

# Parametric Equations of the Theory of Formation of Spherical Micelles

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Using the notion of aggregation work, we construct a system of differential equations for the aggregation number of micelles which is a function of the parameters of micellization (*parametric equations*). There are explicit solutions for two important models of spherical micelles. Based on these solutions, we obtain an analytical expression for the equilibrium concentration of surfactant monomers and consequently for the whole spectrum of equilibrium concentrations of molecular aggregates in this framework. Accuracy of these expressions is discussed, and they are applied to an example of micelles formed by sodium dodecyl sulfate. © 2002 Elsevier Science (USA)

**Key Words:** spherical micelles; micellization; nucleation theory.

## INTRODUCTION

The process of micellization is an important and interesting problem, whose mechanism is not yet understood. Its complexity does not allow it to be described completely. If the concentration  $n_1$  of surfactant monomers (amphiphiles) exceeds the critical micellization concentration (CMC), the monomers can form aggregates called *micelles*. There are different structures of micelles (spherical, cylindrical, disk-like, inverse, etc., see Ref. 1), and they can be classified according to the magnitude of  $n_1$ . For a “relatively small” concentration<sup>2</sup>  $n_1$ , the spherical structure is the most favorable (in this paper we do not consider the supplemental conditions which can be imposed by the packing constraints, see Ref. 1). There are two essential advantages in this case. First, the concentration of monomers is small and therefore one can apply some useful approximations. Second, the geometry of micelles is described by the only parameter—the radius of the sphere. Moreover, this radius can be expressed in terms of aggregation number (the number of monomers which form an aggregate). Consequently, we can use methods of the *classical nucleation theory* and the notion of aggregation work in particular. One can find its description and applications in Refs. 2–6, which investigate thermodynamic properties of mi-

celles. Note that there exist other recent approaches, for example so-called *density-functional theories* (7, 8) and *self-consistent field lattice theories* (9, 10). We do not go deep into comparing them, because that should be the subject of another paper. The present treatment is based on the notion of aggregation work, we thus rest in the framework of the classical nucleation theory.

We propose a method which allows us to determine the dependence of the equilibrium concentration of monomers and micelles on the physical parameters defining the process of micellization (like temperature of solution, length of carbon chain, electric charge of the head of surfactant molecule, etc.). We are going to establish *parametric equations* which can be solved explicitly for the different model expressions of the aggregation work. Therefore, we will be able to determine equilibrium concentration of monomers as a function of physical parameters in the framework of a given model. Consequently, it will allow us to relate different models of spherical micelles among themselves and to compare them with regard to the experimental data.

The first part of this paper is devoted to the introduction of the basic notions and the essential assumptions which will be used to establish parametric equations in the second part. The third and the fourth parts give solutions to these equations for the drop model and Grinin's model of spherical micelles. The final part describes some consequences and the possible generalizations of this formalism.

## 1. BASIC NOTIONS AND ESSENTIAL ASSUMPTIONS

Classical nucleation theory is based upon the notion of *aggregation work*  $F_v$ , i.e., minimal work required to form an aggregate from  $v$  surfactant monomers (amphiphiles), where  $v$  refers the *aggregation number*. Function  $F_v$  essentially defines the dynamics of the system and completely determines the equilibrium distribution of the aggregates  $n_v$  by virtue of the aggregation number  $v$  according to Boltzmann's law

$$n_v = n_1 e^{-F_v}, \quad [1]$$

where  $n_1$  is the concentration of monomers.<sup>3</sup> Note that  $F_1 = 0$  because the monomers already exist. Function  $F_v$  depends on

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<sup>2</sup> We do not specify here what “relatively small concentration” means for the reason that there is no well-defined limitation on the applicability of the theory. Moreover, the “permitted concentrations” significantly depend on the considered amphiphile.

<sup>3</sup> We use dimensionless quantities. In particular, all the concentrations are expressed in convenient units, for example, in units of the critical micellization

different quantities. We classify these dependencies as

- “functional”, on the aggregation number  $v$ ;
- “dynamic”, on the concentration of monomers  $n_1$ ; and
- “parametric”, on the parameters defining micellization (e.g., temperature, molecular properties of solvent, structure of monomers), which are denoted as  $a_1 \dots a_K$ . Note that the aggregation work  $F_v$  does not depend on the concentrations  $n_v$  with  $v > 1$ . Indeed, we are working with spherical micelles; thus the concentration of monomers is relatively small and highly dominates the concentrations of dimers, trimers, etc. Hence, we can assume that aggregates are formed due to gradual attachment/detachment of monomers. In other words, we neglect the possibilities of attachment/detachment of dimers, trimers, etc., to the aggregate. Moreover, for the small concentration (i.e., the dilute solution) the dependence of function  $F_v$  on  $n_1$  is simply

$$F_v = G_v - (v - 1) \ln n_1, \quad [2]$$

where the new function  $G_v$  does not depend at all on the concentrations and is defined only by the parameters  $a_1 \dots a_K$  and  $v$ . This is a direct consequence of the differential form  $dF_v = (\mu_v - \mu_0)dv$  given as the difference of chemical potentials  $\mu_v$  and  $\mu_0$ , where  $\mu_v$  is the chemical potential of any surfactant “inside” the aggregate consisting of  $v$  molecules. Evidently,  $\mu_v$  is independent of the concentration of monomers in the solution and depends only on the internal structure of the aggregate;  $\mu_0$  is the chemical potential of any surfactant in the solution. For the dilute solutions there is a simple expression  $\mu_0 = \ln n_1 + \chi(T)$ , where  $\chi(T)$  is a function of temperature (11). The condition  $F_1 = 0$  implies  $G_1 = 0$ .

We make an important assumption of the *closure* of the system, i.e., the total number of amphiphiles (in monomers and aggregates)  $N$  is fixed. This is an essential condition because one can imagine some processes where this number changes. From now on,  $N$  will be a fixed external parameter. In this case, the law of mass conservation can be written as

$$N = \sum_{v=1}^{\infty} v n_v. \quad [3]$$

Note that in real physical problems the summation is usually limited by a certain value  $v_m$ . However, it is convenient to use this notation, remembering that the finite sum can be “complemented by zeros” (which is equivalent to the rapid growth of  $F_v$  with an increase of  $v$ ). For the convergence of series it is sufficient that  $F_v$  tends to infinity when  $v \rightarrow \infty$  or that  $G_v$  increases faster than a linear function of  $v$ .

