

Thermodynamic and Kinetic Foundations of the Theory of Micellization: 1. General Aspects

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Abstract—A relationship between the work of the aggregate formation and the equilibrium aggregate concentration is established with allowances made for the mobility of molecular aggregates in a solution of a colloidal nonionic surfactant. The relation between the intensities of emission and absorption of surfactant monomers by the aggregates is found. A kinetic equation of the formation of molecular aggregates is obtained. Conditions of aggregation/disaggregation processes are revealed. Kinetic substantiation of the irreversible tendency of a solution to the aggregation equilibrium is given.

INTRODUCTION

Although processes of nucleation (creation of new phases) and micellization are characterized by a common nature (in both cases, aggregation systems of molecules or ions are formed instantaneously), their kinetic theories have been developed in different pathways. The Volmer–Bekker–Döring–Frenkel–Zel'dovich kinetic theory of nucleation [1–4] is based on the phase approach resulting from the Gibbs thermodynamics. The “phase approach” term is also used in the theory of surfactant micellization; however, it has nothing in common with the phase approach used in the theory of nucleation: the array of micelles is considered to be a certain macroscopic “pseudophase”. Such an approach does not stand up under strict scrutiny [5] and it can be assumed to be an approximation only in some aspects. For the theory of micellization, more typical is an approach based on the law of mass action when molecular aggregation is assumed to be a kind of chemical reaction. In essence, all present advances in the theory of micellization (including its kinetic aspect) are based on this approach (see relevant references in [5]). Note that the methods of nucleation kinetics have been virtually unused in the theory of micellization. Above all, it may be explained primarily by the fact that in general micellization kinetics has been developed inadequately.

It can be demonstrated that, from the thermodynamic point of view, approaches of the theories of nucleation and the law of mass action are quite equivalent in their strict formulations differing only in the selection of a standard state (it is true that this selection is rather unusual in the case of nucleation) [6]. At the same time, the approach of the theory of nucleation offers a number of practical advantages and most properly adjusted to the kinetic purposes, to say nothing about the adequately developed apparatus of a theory. Its application to the micellization process, which is strikingly different from the common phase transition,

is of interest to the theory of nucleation itself, which was not yet applied to such a peculiar object.

The aim of this study, which is initiated by this publication, can be determined as the construction of the kinetic theory of micellization based on the current theory of nucleation. Kinetics and thermodynamics will go hand in hand in this way. Just as the theory of nucleation rests to a significant extent on thermodynamics, so too the kinetic theory of micellization needs the data on the equilibrium and non-equilibrium states given by the thermodynamics of micellization. In this communication, we determine the starting points of the study of non-equilibrium micellar systems.

1. THE WORK OF MOLECULAR AGGREGATE FORMATION

Let us consider the solution of one nonionic surfactant capable of forming molecular aggregates. In this case, the role of the solvent is played by the liquid that is passive with respect to aggregate formation. It is assumed that the solution is ideal (infinitely dilute). Considering aggregates to be compact formations and suggesting that their temperature is equal to that of the solution, the aggregation number n is assumed to be the characteristic of the internal state of the aggregate. This discrete characteristic is convenient, because it is also suitable for the smallest aggregates beginning with the lowest value $n = 1$, when the aggregate comprises only one surfactant molecule in a solution.

Let us denote chemical potential and concentration (the number of aggregates per unit volume) of aggregates containing n molecules by μ_n and c_n , respectively. In this case, μ_1 and c_1 represent the chemical potential and concentration of monomers, respectively. In the considered case of nonionic surfactants, all monomers are identical.

