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## Nucleation in Micellization Processes

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**As for our intensive use of calculus . . . , we believe it is unnecessary in the present age to make any apology . . . For any presentation of this subject which is to be both concise and comprehensive, calculus is indispensable . . .**

**Gilbert Newton Lewis, Merle Randall (1923)**

### Abstract

Even though the micelles themselves are not nuclei of a new phase, premicellar molecular aggregates evolve in the course of micellization processes and play the role of critical nuclei (germs) for micelles. This means that nucleation does occur

in micellization and the methods of nucleation theory can be, in fact, successfully applied in micellization kinetics. The present review gives an overview on the kinetics and thermodynamics of formation of spherical micelles on the basis of modern kinetic theory of nucleation. We start with thermodynamic aspects, formulate the kinetic equation of micellization on its basis, consider the characteristic times of aggregation and relaxation processes in surfactant solutions with spherical micelles, and then return back to the thermodynamic modelling of micelles themselves (for the case of non-ionic spherical micelles). This approach allows us to find the relaxation times and other kinetic characteristics of the micellar solutions in an explicit form.

## 7.1 Introduction

Nucleation (the formation of a new phase within a metastable ambient phase) and micellization (formation of micelles in surfactant solutions) have the common feature to proceed through spontaneous aggregation of molecules or ions. Nevertheless, their kinetic theories have been developed in different pathways. The kinetic theory of nucleation, founded by Volmer, Becker, Döring, Frenkel and Zeldovich, is based on the phase approach going back to Gibbs' thermodynamics and considering self-forming molecular aggregates as nuclei of a new stable phase [1, 2].

The phase terminology, used in the theory of micellization, has got initially a different meaning. First, the population of micelles as a whole was considered as a macroscopic "pseudo-phase" participating in a first-order phase transition [3]. Second, the entire micellar solution was considered as a macroscopic phase resulting from a second-order phase transition [4]. Third, a single micelle was considered as a specific microscopic phase not having a macroscopic analogue [5]. The two first approaches do not have a sound basis [5] although can be used for some approximate estimations. The third concept is rigorous and related to the fact that a micelle has a complicated structure resembling a convolute surfactant monolayer [6 - 12], and cannot be viewed as a nucleus of a real phase. The final state of a surfactant solution at micellization is the state of aggregative equilibrium of micelles and monomers, i.e. the equilibrium state of a disperse system. Increasing the brutto-concentration of a surfactant in a solution above the critical micelle concentration (until other polymorphic forms of micelles become favorable) mostly gives only rise to the equilibrium number of spherical micelles.

Even though micelles are not nuclei of a new phase, pre-micellar molecular aggregates arise in the course of the micellization process and play the role of critical nuclei (or germs) for micelles themselves. As an indication of this mechanism, one can consider a maximum in the work of formation of such molecular aggregates (aggregation work) which corresponds to a minimum in the curve of the equilibrium distribution of the aggregates in size [5, 13 - 19]. This maximum precedes the minimum of the work, along the aggregate size axis, associated with micelles. This peculiarity has the consequence that nucleation does occur in micellization, and that the methods of nucleation theory can be in fact successfully applied in micellization kinetics. At the same time, the application of the theory of nucleation to the micellization process, which has features strikingly different from common phase transitions, is of interest for the theory of nucleation itself.

Till recent times, the development of the kinetic theory of micellization was retarded by the fact that, in contrast to the situation with micelles, there is a lack of experimental data on critical pre-micellar nuclei of micelles. According to nucleation theory [20, 21], the main parameters of the maximum of the aggregation work are its height and half-width. These parameters enter the equations for the transition rates and specific times and thus allow one to calculate all kinetic characteristics. Even if direct experimental data are not available, these parameters can be found, relying on the analytic properties of the aggregation work, with the aid of data on the aggregation work in other regions of size of the aggregates [22]. Particularly, in the micellization process, the values of these two parameters have to be consistent with the parameters describing the minimum of the aggregation work that corresponds to the micelles. Therefore, existing experimental data on the equilibrium average micelle size and dispersion of micelle sizes give an essential additional information about the whole behavior of the aggregation work including the region of pre-micellar sizes. This information is needed for solving direct and reverse problems of the micellization kinetics.

The review presents the kinetic and thermodynamic theory of formation of spherical micelles based on the modern kinetic theory of nucleation [18, 19, 22 - 29]. Just as the theory of nucleation is based to a significant extent on thermodynamics, so the kinetic theory of micellization requires data on equilibrium and non-equilibrium states given by the thermodynamics of micellization. This necessity explains the organization of the present review where kinetics and thermodynamics are analyzed hand-in-hand: we will start with questions of thermodynamics of aggregation, formulate the kinetic equation of micellization on this ground, consider the characteristic times of aggregation and relaxation processes in surfactant solutions with spherical micelles, and then return back to

the thermodynamic modelling of micelles themselves (for the case of non-ionic spherical micelles) that allows us to find the relaxation times and other kinetic characteristics of the micellar solutions in an explicit form.

## 7.2 General Aspects of Micellization: the Law of Mass Action and the Work of Aggregation

Let us consider a solution of a single nonionic surfactant capable of forming molecular aggregates. In this case, the role of the solvent is played by a liquid (for example, water) that is passive with respect to aggregation. The solution is assumed to be ideal (infinitely dilute). Considering aggregates to be compact and their temperature equal to that of the solution, the aggregation number,  $n$  (the number of monomers in an aggregate), is assumed to be a characteristic parameter of the internal state of the aggregate. The choice of such a discrete characteristic parameter is convenient because it is also applicable to the description of the smallest aggregates beginning from the value  $n = 1$  for single surfactant molecules. Let us denote further the chemical potential and concentration (i.e. the number of aggregates per unit volume) of aggregates containing  $n$  monomers by  $\mu_n$  and  $c_n$ , respectively. Employing such notation,  $\mu_1$  and  $c_1$  represent the chemical potential and concentration of single monomers. In the considered case of nonionic surfactants, all monomers are identical.