As the mechanism of micelle formation is very complex, it is reasonable to use model expressions for  $G_v$  which should represent the essential properties of micellization. We represent

concentration; the aggregation work is measured in units of  $kT$ , where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature.

function  $G_v$  as a sum of the fractional powers of  $v$ ,

$$G_v = \sum_{m=0}^M c_m v^{\rho m}, \quad [4]$$

where  $\rho > 0$  is constant for a particular model and the coefficients  $c_m$  of this decomposition depend on the parameters  $a_1 \dots a_K$ . This representation is quite reasonable: for example, in the problem of condensation of vapor, the aggregation work is the sum of the powers of  $v^{1/3}$ ; in Grinin’s model of spherical micelles (see below) it is the sum of the powers of  $v^{1/2}$ . We keep only positive powers in the sum. Negative powers of  $v$  have no practical use for the fact that we are interested in the quantity  $G_v$  for large  $v$ . Note that function  $G_v$  has a physical sense only for natural numbers  $v$ . However, Formula [4] allows us to interpolate  $G_v$  for any real number  $v \geq 1$ . Obviously, one can imagine different interpolations but we use the simple one<sup>4</sup> given by [4]. Furthermore, we differentiate some quantities by  $v$ , etc.

The important statement of the nucleation theory is the following: every minimum of aggregation work corresponds to a stable (or quasi-stable) state of the system of aggregates. We are interested in the formation of micelles; therefore, there should be a “deep” minimum of  $F_v$  (potential well). Moreover, this minimum is assumed to be unique and it is denoted as  $v_s$ . Indeed, we are working with a small concentration of monomers, and, consequently, there is only one stable state—spherical micelles. Using Relation [2], one can write the equation on  $v_s$  as

$$0 = \frac{\partial F_v}{\partial v}(v_s) = \frac{\partial G_v}{\partial v}(v_s) - \ln n_1. \quad [5]$$

Physically, the quantity  $v_s$  is the aggregation number of micelles,  $v_s \gg 1$ . In the practically important case the number of amphiphiles in all micelles is comparable (or more) to the concentration of monomers.

Using all previous assumptions, we can establish a formalism which defines the dependence of the equilibrium concentration of monomers on the physical parameters of micellization.

## 2. PARAMETRIC EQUATIONS OF THE THEORY OF FORMATION OF SPHERICAL MICELLES

Let us introduce a set of functions  $f_\alpha(x)$  assuming  $x > 0$ ,

$$f_\alpha(x) = \sum_{v=1}^{\infty} v^\alpha e^{-G_v} x^v = \sum_{v=1}^{\infty} e^{-h(v)}, \quad [6]$$

<sup>4</sup> Nevertheless, sometimes it is convenient to change this *canonical* interpolation a little. Indeed, the limit of  $G_v$  when  $v \rightarrow 1$  is equal to  $c = \sum_{m=0}^M c_m$ , and nothing demands that it equal zero (for example, see the drop model of spherical micelles, part 3). Therefore, we can change expression [4] on the interval  $(1, 2)$  to obtain  $\lim_{v \rightarrow 1} G_v = 0$ . The simple way is to add function  $-c/v^x$  to  $G_v$ , where  $x$  is a large positive number. We are interested in function  $G_v$  for large  $v$ ; thus the addition  $-c/v^x$  has no any influence on our results.

where the new function  $h(v)$  is

$$h(v) = G_v - v \ln x - \alpha \ln v. \quad [7]$$

There are three important properties:

(1) All functions  $f_\alpha(x)$  are defined for any positive  $x$  because of a rapid growth of function  $h(v)$  (since  $G_v$  increases faster than  $v$ ). Moreover,  $f_\alpha(x) \geq 0$  is true for any  $x > 0$ .

(2) Simple verification shows that

$$x \frac{\partial f_\alpha(x)}{\partial x} = f_{\alpha+1}(x). \quad [8]$$

Hereof it follows that all  $f_\alpha(x)$  are smooth monotonously growing functions, with derivatives of all orders.

(3) For  $\alpha \ll v_s$ , function  $h(v)$  has a minimum which is with high accuracy<sup>5</sup> equal to  $v_s$ .

Let us represent  $f_\alpha(x)$  as a sum of three terms which correspond to monomers, small aggregates, and micelles,

$$f_\alpha(x) = x + \sum_{v=2}^{v_0-1} e^{-h(v)} + \sum_{v=v_0}^{\infty} e^{-h(v)} = x + f_\alpha^0(x) + \tilde{f}_\alpha(x). \quad [9]$$

It is necessary to say that the choice of this decomposition is artificial:  $v_0$  depends on the given model. Usually  $v_0$  can be chosen as the maximum of  $F_v$ , i.e., a point where  $n_v$  has its minimum. As we take interest in the formation of micelles, it is reasonable to suppose that the contribution of micelles dominates over the contributions of small aggregates,

$$f_\alpha^0(x) \ll \tilde{f}_\alpha(x). \quad [10]$$

We neglect functions  $f_\alpha^0(x)$ , and the sum [9] becomes

$$f_\alpha(x) \approx x + \tilde{f}_\alpha(x). \quad [11]$$

Now we calculate an approximation to function  $\tilde{f}_\alpha(x)$  (which corresponds to micelles) for small values of  $\alpha$ . For this purpose we represent the corresponding sum in [9] as an integral, decompose  $h(v)$  in the vicinity of its minimum  $v_s$  up to the square terms, and calculate the obtained Gaussian integral after replacing the lower integral limit by  $-\infty$ ,

$$\tilde{f}_\alpha(x) \approx \exp[-\beta(x)], \quad \beta(x) = h(v_s) + \frac{1}{2} \ln h''(v_s) - \frac{1}{2} \ln(2\pi). \quad [12]$$

<sup>5</sup> The equation for the minimum of  $h(v)$  is derived by subtracting  $\alpha/v$  in the right-hand side of Eq. [5]. Under condition  $\alpha \ll v_s$  this term can be neglected by comparison with the positive powers of  $v$ .