Usually, the phase approach does not take into account the multiplicity of phases and the entropy of their mixing. While considering the aggregation processes, we take this fact automatically into account by the introduction of the chemical potential of molecular aggregate [7]:

$$\mu_n = G_n^0 + kT \ln(\Lambda_n^3 c_n f_n), \quad (1.1)$$

where G_n^0 is the Gibbs energy of a single aggregate consisting of n molecules with the quiescent center of mass in a pure medium (in the absence of other aggregates), $k\Lambda_n = h(2\pi m_n kT)^{-1/2}$ is the average de Broglie wavelength of a molecular aggregate (h is Planck's constant, m_n is the mass of the molecular aggregate), and f_n is the activity coefficient of the aggregate. The value of Λ_n^{-3} is the partition function for aggregate translational motion, and $kT \ln \Lambda_n^3$ is its contribution to the free energy. Similarly, $kT \ln f_n$ is the contribution from the interaction of all aggregates (including monomers) with each other.

Following the traditions of physical chemistry, we may write expression (1.1) as

$$\mu_n = G_n + kT \ln(c_n/c_s), \quad (1.2)$$

where G_n is the chemical potential (the Gibbs energy) of the molecular aggregate corresponding to a certain arbitrarily chosen standard concentration c_s . In the thermodynamics of solution, c_s is usually assumed to be equal to unity (in the corresponding measurement units) so that only concentration (in fact, dimensionless value numerically equal to concentration) is placed under the logarithm sign in (1.2). Formula (1.2) is valid both in the absence and the presence of interaction between aggregates in the standard state; however, since we assumed to consider an ideal system, we suggest that the standard state corresponding to concentration c_s is also ideal. Otherwise, we assume that $f_n = 1$, both in formulas (1.1) and (1.2).

For the kinetically important case of fluctuation creation of aggregates with $n = 2, 3, \dots$ in a solution containing originally only surfactant monomers, it is convenient to select standard concentration c_s according to:

$$c_s = c_1. \quad (1.3)$$

In this case, equation (1.2) is reduced to:

$$\mu_n = G_n + kT \ln(c_n/c_1). \quad (1.4)$$

The convenience of definition (1.3) is explained by the fact that the Gibbs energy of monomer G_1 should coincide with its chemical potential μ_1 , in a solution, where monomers are already present, i.e., relation

$$G_1 = \mu_1 \quad (1.5)$$

should be valid. It is this equality that is supported by expression (1.4), which resulted from (1.2) and (1.3).

Addressing the most practically important case, we consider an aggregation system at a constant temperature and pressure and, correspondingly, we shall use the Gibbs energy as the thermodynamic potential (its gain produces the work done over a system). If the molecular aggregate is formed at the selected standard concentration c_1 (both for monomers and forming aggregates), the work of the molecular aggregate formation is given by the formula:

$$W_n = (G_n - n\mu_1)/kT. \quad (1.6)$$

The work W_n is expressed in thermal units of kT energy.

The term $n\mu_1$ in (1.6) representing the Gibbs energy of the array of n monomers corresponds to the fact that the aggregate formation occurs in a solution that originally contained only monomers. However, in this case, the work W_n is independent of concentration c_n of aggregates with $n \geq 2$; however, it is dependent on monomer concentration c_1 . At the same time, equality

$$W_1 = 0, \quad (1.7)$$

which followed from (1.5) and (1.6), also seems to be natural.

Indeed, monomers are already present in a solution, and, hence, no work is needed for their formation.

It follows from (1.4) and (1.6) that

$$\mu_n - n\mu_1 = kT[W_n + \ln(c_n/c_1)]. \quad (1.8)$$

As is known, the condition of aggregation equilibrium in a solution is:

$$\mu_n^{(e)} = n\mu_1, \quad (1.9)$$

where superscript *e* denotes the state of aggregation equilibrium. From (1.8) and (1.9), for the equilibrium aggregate concentration $c_n^{(e)}$ we obtain:

$$c_n^{(e)} = c_1 \exp(-W_n). \quad (1.10)$$

Equality (1.10) corresponds to Boltzmann's fluctuation principle.

Taking into account that chemical potentials μ_n and μ_1 depend (at the ideality of solution) on concentrations c_n and c_1 via the terms $kT \ln c_n$ and $kT \ln c_1$, from the condition of aggregation equilibrium (1.9) we obtain the law of mass action:

$$c_n^{(e)} = K_n c_1^n, \quad (1.11)$$

where coefficient K_n does not depend on concentration c_1 (as well as on concentration c_n with $n \geq 2$).