In the analysis of the aggregation processes, it is convenient to introduce the chemical potential,  $\mu_n$ , of a molecular aggregate in the solution by the relation [18, 23]

$$\mu_n = G_n^0 + k_B T \ln(\Lambda_n^3 c_n f_n), \quad (7.1)$$

where  $G_n^0$  is the Gibbs energy of a single aggregate (consisting of  $n$  surfactant molecules) with fixed center of mass in a pure medium (in the absence of other aggregates),  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature of the solution,  $\Lambda_n = h(2\pi m_n k_B T)^{-1/2}$  is the average de Broglie wavelength of a molecular aggregate ( $h$  is the Planck constant,  $m_n$  is the mass of the molecular aggregate), and  $f_n$  is the activity coefficient of the aggregate.  $\Lambda_n^{-3}$  is the partition function for the translational motion of the aggregates, and  $k_B T \ln \Lambda_n^3$  is its contribution to the free energy. Similarly,  $k_B T \ln f_n$  is the contribution from the interaction of all aggregates with each other.

We may rewrite Eq. (7.1) as

$$\mu_n = G_n + k_B T \ln \left( \frac{c_n}{c_{st}} \right), \quad (7.2)$$

where  $G_n$  is the chemical potential (the Gibbs energy) of the molecular aggregate corresponding to a certain arbitrarily chosen standard concentration  $c_{st}$ . In the thermodynamics of solutions,  $c_{st}$  is usually assumed to be unity (in the corresponding units of measurement) so that only concentration (in fact, a dimensionless number which numerically equals concentration) is retained in the logarithm in Eq. (7.2). Eq. (7.2) is valid both in the absence or presence of any interactions between aggregates in the standard state. However, since we assume to consider an ideal system, we suggest that the standard state, corresponding to the concentration  $c_{st}$ , is also an ideal one. In other words, we assume that, both in Eqs. (7.1) and (7.2), the relation  $f_n = 1$  holds.

We are considering here the situation of fluctuational formation of aggregates consisting of  $n = 2, 3, \dots$  particles in a solution containing originally single surfactant monomers only. By this reason, it is convenient to select a standard concentration  $c_{st}$  as  $c_{st} = c_1$ . In this case, Eq. (7.2) is reduced to

$$\mu_n = G_n + k_B T \ln \left( \frac{c_n}{c_1} \right). \quad (7.3)$$

The convenience of such definition  $c_{st} = c_1$  follows from the following considerations: in a solution, where monomers are already present with the concentration  $c_1$ , the Gibbs energy of a monomer  $G_1$  should coincide with the monomer chemical potential  $\mu_1$ , i.e., the relation

$$G_1 = \mu_1 \quad (7.4)$$

should be valid. This identity is ensured in fact by Eq. (7.3).

Addressing the practically most important case, we consider an aggregating system at constant temperature and pressure and, correspondingly, we shall use the Gibbs energy as the thermodynamic potential (its increase equals the minimal work done on a system to create the same change of its state). If the molecular aggregate is formed at the selected standard concentration,  $c_1$  (both for monomers and aggregates formed), the standard work of molecular aggregate formation (or

shortly aggregation work), expressed in thermal energy units  $k_B T$ , is given by the formula [23]

$$W_n = \frac{(G_n - n\mu_1)}{k_B T} . \quad (7.5)$$

The term  $n\mu_1$  in Eq. (7.5), which represents the Gibbs energy of the ensemble of  $n$  non-interacting monomers, enters this relation due to the fact that aggregation takes place in a solution originally containing single monomers, only. In this case, the work  $W_n$  is independent of the concentrations  $c_n$  of aggregates with particle numbers  $n \geq 2$ . However, it depends on monomer concentration  $c_1$ . At the same time, the relation

$$W_1 = 0 , \quad (7.6)$$

which follows from Eqs. (7.4) and (7.5), seems to be natural as well. Indeed, monomers are already present in a solution, and, hence, no work is required for their formation.

The Gibbs energy per unit volume of a solution,  $G$ , can be written as  $G = \sum_{n \geq 1} \mu_n c_n$ . At constant temperature and pressure in the solution, we have

$$dG = \sum_{n \geq 1} \mu_n dc_n . \quad (7.7)$$

Since the solution is considered as a closed system with respect to particle exchange, the total surfactant concentration,  $c$ , in the solution is constant and determined as

$$c = c_1 + \sum_{n \geq 2} nc_n . \quad (7.8)$$

Eq. (7.8) yields

$$dc_1 = - \sum_{n \geq 2} ndc_n . \quad (7.9)$$

Substituting Eq. (7.9) into the right-hand side of Eq. (7.7) results in

$$dG = - \sum_{n \geq 2} (\mu_n - n\mu_1) dc_n . \quad (7.10)$$

It follows that the condition  $dG = 0$  of aggregation equilibrium in a solution (with constant total concentration  $c$  and at constant temperature and pressure) can be written as

$$\mu_n^{(e)} = n\mu_1, \quad (7.11)$$

where the superscript  $(e)$  specifies aggregation equilibrium.

With Eqs. (7.3) and (7.5), one can write

$$\mu_n - n\mu_1 = k_B T \left[ W_n + \ln \left( \frac{c_n}{c_1} \right) \right]. \quad (7.12)$$

Eqs. (7.11) and (7.12) yield for the equilibrium aggregate concentration  $c_n^{(e)}$

$$c_n^{(e)} = c_1 \exp(-W_n). \quad (7.13)$$

Eq. (7.13) corresponds to the Boltzmann fluctuation principle.