Due to the independence of  $v_s$  of  $\alpha$ , we obtain an important relation between functions  $\tilde{f}_\alpha$ ,

$$\tilde{f}_\alpha / \tilde{f}_\beta = (v_s)^{\alpha-\beta},$$

whence we conclude

$$\tilde{f}_\alpha = (v_s)^{\alpha-1} \tilde{f}_1. \quad [13]$$

In terms of functions  $f_\alpha(x)$  the law of mass conservation [3] can be written as an equation for  $n_1$ ,

$$f_1(x) = N. \quad [14]$$

Due to the continuity and monotone growth of  $f_\alpha(x)$ , for any  $N$  there is a unique solution of [14] which is equal to  $n_1$ ,

$$f_1(n_1) = N. \quad [15]$$

Substituting [12] and [15] in [11], we obtain the transcendental equation for the equilibrium concentration of monomers  $n_1$  (cf. Ref. 5),

$$N = n_1 + \exp[-\beta(n_1)].$$

Practically this equation leads to the same difficulties in solution as the initial Eq. [15]. Therefore we continue to develop our method.

Let us consider Eq. [14]. Once this equation is solved, we shall find the dependence of  $x$  (i.e.,  $n_1$ ) on the parameters  $a_1 \dots a_K$ . One can treat this dependence as a trajectory in the phase space based on parameters  $a_1 \dots a_K$ , where function  $f_1(x)$  is an “integral of motion” (i.e., it is a constant on this trajectory). Fixing all parameters except one and differentiating [14] by this single parameter  $a_k$ , we express the derivatives  $\partial x / \partial a_k$  according to

$$\frac{\partial x}{\partial a_k} = - \left[ \frac{\partial f_1}{\partial x} \right]^{-1} \frac{\partial f_1}{\partial a_k}. \quad [16]$$

The derivative in the denominator can be found with the help of [8]. Now we calculate the derivative in the nominator,

$$\frac{\partial f_1}{\partial a_k} = \sum_{v=1}^{\infty} v e^{-G_v} x^v \left( -\frac{\partial G_v}{\partial a_k} \right).$$

Taking into account the representation of  $G_v$  as a sum of fractional powers of  $v$ , one has

$$\frac{\partial G_v}{\partial a_k} = \sum_m c_{m,k} v^{\alpha m}, \quad c_{m,k} = \frac{\partial c_m}{\partial a_k}. \quad [17]$$

Collecting the previous expressions together, dividing by  $x$ , and

bringing it under the sign of the differential, we obtain

$$\frac{\partial \ln x}{\partial a_k} = \frac{1}{f_2(x)} \sum_m c_{m,k} f_{\rho m+1}. \quad [18]$$

Now we represent functions  $f_\alpha$  according to [9], where all the terms  $\tilde{f}_\alpha$  are expressed by [13] and all the terms  $f_\alpha^0(x)$  are neglected by virtue of [10],

$$\frac{\partial \ln x}{\partial a_k} = \frac{1}{x + v_s \tilde{f}_1} \left( x \sum_m c_{m,k} + \tilde{f}_1 \sum_m c_{m,k} v_s^{\rho m} \right).$$

In the first part we demanded that the number of amphiphiles in micelles ( $\tilde{f}_1$ ) has the same or much greater order than in monomers ( $n_1$ ), therefore we can neglect  $x$  and  $x \sum_m c_{m,k}$  by comparison with  $v_s \tilde{f}_1$  and  $\tilde{f}_1 \sum_m c_{m,k} v_s^{\rho m}$  in nominator and denominator, respectively. Here we make a second approximation, after the Gaussian one in calculation of  $\tilde{f}_\alpha$ . The essential simplification brought by this operation is the independence of derivatives  $\partial \ln x / \partial a_k$  of  $\tilde{f}_1$ . We have

$$\frac{\partial \ln x}{\partial a_k} = \sum_m c_{m,k} v_s^{\rho m-1}. \quad [19]$$

With Eq. [5] we obtain a closed system of equations for two unknown functions:  $\ln x$  and  $v_s$ . Differentiating Eq. [5] by  $a_k$ ,

$$\frac{\partial \ln x}{\partial a_k} = \rho \sum_m m \left( c_{m,k} v_s^{\rho m-1} + c_m (\rho m - 1) v_s^{\rho m-2} \frac{\partial v_s}{\partial a_k} \right),$$

we establish differential equations for  $v_s$ . After simplification, these equations obtain the form

$$\frac{\partial v_s}{\partial a_k} = - \frac{\sum_m c_{m,k} (\rho m - 1) v_s^{\rho m}}{\sum_m c_m \rho m (\rho m - 1) v_s^{\rho m-1}}, \quad (k = 1 \dots K). \quad [20]$$

So, we have obtained a set of equations which define the dependence of the aggregation number of micelles  $v_s$  on the parameters of the theory. We shall call these equations *parametric*. Their solution is connected with the equilibrium concentration of monomers  $n_1$  via [5].

If we are interested only in dependence on one specific parameter,  $a_k$ , it is sufficient to solve one of the Eqs. [20] for this parameter. However, in this case there appears an arbitrary function of the other parameters. On the contrary, if we search for a complete solution, it is necessary to solve all the Eqs. [20] and to accommodate all appearing arbitrary functions. Note that in the case of a large number of parameters this algorithm can be very complicated.

We make another important remark. If one adds an arbitrary function  $g(v)$  to the expression of  $G_v$  which *does not depend* on the set of parameters  $a_1 \dots a_K$  and *does not break a convergence* of the series [6], then Eqs. [20] do not change. Indeed, function  $g(v)$  disappears after differentiation by the parameters  $a_1 \dots a_K$ . Consequently,  $g(v)$  has no influence on the analytic

form of solution of the parametric equations [20] (but it changes the initial conditions, and thus some constants in the solution). On the contrary, the addition of  $g(v)$  affects Eq. [5], and the expression of equilibrium concentration of monomers will change according to the formula

$$n'_1 = n_1 \exp[-g'(v_s)], \quad [21]$$

where  $n_1$  is a solution of [20] without  $g(v)$ . This simple proposition is useful from the practical point of view. We see that the characteristic  $v_s$  is invariant under such transformation of  $G_v$ , because Eqs. [20] are independent of these small variations of function  $G_v$ . On the contrary, the equilibrium concentrations of monomers and micelles depend on the derivative of  $g(v)$  according to [21].