According to (1.10) and (1.11):

$$W_n = -\ln K_n - (n-1) \ln c_1. \quad (1.12)$$

Term $-(n-1) \ln c_1$ in relation (1.12) explicitly governs the dependence of work W_n on monomer concentration c_1 (work W_n is independent of concentrations c_n with $n \geq 2$). Since work W_n , by its meaning, is not related to whether the aggregate concentration is equilibrium or

not, relation (1.12) is valid at the arbitrary aggregate concentration in an ideal solution.

The $-\ln K_n$ value is known to be the work of micellization W_n^M when the standard concentration expressed by the molarity (1 mole l^{-1}) is constant. While comparing this work with W_n (then concentration c_1 should also be expressed via molarity), we can see [from (1.12)] a significant difference between W_n^M and W_n : if, in an ideal system, the former value is independent of monomer concentration, the latter, on the contrary, is dependent on this concentration. This dependence is especially pronounced for the micelles with large aggregation numbers. For the micelles, the values of W_n^M and W_n differ even in signs. For example, the former work is determined experimentally for the micelles of nonionic surfactants via the critical micellization concentration (CMC) c_m as [5]

$$W_n^M \approx (n-1) \ln c_m \quad (1.13)$$

and it is typically negative in view of the CMC smallness expressed by molarity. Relation (1.13) should not be substituted into formula (1.12), because values neglected in (1.13) are significant for W_n . The work W_n is not expressed via the CMC, but it can be expressed via the degree of micellization $\alpha \equiv nc_n/c$ (c is the overall surfactant concentration). For bimodal distribution of monomers and micelles, $c_n = \alpha c/n$ and $c_1 = (1-\alpha)c$; then, formula (1.10) yields

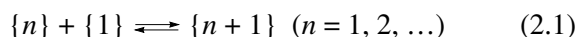
$$W_n = \ln[n(1-\alpha)/\alpha]. \quad (1.14)$$

Critical degree of micellization α_m corresponding to the CMC is easily calculated at the known aggregation number and is usually equal to only a few percentage points [5]. At $n = 50$, the largest of the estimates was equal to $\alpha_m = 0.124$ [5], whereas about 353 stands under the logarithm sign in (1.14). For nonionic surfactants with much larger aggregation numbers, α_m is even smaller (often, $\alpha_m \sim n^{-1/2}$ [5]), and the expression under the logarithm sign is still larger. Therefore, it can be stated that even at the CMC and over the large concentration range above the CMC, work W_n is positive.

Note that (1.8) can also be obtained directly from (1.9) and (1.10), with allowances for relation $\mu_n - \mu_n^{(e)} = kT \ln(c_n/c_n^{(e)})$ of the theory of ideal solutions.

2. KINETIC EQUATION OF THE FORMATION OF MOLECULAR AGGREGATES

According to the principles of classical kinetic theory, the number of molecules in an aggregate varies only as a result of the absorption or emission of a monomer by the aggregate. Let us consider the sequence



of direct and reverse aggregate transitions occurring during this process. Aggregates containing n molecules are denoted by $\{n\}$ ($n = 1, 2, \dots$).

The most important value in the classical kinetic theory is the aggregate flux on a sequence (2.1) occurring due to direct and reverse aggregate transitions. Denoting this flux by J_n , we have

$$J_n = j_n^+ c_n - j_{n+1}^- c_{n+1} \quad (n = 1, 2, \dots), \quad (2.2)$$

where j_n^+ is the number of monomers absorbed by the aggregate $\{n\}$ from solution per unit time; and j_{n+1}^- is the number of monomers emitted from the aggregate $\{n+1\}$ to the solution per unit time. Evidently, $j_n^+ > 0$ and $j_{n+1}^- > 0$.

The importance of aggregate flux J_n in a space of aggregate numbers is explained by the fact that, according to equation

$$\partial c_n / \partial t = J_{n-1} - J_n \quad (n = 2, 3, \dots) \quad (2.3)$$

it is responsible for the variation of aggregate concentration c_n with $n \geq 2$ in time t .