Let us introduce the affinity  $A_n$  via

$$A_n \equiv -(\mu_n - n\mu_1), \quad n = 1, 2, \dots \quad (7.14)$$

Eqs. (7.14) and (7.11) show that, at aggregation equilibrium, the relation

$$A_n^{(e)} = 0 \quad n = 1, 2, \dots \quad (7.15)$$

holds. With Eq. (7.12), we can express the affinity (defined via Eq. (7.14)) as

$$A_n = -k_B T \left[ W_n + \ln \left( \frac{c_n}{c_1} \right) \right]. \quad (7.16)$$

According to Eq. (7.16), the lower the work  $W_n$  and the  $c_n/c_1$  ratio are, the larger is the affinity  $A_n$ . With Eq. (7.14), Eq. (7.10) can be rewritten as

$$dG = - \sum_{n \geq 2} A_n dc_n. \quad (7.17)$$

Taking into account that the chemical potentials  $\mu_n$  and  $\mu_1$  depend (for the considered ideal solutions) on the concentrations  $c_n$  and  $c_1$  via the terms  $k_B T \ln c_n$



and  $k_B T \ln c_1$ , the condition of aggregation equilibrium, Eq. (7.11), is transformed into the law of mass action

$$c_n^{(e)} = K_n c_1^n . \quad (7.18)$$

Here the coefficient  $K_n$  does not depend neither on the concentration  $c_1$  nor on the concentrations  $c_n$  with  $n \geq 2$ , but depends on the aggregation number  $n$ . According to Eqs. (7.13) and (7.18), we have

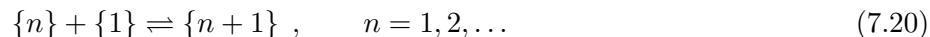
$$W_n = -\ln K_n - (n - 1) \ln c_1 . \quad (7.19)$$

The term  $-(n - 1) \ln c_1$  in Eq. (7.19) explicitly determines the dependence of the work  $W_n$  on monomer concentration  $c_1$  (the work  $W_n$  is independent of the concentrations  $c_n$  with  $n \geq 2$ ). Since the work  $W_n$  is, by its meaning, not affected by the condition whether the aggregate concentration is in equilibrium or not, Eq. (7.19) is valid at arbitrary aggregate concentrations in an ideal solution.

The value of the parameter  $-\ln K_n$  is known as the work of micellization,  $W_n^M$ , for the case when the standard concentration is expressed by the molarity (1 mol/l). While comparing this work with  $W_n$  (then the concentration  $c_1$  should also be expressed in moles), we can see from Eq. (7.19) a significant difference between  $W_n^M$  and  $W_n$ : if, in an ideal system, the former work is independent of monomer concentration, the latter, on the contrary, is dependent on this concentration. This dependence is especially pronounced for micelles with large aggregation numbers.

### 7.3 General Kinetic Equation of Molecular Aggregation: Irreversible Behavior in Micellar Solutions

According to the basic assumptions of the classical kinetic theory of nucleation [1, 2], the number of molecules in an aggregate varies only as a result of absorption or emission of monomers by the aggregate. This way the kinetics is determined by the sequences



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

The most important quantity in the classical kinetic theory is the flux of aggregates in the space of cluster sizes according to the mechanism as illustrated in Eq. (7.20), i.e., occurring due to direct and reverse transitions of the aggregates. Denoting this flux by  $J_n$ , we have

$$J_n = j_n^+ c_n - j_{n+1}^- c_{n+1}, \quad n = 1, 2, \dots, \quad (7.21)$$

where  $j_n^+$  is the number of monomers absorbed by the aggregate  $\{n\}$  from the 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, the inequalities  $j_n^+ > 0$  and  $j_{n+1}^- > 0$  hold.

The importance of the flux of aggregates  $J_n$  in the aggregate size space is due to the fact that, according to equation

$$\frac{\partial c_n}{\partial t} = J_{n-1} - J_n, \quad n = 2, 3, \dots, \quad (7.22)$$

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

Let us find the relationship between the rates of emission,  $j_{n+1}^-$ , and absorption,  $j_n^+$ , of monomers by the molecular aggregate. At aggregation equilibrium, i.e., under the condition expressed in Eq. (7.11), a detailed balance of direct and reverse transitions of aggregates on each sequence Eq. (7.20) should be established, i.e., the relationship

$$J_n^{(e)} = 0, \quad n = 1, 2, \dots \quad (7.23)$$

should be fulfilled. Here,  $J_n^{(e)}$  is given by Eq. (7.21), where  $c_n$  has to be replaced by  $c_n = c_n^{(e)}$ . Taking into account that, at the suggested high density of matter in the aggregates, the rates  $j_{n+1}^-$  are independent of whether the solution is at aggregation equilibrium at a given concentration  $c_1$  or not, we obtain from Eqs. (7.21) and (7.23)

$$j_{n+1}^- = j_n^+ \left( \frac{c_n^{(e)}}{c_{n+1}^{(e)}} \right), \quad n = 1, 2, \dots \quad (7.24)$$

Substituting Eq. (7.13) into Eq. (7.24), we arrive at

$$j_{n+1}^- = j_n^+ \exp(W_{n+1} - W_n), \quad n = 1, 2, \dots \quad (7.25)$$

Then, substituting Eqs. (7.25) into (7.21), we obtain

$$J_n = j_n^+ [c_n - c_{n+1} \exp(W_{n+1} - W_n)] , \quad n = 1, 2, \dots . \quad (7.26)$$

Finally, a substitution of Eq. (7.26) into Eq. (7.22) leads to the general kinetic equation of formation of molecular aggregates. It is also called the Becker-Döring step-by-step equation.

Using Eq. (7.16), let us represent Eq. (7.26) in the following form

$$J_n = j_n^+ c_n \left\{ 1 - \exp \left[ -\frac{(A_{n+1} - A_n)}{k_B T} \right] \right\} , \quad n = 1, 2, \dots . \quad (7.27)$$

In the case of aggregation equilibrium, when Eq. (7.15) is valid, Eq. (7.27) confirms the relation of detailed balance, Eq. (7.23).

Applying the kinetic theory to the description of a non-equilibrium process in a disperse system, it seems natural to generally refer the problem of the occurrence of aggregation or disaggregation to a single link in the sequence Eq. (7.20) of direct and reverse transitions performed by the aggregates, and, moreover, to refer this problem to each current moment of process development. Evidently, the occurrence of aggregation or disaggregation on this particular link of the transition sequence depends on the fact whether the inequality  $J_n > 0$  or the inequality  $J_n < 0$  holds at each moment. In view of inequality  $j_n^+ > 0$ , Eq. (7.27) allows us to state that

$$\begin{aligned} J_n > 0 \quad (\text{aggregation}) \quad & \text{if } A_{n+1} > 0 \\ & \text{for } n = 1, 2, \dots . \quad (7.28) \\ J_n < 0 \quad (\text{dissolution}) \quad & \text{if } A_{n+1} < 0 \end{aligned}$$

Rewriting Eq. (7.16) as

$$A_{n+1} - A_n = -k_B T \left[ W_{n+1} - W_n + \ln \left( \frac{c_{n+1}}{c_n} \right) \right] , \quad n = 1, 2, \dots , \quad (7.29)$$

we can see that the sign of the difference  $A_{n+1} - A_n$  (important in the conditions given by Eqs. (7.28) for the occurrence of aggregation or disaggregation) depends not only on the value of  $W_{n+1} - W_n$ , i.e., on the energy factor, but also on the value  $\ln(c_{n+1}/c_n)$ , i.e., on the fluctuation-probability factor. The conditions, as given by Eqs. (7.28) and (7.29), are valid for the whole course of the evolution of the disperse system from arbitrary initial states.