The common property of the set of equations [20] is their independence of the linear term  $v$  which disappears by virtue of the factor  $(\rho m - 1)$  when  $m$  equals  $m_0 = 1/\rho$  corresponding to a linear term (in the case when  $1/\rho$  is not a natural number, a priori there is no linear term). Nevertheless sometimes there is a dependence of Eqs. [20] on the coefficient  $c_{m_0}$  by virtue of the term  $c_0$  which can contain this coefficient. However, usually one can neglect the term  $c_0$  by comparison with  $v_s^{\rho m}$  ( $v_s \gg 1$ ). Note that every case should be analyzed individually.

What is the qualitative information that is contained in Eqs. [20]? It seems possible to use this equation (and the whole method) to verify the following important hypothesis in the theory of micellization. As it was mentioned above, exact expression for the aggregation work is unknown, therefore we use model expressions (like [31]). However, one can suppose that all physically measured quantities depend on *global characteristics* of the aggregation work (such as minimum of  $F_v$ , depth of this minimum, activation barrier height, etc.), rather than on a choice of its particular expression. If this hypothesis works, it is sufficient to take a simple expression for  $F_v$  satisfying to the qualitative requests and to solve the problems with the use of this expression.

### 3. SOLUTION OF THE PARAMETRIC EQUATIONS FOR THE DROP MODEL OF SPHERICAL MICELLES

Let us consider the *drop model* of spherical micelles, first elaborated by Tanford (12), studied by Israelachvili *et al.* (13), and reformulated independently by Rusanov in terms of the aggregation work (14). The basic ideas of this model are simple:

- (1) Hydrophilic electrically charged heads form the surface of a micelle (sphere).
- (2) Hydrophobic tails are very flexible; therefore they form a “liquid drop” in the micellar core.

We briefly describe the drop model in the Appendix (Section 6.1), in particular, we deduce a formula for the

aggregation work following (12),

$$G_v = b_1 v^{4/3} - \left( \frac{4}{3} \sqrt{2b_1 b_3} \right) v + b_3 v^{2/3}, \quad [22]$$

where the parameters  $b_1$  and  $b_3$  (in Rusanov's notation) are defined through the physical characteristics

$$b_1 = \frac{(ez)^2 \delta}{8\pi \varepsilon_0 \varepsilon \lambda^2 kT}, \quad b_3 = \frac{4\pi \lambda^2 \gamma_0}{kT}, \quad [23]$$

where  $\lambda = (3v/4\pi)^{1/3}$  is the radius of a sphere which has the same volume  $v$  as one hydrocarbon chain,  $ez$  is the electric charge of one amphiphile,  $\varepsilon_0$  is the dielectric constant,  $\varepsilon$  is the dielectric permittivity,  $\delta$  is the separation of the capacitor plates,  $\gamma_0$  is the surface tension of the hydrocarbon–water interface.

Equation [22] defines the coefficients of decomposition of the aggregation work by the powers of  $v$  with  $\rho = 1/3$ ,

$$c_0 = 0, \quad c_1 = 0, \quad c_2 = b_3, \quad c_3 = -\frac{4}{3} \sqrt{2b_1 b_3}, \quad c_4 = b_1.$$

In the framework of this model the parametric equations [20] can be solved exactly, without any approximation (however, the parametric equations themselves remain approximate ones). Substituting the values of  $c_m$  into Eqs. [20], we obtain

$$\frac{\partial v_s}{\partial b_1} = -\frac{3}{2} \frac{v_s^{4/3}}{2b_1 v_s^{1/3} - b_3 v_s^{-1/3}}, \quad [24]$$

$$\frac{\partial v_s}{\partial b_3} = \frac{3}{2} \frac{v_s^{2/3}}{2b_1 v_s^{1/3} - b_3 v_s^{-1/3}}. \quad [25]$$

The substitution

$$v_s = (b_3/b_1)^{3/2} \varphi^3(b_1, b_3)$$

leads to

$$2b_1 \frac{\partial \varphi}{\partial b_1} = \frac{\varphi(\varphi^2 - 1)}{2\varphi^2 - 1}, \quad -b_3 \frac{\partial \varphi}{\partial b_3} = \frac{\varphi(\varphi^2 - 1)}{2\varphi^2 - 1},$$

and we obtain the solution

$$\varphi^2(\varphi^2 - 1) = \gamma_3(b_3)b_1, \quad [26]$$

$$\varphi^2(\varphi^2 - 1) = \gamma_1(b_1)b_3^{-2}. \quad [27]$$

Equaling the right-hand sides, we relate functions  $\gamma_1(b_1)$  and  $\gamma_3(b_3)$ ,

$$\gamma_1(b_1)b_1^{-1} = \gamma_3(b_3)b_3^2.$$

As the parameters  $b_1$  and  $b_3$  are independent, both sides of this

TABLE 1  
The Values of Constant  $\gamma(N)$  and of Equilibrium Concentration of Monomers  $n_1$  as Functions of  $N$

$N$							
	2.0	2.5	3.0	3.5	4.0	4.5	5.0
$n_1$	1.9865	2.1159	2.1471	2.1648	2.1771	2.1865	2.1942
$\gamma$	-32.774	-22.852	-20.486	-19.156	-18.232	-17.525	-16.953

Note. For these simulations we have used  $b_1 = 2.0$ ,  $b_3 = 30$  corresponding to sodium dodecyl sulfate in water.

equality are constant, whence

$$\gamma_1(b_1) = \gamma(N)b_1, \quad \gamma_3(b_3) = \gamma(N)b_3^{-2},$$

where a constant  $\gamma(N)$  can be determined numerically for any  $N$  (see Table 1). Substituting function  $\gamma_1(b_1)$  in Eq. [27], one finds the dependence of the aggregation number of micelles  $v_s$  on the parameters of micellization,

$$v_s = (\alpha b_3 / 2b_1)^{3/2}, \quad \alpha = 1 + \sqrt{1 + 4\gamma(N)b_1 b_3^{-2}}. \quad [28]$$