Let us find the relationship between the intensities of emission j_{n+1}^- and absorption j_n^+ of monomers by the molecular aggregate.

Under aggregation equilibrium, i.e., under condition (1.9), the detail equilibrium of aggregates on each sequence of direct and reverse transitions should be established, i.e., the relationship

$$J_n^{(e)} = 0 \quad (n = 1, 2, \dots) \quad (2.4)$$

should be fulfilled. Here, $J_n^{(e)}$ is given by expression (2.2) at $c_n = c_n^{(e)}$. Taking into account that, at the suggested high density of a matter in aggregates, values j_n^+ and j_{n+1}^- are independent of whether the solution is under an aggregation equilibrium at the given concentration c_1 or not, we obtain from (2.2) and (2.4):

$$j_{n+1}^- = j_n^+ c_n^{(e)} / c_{n+1}^{(e)} \quad (n = 1, 2, \dots). \quad (2.5)$$

Substituting (1.10) into (2.5), we arrive at the desired relation

$$j_{n+1}^- = j_n^+ \exp(W_{n+1} - W_n) \quad (n = 1, 2, \dots). \quad (2.6)$$

Substituting (2.6) into (2.2), we obtain

$$J_n = j_n^+ [c_n - c_{n+1} \exp(W_{n+1} - W_n)] \quad (n = 1, 2, \dots). \quad (2.7)$$

Relation (2.7), together with (2.3), yields the kinetic equation of the formation of molecular aggregates.

3. CONDITIONS OF AGGREGATION AND DISAGGREGATION

According to definition (15) in [6], let us introduce the affinity A_n

$$A_n = -(\mu_n - n\mu_1) \quad (n = 1, 2, \dots). \quad (3.1)$$

Under the aggregation equilibrium, it follows from (3.1) and (1.9) that

$$A_n^{(e)} = 0 \quad (n = 1, 2, \dots). \quad (3.2)$$

Opening the definition (3.1) with the aid of (1.8), we obtain

$$A_n = -kT[W_n + \ln(c_n/c_1)] \quad (n = 1, 2, \dots). \quad (3.3)$$

Expression (3.3) describes the dependence of affinity A_n on the work of formation and the aggregate concentration. According to (3.3), the lower work W_n and the c_n/c_1 ratio, the larger is affinity A_n .

Using (3.3), let us represent (2.7) in the following form

$$J_n = j_n^+ c_n \{1 - \exp[-(A_{n+1} - A_n)/kT]\} \quad (3.4)$$

$$(n = 1, 2, \dots).$$

In the case of aggregation equilibrium, when (3.2) is valid, formula (3.4) confirms the relation of detailed equilibrium (2.4).

At the detailed description of the non-equilibrium process in a disperse system given by the kinetic theory, it seems natural to generally refer the problem of the occurrence of aggregation or disaggregation to a single sequence (2.1) of direct and reverse transitions done by the aggregates; moreover, to refer this problem to each current moment of process development.

Evidently, the occurrence of aggregation or disaggregation on this particular sequence depends on the fact whether $J_n > 0$ or $J_n < 0$ at each current moment. In view of $j_n^+ > 0$, formula (3.4) allows us to state that

$$\left. \begin{array}{l} J_n > 0 \text{ (aggregation), if } A_{n+1} - A_n > 0 \\ J_n < 0 \text{ (disaggregation), if } A_{n+1} - A_n < 0 \end{array} \right\} \quad (3.5)$$

$$(n = 1, 2, \dots).$$

Using (3.3) to express relation

$$A_{n+1} - A_n = -kT[W_{n+1} - W_n + \ln(c_{n+1}/c_n)] \quad (3.6)$$

$$(n = 1, 2, \dots),$$

we can see that the sign of difference ($A_{n+1} - A_n$) [important in conditions (3.5) for the occurrence of aggregation or disaggregation] depends not only on the ($W_{n+1} - W_n$) value, i.e., on the energy factor, but also on the $\ln(c_{n+1}/c_n)$ value, i.e., on the fluctuation probability factor. Conditions (3.5) and relation (3.6) are valid during the evolution of the disperse system from its arbitrary initial state.