In particular, if only monomers are present in the systems at the initial moment, then, at least at the consecutive moments, the inequalities  $c_1 \gg c_2 \gg c_3 \gg c_4 \dots$ , are fulfilled with increasing strength. At the same time (cf. Eq. (7.29)), the inequalities  $0 < A_2 - A_1 < A_3 - A_2 < A_4 - A_3 \dots$ , hold. This result is valid despite a possible increase in the work  $W_n$  with an increase in  $n$  beginning with  $n = 1$  where, according to Eq. (7.6), the work  $W_n$  is equal to zero. Then, as it is seen from Eq. (7.28), at the consecutive moments close to the initial one, the aggregation occurs at all levels  $n$  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.

Let us demonstrate that, irrespective of the initial state of a solution, the kinetic theory shows a monotonic decrease in the Gibbs energy of a solution with time (total concentration, temperature and pressure are assumed to be constant, again). Rewriting Eq. (7.17) as

$$\frac{\partial G}{\partial t} = - \sum_{n \geq 2} A_n \frac{\partial c_n}{\partial t} \quad (7.30)$$

and using Eq. (7.22), we obtain (after changing the summation index and taking into account  $A_1 = 0$ )

$$\frac{\partial G}{\partial t} = - \sum_{n \geq 1} (A_{n+1} - A_n) J_n . \quad (7.31)$$

According to Eq. (7.28), the sign of the flux  $J_n$  coincides with that of the difference  $A_{n+1} - A_n$  at all  $n \geq 1$ . Then it follows from Eq. (7.31) that

$$\frac{\partial G}{\partial t} \leq 0 . \quad (7.32)$$

The equality sign in Eq. (7.32) holds only when  $J_n = 0$ , and, correspondingly,  $A_{n+1} - A_n = 0$  at all  $n \geq 1$ , i.e., when (in agreement with Eqs. (7.23) and (7.27)) the aggregation equilibrium of the solution is established.

Thus, irrespective of the initial state of a solution, the kinetic theory indeed shows (according to Eq. (7.32)) a monotonic decrease in the Gibbs energy of a solution with time up to the moment when the Gibbs energy reaches its minimum value at the final state of the aggregation equilibrium of the solution. Since, at the assumed conditions of constant total concentration, constant temperature

and pressure, a monotonic decrease in the Gibbs energy implies, according to thermodynamic principles, the irreversible tendency of evolution of the system to the state of thermodynamic equilibrium, the inequality Eq. (7.32) obtained is the kinetic substantiation of the irreversible tendency of a solution to its aggregation equilibrium. As it is well-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 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, Eqs. (7.22) and (7.26) constitute precisely such an equation.

In the outline of the results in the present section, we followed widely Ref. 23. Other aspects of applying the Becker-Döring step-by-step equation to micellization processes as well as the analysis of general properties of this equation can be found in Refs. 30 - 33.

## 7.4 Thermodynamic Characteristics of Micellization Kinetics in the Near-critical and Micellar Regions of Aggregate Sizes

According to Eq. (7.19) the aggregation work  $W_n$  depends on the monomer concentration  $c_1$  via the term  $-(n-1)\ln c_1$ . The behavior of the work  $W_n$  as a function of  $n$  at variable concentration  $c_1$  is shown in Fig. 7.1. Curve (1) corresponds to the case when the surfactant concentration has values below the critical micelle concentration (CMC), i.e. the concentration at which the micelles accumulate the noticeable part of the surfactants in the solution. Curve (2) corresponds to the case when the surfactant concentration is near to the CMC, but from below. Curve (3) corresponds to the practically important case when the surfactant concentration exceeds the CMC, but is lower than the concentration that gives rise to the micelle non-spherical polymorphic transformations in surfactant solutions [5, 9, 12, 34]. It is this curve that will be used in our further analysis.

The positions of the maximum and minimum of the work  $W_n$  along the  $n$ -axis, i.e., the aggregation numbers of critical and stable molecular aggregates, are denoted

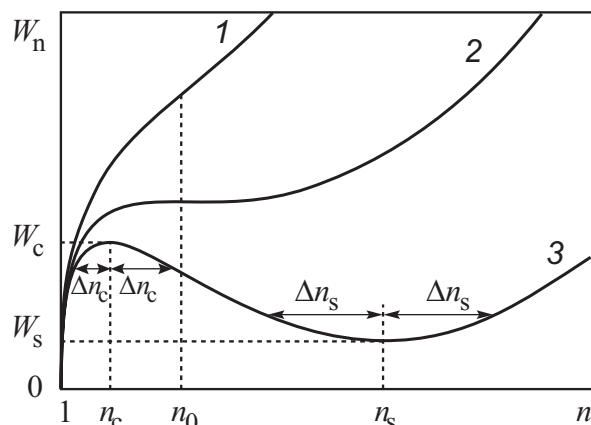


Fig. 7.1 Behavior of the work,  $W_n$ , of formation of a surfactant molecular aggregate as a function of the aggregation number,  $n$ , at a variation of concentration,  $c_1$ , of surfactant monomers (see text).

by  $n_c$  and  $n_s$ , respectively. The values of the barrier height and the well depth of the work,  $W_n$ , are denoted by  $W_c \equiv W_n|_{n=n_c}$  and  $W_s \equiv W_n|_{n=n_s}$ . The potential barrier gives rise to the activation barrier of micellization. The half-widths of the potential barrier and potential well of the aggregation work are denoted by  $\Delta n_c$  and  $\Delta n_s$ . They are determined by

$$\Delta n_c = \left[ 2 / \left| \partial^2 W_n / \partial n^2 \right|_{n=n_c} \right]^{1/2}, \quad \Delta n_s = \left[ 2 / \left| \partial^2 W_n / \partial n^2 \right|_{n=n_s} \right]^{1/2}. \quad (7.33)$$

The physical meaning of the half-widths  $\Delta n_c$  and  $\Delta n_s$ , introduced by Eq. (7.33), will be disclosed below. Fig. 7.1 takes into account Eq. (7.6) which implies that the formation of surfactant monomers, present initially in a micellar solution, does not require any work. For definiteness, curve (3) in Fig. 7.1 refers to the case when  $W_s > 0$  (when the concentration  $c_1$  is not too high).