The equilibrium concentration of monomers can be found by substitution of [28] in Eq. [5],

$$n_1 = \exp\left(\frac{2}{3} \sqrt{2b_1 b_3} [\alpha^{1/4} - \alpha^{-1/4}]^2\right). \quad [29]$$

Now it is useful to estimate the values of parameters  $b_1$  and  $b_3$  for a particular surfactant molecule. We take the well-known molecules of sodium dodecyl sulfate (SDS) ( $C_{12}H_{25}OSO_3Na$ ) in water at the ambient temperature ( $T = 300$  K). Using characteristic values of the following parameters (1, 13, 17, 18):  $v = 0.350 \text{ nm}^3$ ,  $\lambda = 0.437 \text{ nm}$ ,  $\delta \approx 0.07 \text{ nm}$ ,  $\varepsilon = 50$ ,  $z = 1$ ,  $\gamma_0 = 0.05 \text{ N/m}^2$ , we can obtain with the help of [23],

$$b_1 \approx 2, \quad b_3 \approx 30. \quad [30]$$

Note that these estimations are quite sufficient for our purposes. Indeed, we are working with a simple model; therefore, we cannot expect high accuracy of predicted results. Our main interest is not to concentrate attention on the *numerical* predictions, but rather on the *functional* dependencies of some physical quantities on other physical quantities (like the result [29]). Comparing theoretical dependencies with experimental ones, we can understand which model is more realistic for a given surfactant. In its turn, every model is based on some physical assumptions. If we find an adequate model for the considered surfactant, we can make certain conclusions about its physical properties. For example, if experimentation confirms that the dependency of  $n_1$  on other physical parameters (e.g., temperature) is given by [29] for SDS, we can conclude that the hydrophobic tails of SDS form a “liquid drop”

in the micellar core (this statement was assumed for the drop model). But experimentation can confirm another dependency, say, Eq. [39], of Grinin's model (see below). In this case we conclude that the hydrophobic tails of SDS are ordered in the micellar core (the assumption of Grinin's model). Analyzing different models, we can extract the important information about the geometrical structure of micelles and their physical properties.

We have determined the dependence of the equilibrium concentration of monomers on the parameters  $b_1$  and  $b_3$ . The dependence on the total concentration of amphiphiles  $N$  is contained in the constant  $\gamma(N)$  which can be numerically calculated for any  $N$ . Indeed, it is sufficient to find  $n_1^0$  for one set of  $b_1^0$ ,  $b_3^0$ , and  $N$  by solving Eq. [3] or [15], then to substitute the value of  $n_1^0$  in expression [29] and to express the constant  $\gamma$ . With the help of numerical simulations we obtain the values of  $\gamma(N)$  for some  $N$  represented in Table 1.

Note that the aggregation work  $F_v$  for this model grows rapidly for small  $v$ ; thus dimers, trimers, and other small aggregates are completely negligible. Consequently, the number of amphiphiles in micelles can be well approximated as  $N - n_1$ .

The essential advantage of Eq. [29] is its explicit form which allows us to analyze dependencies of all the equilibrium concentrations on parameters  $b_1$  and  $b_3$ . Moreover, this formula has quite a high precision in the framework of the drop model. Table 2 shows its relative errors (with respect to the numerical solution of [3]) when parameters  $b_1$  and  $b_3$  are widely varied.

Note that the small variation of  $b_3$  from 30 to 32 (or 28) can be caused by decreasing (increasing) the temperature by 20°C (i.e., the domain of variation of temperature is between 5 and 45°C). On the contrary, the parameter  $b_1$  can be varied in a wide enough region. Indeed, if one adds salts (for example, NaCl) in solution, they will screen electrostatic repulsion of amphiphile heads; i.e., the parameter  $b_1$  will be decreased. Normally, it is difficult to increase  $b_1$  considerably; thus the right upper corner of Table 2 is not physical. We can conclude that Formula [29] approximates the equilibrium concentration of monomers with relative errors less than 1% in the framework of the drop model.

TABLE 2

The Relative Errors (in Percentage) of Formula [29] When  $b_1$  Changes from 1.0 to 2.5 and  $b_3$  Changes from 28 to 32

$b_3 \setminus b_1$	1.0	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5
28	0.9	0.5	0.3	0.1	0.0	0.3	0.5	0.7	1.0	1.3	1.6	1.9
29	0.9	0.6	0.4	0.3	0.1	0.0	0.2	0.4	0.7	0.9	1.2	1.5
30	0.9	0.7	0.6	0.4	0.3	0.2	0	0.2	0.4	0.9	0.8	1.0
31	0.9	0.7	0.7	0.6	0.5	0.3	0.2	0.1	0.1	0.6	0.4	0.6
32	0.9	0.8	0.7	0.7	0.6	0.5	0.4	0.3	0.2	0.0	0.1	0.2

Note. Generally, these errors are less than 1% (besides the right upper corner marked in italic that is not physical).

#### 4. SOLUTION OF THE PARAMETRIC EQUATIONS FOR GRININ'S MODEL OF SPHERICAL MICELLES

There is another model of spherical micelles elaborated by Grinin (17). The hydrophobic tails of amphiphiles are assumed to be ordered enough in the core of a micelle (on the contrary, for the drop model we assumed that hydrophobic tails are completely flexible as a liquid). We briefly describe Grinin's model in the Appendix Section 6.2 (a more detailed description can be found in the original article (17)). In particular, the expression of aggregation work is obtained,<sup>6</sup>

$$G_v = \frac{b}{2}v^2 - \frac{2a}{3}v^{3/2} + \frac{a^2}{4b}v. \quad [31]$$

As for the drop model, the parameters  $a_1 = a$  and  $a_2 = b$  are not physical, but they are connected with physical characteristics,

$$a = \frac{3}{2}B \frac{d + d_{\text{H}_2\text{O}} - s^{1/2}}{(4\pi)^{1/2}l_c}, \quad b = \frac{(ze)^2\delta}{4\pi\varepsilon_0\varepsilon kTl_c^2n_c^2}, \quad [32]$$

where  $B$  is the empiric factor (which equals 1.4 under normal conditions, see Ref. 14),  $d$  is the minimal distance between the hydrophobic tail and the water molecule,  $d_{\text{H}_2\text{O}}$  is the characteristic size of the water molecule,  $s$  is the effective surface area of the hydrophobic tail,  $n_c$  is the number of carbon atoms in the hydrophobic tail, and  $n_c l_c$  is the length of the hydrocarbon chain.

