the nonlinear Poisson–Boltzmann equation for a charged sphere and allow the W_q^{el} contribution to be calculated as a function of aggregation numbers n_1 and volume concentrations of surface-active ions, counterions, and co-ions in solution [2, 4, 15, 16].

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