The quantities  $n_c$ ,  $n_s$ ,  $W_c$ ,  $W_s$ ,  $\Delta n_c$  and  $\Delta n_s$  (as well as the work  $W_n$  itself) depend on the monomer concentration,  $c_1$ . They represent thermodynamic characteristics of the micellization kinetics. Further, we assume the conditions

$$\Delta n_c \gg 1, \quad \frac{\Delta n_c}{n_c} \ll 1, \quad \frac{\Delta n_c}{(n_s - n_c)} \ll 1, \quad (7.34)$$

$$\Delta n_s \gg 1, \quad \frac{\Delta n_s}{(n_s - n_c)} \ll 1 \quad (7.35)$$

to be fulfilled. The first conditions in Eqs. (7.34) and (7.35) allow us to consider the aggregation number  $n$  as a continuous variable in the regions of potential barrier and potential well of the work  $W_n$ . The remaining conditions in Eqs. (7.34) and (7.35) imply that the potential barrier and potential well of the work  $W_n$  are fully exhibited. As it is qualitatively shown in Fig. 7.1, they are separated from the initial point  $n = 1$  at the  $n$ -axis and from each other. This property can also be expressed by the inequalities

$$\exp(W_c) \gg 1, \quad \exp(W_c) \gg \exp(W_s), \quad (7.36)$$

which result from the conditions given in Eqs. (7.34) and (7.35).

Eqs. (7.34) and (7.35) are fulfilled when the total surfactant concentration sufficiently exceeds the CMC (at this, possibly, the second condition in Eq. (7.34) is valid at its breaking point). In particular, the conditions in Eq. (7.34) and (7.35) imply that the aggregation numbers  $n_c$  and  $n_s$  are much larger than unity.

Eqs. (7.34) and (7.35) make it possible (employing Eqs. (7.33)) to derive the following quadratic approximations for the work  $W_n$  in the regions of its potential barrier and well

$$W_n = W_c - \left( \frac{n - n_c}{\Delta n_c} \right)^2 \quad \text{for} \quad n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c, \quad (7.37)$$

$$W_n = W_s + \left( \frac{n - n_s}{\Delta n_s} \right)^2 \quad \text{for} \quad n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s. \quad (7.38)$$

According to Eq. (7.37), the work  $W_n$  decreases by a thermal unit when the variable  $n$  deviates from  $n_c$  by  $\Delta n_c$ . In accordance with Eq. (7.38), the work  $W_n$  increases by a thermal unit when the variable  $n$  deviates from  $n_s$  by  $\Delta n_s$ . These facts clarify the physical meaning of  $\Delta n_c$  and  $\Delta n_s$ .

The conditions expressed in Eqs. (7.34)-(7.36) allow us to employ a macroscopic description of the micellization kinetics. They generalize the conditions for a macroscopic description revealed previously [20] in the kinetic theory of nucleation. The regions in aggregate size space  $n \lesssim n_c - \Delta n_c$ ,  $n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c$  and  $n \gtrsim n_c + \Delta n_c$  are called pre-critical, near-critical, and super-critical regions, respectively. Micelles are accumulated mainly in the region  $n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s$ . This region is called the micellar one. It is located within the super-critical region. The quantities  $n_s$  and  $\Delta n_s$  have the meaning of the average aggregation number of micelles and the variance of the aggregation number of micelles

around this average value, respectively. As for the regions of potential barrier and potential well of the work  $W_n$ , we imply that these regions are the near-critical and micellar regions, respectively.

Molecular aggregates gather mostly in the regions of their sizes, where the work of aggregate formation is minimal. These regions are located to the left- and right-hand sides of the potential barrier of work, i.e., they are the pre-critical and super-critical regions. We are not concerned about the part of the super-critical region where  $n > n_s + \Delta n_s$ , because the concentrations of molecular aggregates in this region are rather low.

The large amount of molecular aggregates in the pre-critical and super-critical regions may be assumed to be varied in its relative proportions so slowly that the aggregate concentrations in each of these separate regions are maintained as quasi-equilibrium concentrations irrespective of a permanent decrease or increase in the number of aggregates by their fluxes over the potential barrier of the aggregation work. However, the mutual quasi-equilibrium between molecular aggregates in the pre-critical and super-critical regions is absent due to these fluxes. Mutual quasi-equilibrium is only reached as soon as the final equilibrium of micellar solution is established when quasi-equilibrium concentrations of molecular aggregates in the pre-critical and super-critical regions as well as the concentrations of molecular aggregates within the entire range of their sizes come to complete equilibrium.