Equation [31] is the decomposition of the aggregation work by the powers of  $v$  with  $\rho = 1/2$  and with the coefficients

$$c_0 = 0, \quad c_1 = 0, \quad c_2 = \frac{a^2}{4b}, \quad c_3 = -\frac{2a}{3}, \quad c_4 = \frac{b}{2}.$$

After calculating a matrix of derivatives  $c_{m,k}$  and substituting it in [20], we obtain two equations:

$$\frac{\partial v_s}{\partial a} = \frac{2}{3} \frac{v_s^{3/2}}{2bv_s - av_s^{1/2}}, \quad [33]$$

$$\frac{\partial v_s}{\partial b} = -\frac{v_s^2}{2bv_s - av_s^{1/2}}. \quad [34]$$

The substitution

$$v_s = (a/b)^2 \varphi^2(a, b) \quad [35]$$

reduces these equations to the quadratures

$$-\frac{2da}{a} = \frac{d\varphi(2\varphi - 1)}{\varphi(\varphi - 2/3)}, \quad \frac{3db}{2b} = \frac{d\varphi(2\varphi - 1)}{\varphi(\varphi - 2/3)},$$

<sup>6</sup> Recently Professor A. P. Grinin introduced some modifications in the original expression of aggregation work. Here the corrected expression is used. We are grateful to Professor A. P. Grinin who informed us about these modifications.

which give after integration two equations of fourth degree connecting  $\varphi$  with  $a$  and  $b$ ,

$$\begin{aligned}\varphi^3|\varphi - 2/3| &= \gamma_1(b)a^{-4}, \\ \varphi^3|\varphi - 2/3| &= \gamma_2(a)b^3,\end{aligned}$$

where  $\gamma_1(b)$ ,  $\gamma_2(a)$  are arbitrary functions. Equaling the right-hand sides, one obtains  $\gamma_1(b) = Cb^3$ ,  $\gamma_2(a) = Ca^{-4}$ ; i.e., the equation is

$$\varphi^3|\varphi - 2/3| = Ca^{-4}b^3, \quad [36]$$

with an arbitrary constant  $C$ . Taking small variations from the initial parameters, one can conclude that the factor  $\varphi^3$  changes a little. Indeed, using the explicit expression [31] for function  $G_v$  we obtain an equation for extrema,  $bv - av^{1/2} + a^2/4b = \ln n_1$ , with a larger solution (corresponding to the minimum  $v_s$ )

$$v_s = (a/2b + \sqrt{(\ln n_1)/b})^2.$$

It follows that  $\varphi \geq 1/2$ , so all changes occur in the vicinity of the point 2/3.

Then we obtain an approximate solution

$$\varphi = 2/3 + (Ca_0^4b_0^{-3})a^{-4}b^3, \quad [37]$$

or, with the help of [35], we have

$$v_s = (2a/3b + \gamma_G(N)a^{-3}b^2)^2, \quad [38]$$

where a constant  $\gamma_G$  can be defined for any  $N$ , and once defined (by the numerical solution of the initial Eq. [3] for certain fixed parameters  $a_0, b_0$ ), it becomes the universal characteristic for the model under consideration. Table 3 shows the values of  $\gamma_G(N)$  for some  $N$ . Now one can use Eq. [5] to calculate  $n_1$ ,

$$n_1 = \exp\left[\frac{a^2}{36b}(1 + \gamma_G(N)a^{-4}b^3)^2\right]. \quad [39]$$

Thus we have found the complete dependence of the equilibrium concentration of monomers on the parameters for Grinin's model of spherical micelles.

As for the drop model, we can estimate the characteristic values of  $a$  and  $b$  for SDS with the help of [32]. Using the following supplemental parameters (17, 18)  $d = 0.5$  nm,  $d_{H_2O} = 0.3$  nm,  $l_c = 0.13$  nm,  $s = v/l_c \approx 0.21$  nm<sup>2</sup>, and  $n_c = 12$ , we obtain

$$a \approx 1.5, \quad b \approx 0.1. \quad [40]$$

As it was mentioned previously, we use these estimations just to verify the accuracy of our approximation [39].

TABLE 3

Grinin's Model: Values of the Constant  $\gamma_G$  and of the Equilibrium Concentration of Monomers  $n_1$  for Some  $N$  Calculated with the Parameters  $a = 1.5$  and  $b = 0.1$

$n_1$	$N$						
	2.0	2.5	3.0	3.5	4.0	4.5	5.0
$\gamma_G$	-592.08	-541.82	-517.62	-501.66	-489.76	-480.29	-472.42

With the help of numerical simulations, we calculate the values of the constant  $\gamma_G$  for some  $N$  for these characteristic values of the parameters  $a$  and  $b$ ; see Table 3.

Table 4 contains relative errors (in percentage) of Eq. [39]. To fill this table, the equilibrium concentration of monomers  $n_1$  for some values of parameters  $a$  and  $b$  was calculated by two different methods: by numerical solution of Eq. [15] and with the help of an approximate formula [39].

The absence of the values in the left lower corner is caused by the condition  $n_1 > 1$  (otherwise there are no stable aggregates). The right upper corner is empty by virtue of the condition  $n_1 < N$  (the opposite case has no physical sense). We see that the relative error of the approximate solution [39] changes in an irregular way; however, it does not exceed 2% when the parameters  $a$  and  $b$  take all physically reasonable values. This accuracy can be considered a high one; thus, we conclude that Formula [39] is a good approximation for the equilibrium concentration of monomers in Grinin's model. Nevertheless, there are problems which demand more accurate results. For this reason we stress that the main advantage of our expressions is the explicit functional dependency of  $n_1$  on  $a$  and  $b$ ; therefore, it is possible to analyze the results qualitatively and to compare different models.