In particular, if only monomers are present in disperse systems at the initial moment, then, at least during the consecutive moments (close to the preceding moment), inequalities $c_1 \gg c_2 \gg c_3 \gg c_4 \dots$, are to be fulfilled with ever increasing strength; at the same time, in view of (3.6), inequalities $0 < A_2 - A_1 < A_3 - A_2 < A_4 - A_3 \dots$, will be fulfilled, despite a possible increase in work W_n with an increase in n beginning with $n = 1$ when, according to (1.7), work W_n is equal to zero. Then, as is seen from (3.5), at the consecutive moments close to the initial moment, the aggregation occurs at all sequences of the non-equilibrium process in a disperse system. The aggregation is caused by the probability fluctuation factor, which can be counteracted (and even noticeably) by the energy factor.

4. KINETIC SUBSTANTIATION OF IRREVERSIBLE TENDENCY OF A SOLUTION TO AGGREGATION EQUILIBRIUM

Let us demonstrate that, irrespective of the initial state of a solution, the kinetic theory results in a monotonic decrease in the Gibbs energy of a solution with time at the material isolation of a solution and at its constant temperature and pressure.

We refer our consideration to unit volume of a solution. The Gibbs energy of a solution unit volume we denote by G . The numbers of aggregates with $n = 1, 2, \dots$ per solution unit volume are equal to c_n . Material isolation of a solution implies that the overall surfactant concentration c in a solution determined by the evident equality

$$c_1 + \sum_{n \geq 2} n c_n = c \quad (4.1)$$

is a preset magnitude.

According to relations (15) from [6], at the material isolation of a solution [at preset overall concentration c in (4.1)] and constant temperature and pressure, we arrive at the following differential thermodynamic relation

$$dG = -\sum_{n \geq 2} A_n d c_n. \quad (4.2)$$

Expressing this relation as

$$\partial G / \partial t = -\sum_{n \geq 2} A_n \partial c_n / \partial t \quad (4.3)$$

and using (2.3), we obtain (after changing the designation of the summation index and allowing for $A_1 = 0$):

$$\partial G / \partial t = -\sum_{n \geq 1} (A_{n+1} - A_n) J_n. \quad (4.4)$$

According to (3.5), the sign of flux J_n coincides with that of the difference $(A_{n+1} - A_n)$ at all $n \geq 1$. Then it follows from (4.4) that:

$$\partial G / \partial t \leq 0. \quad (4.5)$$

The sign of equality in (4.5) is meaningful only when $J_n = 0$, and, correspondingly, $A_{n+1} - A_n = 0$ at all $n \geq 1$, i.e., when [in agreement with (2.4) and (3.2)] the aggregation equilibrium of a solution is established.

Thus, irrespective of the initial state of a solution, the kinetic theory indeed results [according to (4.5)] in a monotonic decrease in the Gibbs energy of a solution with time at its material isolation and constant temperature and pressure, up to the moment when the Gibbs energy reaches its minimum value at the final state of the aggregation equilibrium of a solution. Since at the material isolation of a system and its constant temperature and pressure, a monotonic decrease in the Gibbs energy implies, according to thermodynamic principles, the irreversible tendency of a system to the state of detailed thermodynamic equilibrium, the obtained inequality (4.5) results in the kinetic substantiation of the irreversible tendency of a solution to its aggregation equilibrium.

As is known, the statement of the irreversible tendency of a system to thermodynamic equilibrium is one of the most important postulates of thermodynamics. In particular, the derivation of the conditions of thermodynamic stability of a system under thermodynamic equilibrium is based on this postulate.

The substantiation of the thermodynamic postulate of the irreversible tendency of a system to thermodynamic equilibrium may be done only by the kinetic theory, for example, by the kinetic Boltzmann equation, the Fokker–Planck equations, and the equations of Markovian processes. In our treatment of disperse systems, relations (2.3) and (2.7) were precisely such equations.

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