Denoting the quasi-equilibrium concentration of molecular aggregates with the aggregation number  $n$  by  $c_n^{(e)}$  (similar to the equilibrium concentration), we have in the pre-critical and super-critical regions

$$c_n = c_n^{(e)} \quad \text{for } n \lesssim n_c - \Delta n_c, \quad c_n = c_n^{(e)} \quad \text{for } n \gtrsim n_c + \Delta n_c. \quad (7.39)$$

In accordance with Boltzmann's fluctuation principle, similar to Eq. (7.13), we can write

$$c_n^{(e)} = \text{const} \cdot \exp(-W_n). \quad (7.40)$$

Thus we have in the pre-critical and super-critical regions:

$$c_n^{(e)} = c_1 \exp(-W_n) \quad \text{for } n \lesssim n_c - \Delta n_c, \quad (7.41)$$

$$c_n^{(e)} = c_s \exp[-(W_n - W_s)] \quad \text{for } n \gtrsim n_c + \Delta n_c, \quad (7.42)$$



where  $c_s \equiv c_n|_{n=n_s}$  is the concentration of molecular aggregates at the point of minimal work of their formation. The fact that the pre-exponential factor in Eq. (7.41) is equal to  $c_1$  results from  $c_1 \equiv c_n|_{n=1}$  and equality  $W_n|_{n=1} = 0$ . The fact that the pre-exponential factor in Eq. (7.42) is equal to  $c_s$  results from the definition of the concentration  $c_s$  and the evident equality  $(W_n - W_s)|_{n=n_s} = 0$ . Because micelles are accumulated in the micellar region, their total concentration  $c_M$  is

$$c_M = \int_{n_s - \Delta n_s}^{n_s + \Delta n_s} c_n dn . \quad (7.43)$$

Employing Eq. (7.42), the quadratic approximation Eq. (7.38) and replacing, with a high degree of precision, the integration limits by  $-\infty$  and  $\infty$ , we get from Eq. (7.43)

$$c_M = \pi^{1/2} c_s \Delta n_s . \quad (7.44)$$

Using Eq. (7.44), we may rewrite Eq. (7.42) as [19]

$$c_n^{(e)} = \left( \frac{c_M}{\pi^{1/2} \Delta n_s} \right) \exp[-(W_n - W_s)] \quad \text{for} \quad n \gtrsim n_c + \Delta n_c . \quad (7.45)$$

## 7.5 Kinetic Equation of Aggregation in the Near-critical and Micellar Regions of Aggregate Sizes

Employing the first conditions in Eqs. (7.34) and (7.35), the aggregation number  $n$  may be considered as a continuous variable in the near-critical and micellar regions of the sizes of molecular aggregates. Thus in these regions, Eq. (7.22) may be written as a continuity equation

$$\frac{\partial c_n(t)}{\partial t} = - \frac{\partial J_n(t)}{\partial n} . \quad (7.46)$$

Taking into account Eqs. (7.37), (7.38) and  $W_{n+1} - W_n = \partial W_n / \partial n$ , we obtain

$$W_{n+1} - W_n = -2 \frac{(n - n_c)}{(\Delta n_c)^2} \quad \text{for} \quad n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c , \quad (7.47)$$

$$W_{n+1} - W_n = 2 \frac{(n - n_s)}{(\Delta n_s)^2} \quad \text{for} \quad n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s . \quad (7.48)$$

Due to the first conditions in Eqs. (7.34) and (7.35), the absolute values of the terms in the right-hand sides of Eqs. (7.47) and (7.48) are much smaller than unity in the near-critical and micellar regions of aggregate sizes. Then, with a high degree of accuracy, we have from Eqs. (7.47) and (7.48) in these regions

$$\exp(W_{n+1} - W_n) = 1 - 2 \frac{(n - n_c)}{(\Delta n_c)^2} \quad \text{for} \quad n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c , \quad (7.49)$$

$$\exp(W_{n+1} - W_n) = 1 + 2 \frac{(n - n_s)}{(\Delta n_s)^2} \quad \text{for} \quad n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s . \quad (7.50)$$

Using the approximation  $c_{n+1} = c_n + \partial c_n / \partial n$  and Eqs. (7.49)-(7.50), ignoring the products of the small quantities  $\partial c_n / \partial n$ ,  $2(n - n_c) / (\Delta n_c)^2$  and  $2(n - n_s) / (\Delta n_s)^2$ , we obtain from Eq. (7.26)

$$J_n(t) = j_c^+ \left[ 2 \frac{(n - n_c)}{(\Delta n_c)^2} - \frac{\partial}{\partial n} \right] c_n(t) \quad \text{for} \quad n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c , \quad (7.51)$$

$$J_n(t) = -j_s^+ \left[ 2 \frac{(n - n_s)}{(\Delta n_s)^2} + \frac{\partial}{\partial n} \right] c_n(t) \quad \text{for} \quad n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s , \quad (7.52)$$

where  $j_c^+ \equiv j_n^+|_{n=n_c}$  and  $j_s^+ \equiv j_n^+|_{n=n_s}$  are the rates of monomer absorption by critical and stable aggregates, respectively. Eqs. (7.51), (7.52) and (7.46) result in the differential kinetic equation describing the formation of molecular aggregates in the near-critical and micellar regions of their sizes.

Let us briefly sketch also another way of deriving Eqs. (7.51) and (7.52). The variation of the aggregation number  $n$  with respect to time,  $\dot{n}$ , is given by

$$\dot{n} = j_n^+ - j_n^- . \quad (7.53)$$

Assuming  $n$  to be a continuous variable, Eq. (7.25) yields approximately

$$j_n^- = j_n^+ \exp \left( \frac{\partial W_n}{\partial n} \right) . \quad (7.54)$$

As was already mentioned, the derivative  $\partial W_n/\partial n$  is small in the near-critical and micellar regions of aggregate sizes. Then, from Eqs. (7.53) and (7.54) we have in these regions with a high degree of accuracy

$$\dot{n} = -j_n^+ \frac{\partial W_n}{\partial n} . \quad (7.55)$$

One can also write the flux of molecular aggregates,  $J_n(t)$ , as

$$J_n(t) = \left( \dot{n} + \beta \frac{\partial}{\partial n} \right) c_n(t) . \quad (7.56)$$

The term containing  $\dot{n}$  describes the regular evolution of a single molecular aggregate. The term including the differential operator  $\partial/\partial n$  describes the fluctuation evolution of the ensemble of molecular aggregates. This fluctuational contribution on the evolution is superimposed on the regular one and broadens the regular evolution. Further, we substitute Eq. (7.55) into Eq. (7.56) in the near-critical and micellar regions. Then, determining the unknown coefficient  $\beta$  from the condition of vanishing of the flux of molecular aggregates at their equilibrium concentrations given by Eq. (7.40), we obtain

$$J_n(t) = -j_n^+ \left( \frac{\partial W_n}{\partial n} + \frac{\partial}{\partial n} \right) c_n(t) . \quad (7.57)$$

Expressing the derivative  $\partial W_n/\partial n$  in Eq. (7.57) in the near-critical and micellar regions by means of Eqs. (7.37) and (7.38), we arrive at the previously obtained Eqs. (7.51) and (7.52), again.