Note that the form of Solution [39] is different if compared with the drop's one [29]. We cannot compare them directly because of the difference of origin of parameters  $a, b$  and  $b_1, b_3$ . Indeed, these two models of formation of spherical micelles are

TABLE 4

Relative Errors (in Percentage) of Eq. [39] Calculated for a Wide Domain of the Parameters  $a$  and  $b$  ( $N = 2$ )

$b/a$	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
0.05	0.0	0.9	—	—	—	—	—	—	—	—	—
0.06	0.7	0.0	0.8	—	—	—	—	—	—	—	—
0.07	1.2	0.8	0.1	0.8	—	—	—	—	—	—	—
0.08	0.9	1.3	0.9	0.1	0.8	—	—	—	—	—	—
0.09	1.3	1.2	1.4	0.9	0.0	0.9	—	—	—	—	—
0.10	—	0.2	1.4	1.4	0.8	0	1.0	—	—	—	—
0.11	—	—	0.6	1.6	1.4	0.7	0.1	1.2	—	—	—
0.12	—	—	—	1.1	1.5	1.3	0.6	0.3	1.5	—	—
0.13	—	—	—	0.4	1.5	1.7	1.3	0.5	0.5	1.8	—
0.14	—	—	—	—	0.5	1.7	1.7	1.1	0.3	0.7	2.2
0.15	—	—	—	—	—	1.1	1.8	1.6	1.0	0.0	1.0

based on different physical assumptions. Whereas the electric terms (corresponding to  $b_1$  and  $b$ ) have the same origin (capacitor energy), two of the other terms (corresponding to  $b_3$  and  $a$ ) have different origins. However, there exists a way to compare the two models. For this, one can express  $b_1$ ,  $b_3$  and  $a$ ,  $b$  in terms of physical quantities (e.g., temperature), substitute expressions in [29] and [39], and after that compare the results. This work is not yet finished.

## 5. CONCLUSIONS

Based on the classical nucleation theory, we have developed a method which allows us to obtain the parametric equations under rather general assumptions:

- closure of the system,
- dilute solution of the surfactants,
- general model expression of  $G_v$  as a sum of the fractional powers of  $v$ , and
- comparability of the numbers of amphiphiles in monomers and micelles.

To deduce the parametric equations we have used these assumptions, but they have rather different significances. The most important hypothesis is the closure of the system. Others are necessary to be mathematically rigorous. Finally, there are certain conditions which are used to specify the differential equations in order to obtain concrete results (such as the Solutions [29] and [39]), but they are not strictly necessary for the method's work. For example, the decomposition of function  $G_v$  by the fractional powers of  $v$  is physically reasonable and it simplifies the method significantly. But this assumption can be diminished; i.e., the expression of  $G_v$  can be generalized. In other words, by concretizing the form of some expressions (for example, [2], [4], etc.), we simplify mathematically our problem, physically leaving it in a general form.

We have obtained the differential equation for the important characteristic of micellization—for the aggregation number of micelles. Taking into account the remark in Section 2 about the invariance of the parametric equations by the addition of some function  $g(v)$  to the aggregation work, we can conclude that  $v_s$  is also invariant under this transformation. On the contrary, equilibrium concentrations of monomers and micelles essentially depend on the concrete expression of  $G_v$ ; consequently, they are not invariant in this sense.

The system of parametric equations was solved for two practically important models of spherical micelles: the drop model and Grinin's model. We have obtained an explicit dependence of the equilibrium concentration of monomers on the parameters of micellization. The numerical simulations showed that these formulae have a high accuracy. We would like to mention again that in this paper we do not determine the limitations of the present approach. Using our approximations, one should take them into account. For example, in Table 1 we give  $n_1$  for  $N = 5$  (in CMC units). But it is possible that the concentration

$5 \times CMC$  is not "relatively small," and in this case nonspherical micelles may appear which invalidate our treatment. In order to verify physical admittance of this formalism one should refer to the experiments. For the moment, the work on comparing theoretical and experimental data is not yet done.

At last, there appears to be a real possibility of verifying the hypothesis that the physically measured quantities of micellization (e.g., the relaxation times) are independent of the *concrete* analytical expression of the aggregation work, but they are defined by its global characteristic (such as minimum point, activation barrier height, etc.). If this hypothesis is confirmed, it will justify the use of the simple model expressions of the aggregation work (such as [22] for the drop model, or [31] for Grinin's model). In the opposite case, our method will allow the comparison of different model expressions and the solutions based on them and the determination of the substantiality of the model and its accuracy.

We can conclude that the elaborated method is effective enough to determine the dependencies of the equilibrium concentration of monomers on physical parameters in the framework of the considered model of spherical micelles. We hope that it will allow some problems in the theory of micelles to be solved and the mechanism of micellization to be comprehended profoundly.

## 6. APPENDIX

Here we present a brief description of the drop model and Grinin's model. As our main interest is concentrated on the analytical expression of aggregation work, we would not like to disperse the attention on other aspects of these interesting models (one can find details in the original papers (12, 14, 17)).

### 6.1. The Drop Model

We assume that hydrophobic tails are flexible; i.e., they form a "liquid drop" in the micellar core, see Fig. 1a. There are three terms which we consider in turn.