## 7.6 Direct and Reverse Fluxes of Molecular Aggregates over the Activation Barrier of Micellization

As was already mentioned above, in contrast to nucleation at micellization we observe, in addition to the direct flux of molecular aggregates overcoming (by fluctuation) the activation barrier of micellization from the side of the pre-critical region, the reverse flux of molecular aggregates overcoming (by fluctuation) the activation barrier of micellization from the side of the super-critical region. Let us denote the direct and reverse fluxes of molecular aggregates in the region

of the potential barrier of the work of their formation, i.e., in the near-critical region, by  $J'_n(t)$  and  $J''_n(t)$ , respectively. Similarly, the concentrations of molecular aggregates participating in these fluxes in the near-critical region are  $c'_n(t)$  and  $c''_n(t)$ . We have in this case for the total flux  $J_n(t)$  of molecular aggregates and their total concentrations  $c_n(t)$  in the near-critical region  $n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c$

$$J_n(t) = J'_n(t) + J''_n(t) , \quad (7.58)$$

$$c_n(t) = c'_n(t) + c''_n(t) . \quad (7.59)$$

The approach employed in the previous sections to derive the kinetic equation of micellization can be applied separately for the molecular aggregates transferred (by fluctuations) from the pre-critical to super-critical regions and for molecular aggregates transferred (by fluctuations) from the super-critical to pre-critical regions. Therefore, similarly to Eqs. (7.46) and (7.51), we have in the near-critical region  $n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c$

$$\frac{\partial c'_n(t)}{\partial t} = -\frac{\partial J'_n(t)}{\partial n} , \quad (7.60)$$

$$J'_n(t) = j_c^+ \left[ 2\frac{(n - n_c)}{(\Delta n_c)^2} - \frac{\partial}{\partial n} \right] c'_n(t) \quad (7.61)$$

as well as

$$\frac{\partial c''_n(t)}{\partial t} = -\frac{\partial J''_n(t)}{\partial n} , \quad (7.62)$$

$$J''_n(t) = j_c^+ \left[ 2\frac{(n - n_c)}{(\Delta n_c)^2} - \frac{\partial}{\partial n} \right] c''_n(t) . \quad (7.63)$$

Let us formulate the boundary conditions to Eqs. (7.60)-(7.63). Based on the ideas of the kinetic theory of nucleation [21] and taking into account the boundary conditions Eq. (7.39), we conclude that the boundary conditions to Eqs. (7.60) and (7.61) for the concentrations  $c'_n(t)$  in the near-critical region are [19]

$$\frac{c'_n(t)}{c_n^{(e)}} \cong \begin{cases} 1 & \text{for } n \simeq n_c - \Delta n_c , \\ 0 & \text{for } n \simeq n_c + \Delta n_c , \end{cases} \quad (7.64)$$

and the boundary conditions to Eqs. (7.62) and (7.63) for the concentrations  $c_n''(t)$  in the near-critical region are [19]

$$\frac{c_n''(t)}{c_n^{(e)}} \cong \begin{cases} 0 & \text{for } n \simeq n_c - \Delta n_c, \\ 1 & \text{for } n \simeq n_c + \Delta n_c. \end{cases} \quad (7.65)$$

The quasi-equilibrium concentrations  $c_n^{(e)}$  in the boundary conditions Eqs. (7.64) and (7.65) are determined by Eqs. (7.41) (at  $n \simeq n_c - \Delta n_c$ ) and (7.45) (at  $n \simeq n_c + \Delta n_c$ ).

According to Eqs. (7.59), (7.64) and (7.65), the boundary conditions to Eqs. (7.46) and (7.51) for the total concentrations  $c_n(t)$  of molecular aggregates in the near-critical region are

$$\frac{c_n(t)}{c_n^{(e)}} \cong 1 \quad \text{for } n \simeq n_c \mp \Delta n_c, \quad (7.66)$$

where the quasi-equilibrium concentrations  $c_n^{(e)}$  are given by Eqs. (7.41) (at  $n \simeq n_c - \Delta n_c$ ) and (7.45) (at  $n \simeq n_c + \Delta n_c$ ).

At the quasi-equilibrium concentrations of molecular aggregates in the pre-critical and super-critical regions, the concentrations  $c_n$  of molecular aggregates in the near-critical region will be quasi-stationary ones. The prefix "quasi" to the words "equilibrium", "steady" and "stationary" specifies the absence of a significant time dependence of the concentrations  $c_n$  within the time intervals, during which the concentrations  $c_1$  and  $c_M$  do not vary noticeably in the course of the slow tendency of evolution of the micellar solution to its final state of complete equilibrium.

Let us study the quasi-steady state of molecular aggregates in the near-critical region. The concentrations  $c_n'(t)$ ,  $c_n''(t)$  and  $c_n(t)$  of the aggregates are independent of time  $t$  in this state, whereas the aggregate fluxes  $J_n'(t)$ ,  $J_n''(t)$  and  $J_n(t)$  are also independent of the aggregation number  $n$  (cf. Eqs. (7.60), (7.62) and (7.46)). We denote the concentrations  $c_n'(t)$ ,  $c_n''(t)$  and  $c_n(t)$  in a quasi-steady state by  $c_n'^{(s)}$ ,  $c_n''^{(s)}$  and  $c_n^{(s)}$ , and the fluxes  $J_n'(t)$ ,  $J_n''(t)$  and  $J_n(t)$  in this state by  $J'$ ,  $J''$  and  $J$  (for simplicity of the notations, the quasi-steady state of fluxes is specified by the omission of the argument  $n$  and  $t$ ). Then, in the near-critical region,  $n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c$ , we have

$$c_n'(t) = c_n'^{(s)}, \quad c_n''(t) = c_n''^{(s)}, \quad c_n(t) = c_n^{(s)} \quad (7.67)$$