The first contribution,  $G_e$ , is due to electrostatic repulsion of electrically charged hydrophilic heads of amphiphiles. To evaluate this term, Tanford (12) proposed a simple model of spherical capacitor with energy:

$$G_e = \frac{Z^2}{8\pi\varepsilon_0\varepsilon kT} \frac{\delta}{R^2}$$

(as usual, we write the quantities in dimensionless units). Here  $Z$  is the total charge of the capacitor plates,  $\delta$  is the distance between them,  $R$  is the radius of the capacitor,  $\varepsilon_0$  is the dielectric constant, and  $\varepsilon$  is the dielectric permittivity. In the framework of the drop model,

$$Z = (ez)v, \quad R = \left( \frac{3vv}{4\pi} \right)^{1/3} = \lambda v^{1/3},$$

where  $ez$  is the electric charge of one hydrophobic head and

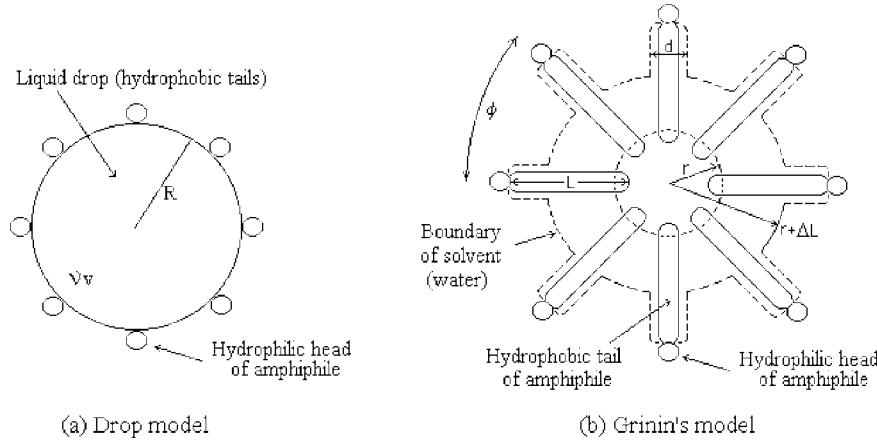


FIG. 1. Schematic presentation of spherical micelles in the framework of the drop model (a) and Grinin's model (b).

$\lambda = (3v/4\pi)^{1/3}$  is the radius of a sphere which has the same volume  $v$  as one hydrocarbon chain. So, we have

$$G_e = b_1 v^{4/3} \quad \text{with} \quad b_1 = \frac{(ez)^2 \delta}{8\pi \varepsilon_0 \varepsilon \lambda^2 kT}.$$

Second, the surface tension is simply

$$G_s = S \gamma_0 / kT,$$

where  $\gamma_0$  is the surface tension of the hydrocarbon–water interface,  $S$  is the micelle's surface, and  $S = 4\pi R^2$ ; thus,

$$G_s = b_3 v^{2/3} \quad \text{with} \quad b_3 = \frac{4\pi \lambda^2 \gamma_0}{kT}.$$

Third, the bulk term is proportional to the volume of the micelle; thus we can write

$$G_b = b_2 v.$$

Collecting all these terms, we obtain

$$G_v = b_1 v^{4/3} + b_2 v + b_3 v^{2/3}. \quad [41]$$

Now let us find the inflection point of this curve, when  $G''(v_0) = 0$ ,

$$v_0 = (b_3/2b_1)^{3/2}.$$

In the classical nucleation theory the CMC can be defined<sup>7</sup> as such a concentration when there appears the minimum of aggregation work corresponding to micelles. Mathematically it

means that

$$F'_v(v_0) = 0 \quad \text{or} \quad b_2 = \ln(CMC/c_{\text{unit}}) - \frac{4}{3}\sqrt{2b_1 b_3}$$

( $c_{\text{unit}}$  is the chosen concentration unit). Now we can substitute  $b_2$  in [41] to obtain the aggregation work  $F_v$ ,

$$F_v = b_1 v^{4/3} - \left(\frac{4}{3}\sqrt{2b_1 b_3}\right)v + b_3 v^{2/3} - (v - 1) \ln \frac{n_1}{CMC}$$

(here we neglected the insignificant constant  $\ln CMC/c_{\text{unit}}$ ). We thus obtain (22) just as required.

## 6.2. Grinin's Model

Here we assume that hydrophobic tails are ordered, see Fig. 1b. In this case, the radius of the capacitor is  $R = l_c n_c$ , where  $l_c$  is the length of one segment  $C-C$  and  $n_c$  is the number of hydrocarbon groups in the hydrophobic tail. Using the capacitor model, we obtain the electrostatic contribution

$$G_e = \frac{b}{2} v^2 \quad \text{with} \quad \frac{b}{2} = \frac{(ez)^2 \delta}{8\pi \varepsilon_0 \varepsilon kT (l_c n_c)^2}$$

(here we preserve Grinin's notations  $b/2$  and  $2a/3$ ).

In this model part of the hydrophobic tail lies in the water, and we should estimate the corresponding energy. It is known (12, 17) that the hydrophobic energy is well approximated by the linear function of  $\Delta n_c$ —the number of hydrocarbon groups lying in the water,  $G_h = B \Delta n_c$ , where  $B$  is the empiric factor (which equals 1.4 under normal conditions, see Refs. 14 and 17). Simple geometry gives the length of the part standing above the border level (see Fig. 1b),

$$\Delta L = \frac{d + d_{H_2O}}{2 \sin(\phi/2)} - r,$$

where  $d$  is the minimal distance between the hydrophobic tail

<sup>7</sup> Some authors give a little different definition of CMC, see Refs. 2–6 on this discussion.

and the water molecule,  $d_{\text{H}_2\text{O}}$  is the characteristic size of the water molecule,  $\phi \approx (4\pi/v)^{1/2}$  is the angle between the two nearest hydrophobic tails, and  $r$  is the radius of the inner sphere. We express  $r = (vs/4\pi)^{1/2}$ , where  $s$  is the effective surface area of the hydrophobic tail. For small  $\phi$  (large  $v$ ) we can rewrite

$$\Delta L = \frac{d + d_{\text{H}_2\text{O}} - s^{1/2}}{(4\pi)^{1/2}} v^{1/2}.$$

Expressing the number of hydrocarbon groups standing above the border level as  $\Delta n_c = \frac{\Delta L}{l_c} v$ , we obtain

$$G_h = \frac{2a}{3} v^{3/2} \quad \text{with} \quad \frac{2a}{3} = B \frac{d + d_{\text{H}_2\text{O}} - s^{1/2}}{(4\pi)^{1/2} l_c}.$$

The bulk term is  $c v$ , and we obtain

$$G_v = \frac{b}{2} v^2 - \frac{2a}{3} v^{3/2} + cv.$$

Using the same ideas as for the drop model, we can get

$$G_v = \frac{b}{2} v^2 - \frac{2a}{3} v^{3/2} + \frac{a^2}{4b} v,$$

and all concentrations are measured in CMC units.

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