as well as

$$J'_n(t) = J', \quad J''_n(t) = J'', \quad J_n(t) = J. \quad (7.68)$$

The right-hand sides of the continuity equations Eqs. (7.60) and (7.62) are equal to zero in the quasi-steady state of molecular aggregates. We employ further Eqs. (7.61) and (7.63) for the fluxes of molecular aggregates and the boundary conditions Eq. (7.64) and (7.65) (with Eqs. (7.41) and (7.45)). Then, performing the integration, we obtain in the near-critical region  $n_c - \Delta n_c \lesssim n \lesssim n_c + \Delta n_c$  [19]

$$c_n^{I(s)} = \frac{c_1 \exp(-W_c)}{\pi^{1/2} \Delta n_c} \exp \left[ \left( \frac{n - n_c}{\Delta n_c} \right)^2 \right] \int_n^\infty \exp \left[ - \left( \frac{n' - n_c}{\Delta n_c} \right)^2 \right] dn', \quad (7.69)$$

$$J' = c_1 j_c^+ \exp(-W_c) / \pi^{1/2} \Delta n_c, \quad (7.70)$$

$$c_n^{II(s)} = \frac{c_M \exp[-(W_c - W_s)]}{\pi \Delta n_c \Delta n_s} \exp \left[ \left( \frac{n - n_c}{\Delta n_c} \right)^2 \right] \times \quad (7.71)$$

$$\times \int_{-\infty}^n \exp \left[ - \left( \frac{n' - n_c}{\Delta n_c} \right)^2 \right] dn',$$

$$J'' = -c_M j_c^+ \exp[-(W_c - W_s)] / \pi \Delta n_c \Delta n_s. \quad (7.72)$$

For the total concentrations of molecular aggregates and their total flux in the quasi-steady state in the near-critical region, we have according to Eqs. (7.59) and (7.58)

$$c_n^{(s)} = c_n^{I(s)} + c_n^{II(s)}, \quad J = J' + J''. \quad (7.73)$$

Direct  $J'$  and reverse  $J''$  fluxes, given by Eqs. (7.70) and (7.72), are, naturally, positive and negative, respectively. In accordance with Eq. (7.70), higher values of  $c_1$ ,  $j_c^+$  and lower values of  $W_c$  and  $\Delta n_c$  result in larger values of the direct flux  $J'$ . According to Eq. (7.72), the higher  $c_M$ ,  $j_c^+$  and the lower  $W_c - W_s$ ,  $\Delta n_c$  and  $\Delta n_s$ , the larger is the absolute value of the reverse flux  $J''$ .

## 7.7 Times of Establishment of Quasi-equilibrium Concentrations

### 7.7.1 Pre- and Super-critical Sizes

Let us consider the initial stages of micellization. At these stages, the quasi-equilibrium concentrations of surfactant molecular aggregates in the pre-critical and super-critical regions of their sizes, as well as the quasi-steady concentrations of molecular surfactant aggregates in the near-critical region of their sizes, are established. We will analyze here how this process of establishment of the quasi-equilibrium concentrations proceeds with time in the pre-critical and super-critical regions.

Let us consider first the establishment of the quasi-equilibrium state in the micellar region  $n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s$ . This range of sizes is a part of the super-critical region. The variations in the concentrations  $c_n$  of the molecular aggregates with time  $t$  are governed then by the continuity equation Eq. (7.46) with fluxes  $J_n(t)$  determined by Eq. (7.52). The boundary conditions to the kinetic equation can be written in the form

$$c_n(t) \simeq 0 \quad \text{for} \quad n \simeq n_s \mp \Delta n_s . \quad (7.74)$$

The approximate equality Eq. (7.74) should be interpreted as if the concentrations of molecular aggregates at the boundaries  $n \simeq n_s \mp \Delta n_s$  of the micellar region are negligible as compared to the concentration at  $n = n_s$ . For the description of the quasi-equilibrium aggregate concentrations, which are established with time in the micellar region, we have at our disposal Eq. (7.45). Taking into account the approximation for  $W_n$ , as given by Eq. (7.38), we can see from Eq. (7.45) that the quasi-equilibrium concentrations rather rapidly decrease as  $n$  approaches the boundaries  $n \simeq n_s \mp \Delta n_s$  of the micellar region. Thus, the boundary conditions Eq. (7.74) are fulfilled.

Let us go over in the micellar region from the variable  $n$  to the variable

$$u \equiv \frac{(n - n_s)}{\Delta n_s} \quad \text{for} \quad -1 \lesssim u \lesssim 1 . \quad (7.75)$$

Assuming that

$$c(u, t) \equiv c_n(t) , \quad c^{(e)}(u) \equiv c_n^{(e)} \quad \text{for} \quad -1 \lesssim u \lesssim 1 , \quad (7.76)$$

with Eqs. (7.46) and (7.52) we arrive at the kinetic equation

$$\frac{\partial c(u, t)}{\partial t} = \frac{j_s^+}{(\Delta n_s)^2} \frac{\partial}{\partial u} \left( 2u + \frac{\partial}{\partial u} \right) c(u, t) \quad \text{for} \quad -1 \lesssim u \lesssim 1. \quad (7.77)$$

In this case, the boundary conditions in Eq. (7.74) can be rewritten as

$$\overline{c(u, t)} \approx 0 \quad \text{for} \quad u \approx \mp 1. \quad (7.78)$$

According to Eqs. (7.45), (7.75) and (7.76), we also have

$$c^{(e)}(u) = \text{const} \cdot \exp(-u^2) \quad \text{for} \quad -1 \lesssim u \lesssim 1. \quad (7.79)$$

To solve Eq. (7.77), we first recall some properties of the Hermitean polynomials  $H_i(\xi)$  ( $i = 0, 1, \dots$ ):  $H_0(\xi) = 1$ ,  $H_1(\xi) = 2\xi$ ,  $H_2(\xi) = 4\xi^2 - 2, \dots$ . They satisfy the recurrent relations,

$$\frac{\partial}{\partial \xi} H_i(\xi) = 2i H_{i-1}(\xi), \quad \left( 2\xi - \frac{\partial}{\partial \xi} \right) H_i(\xi) = H_{i+1}(\xi), \quad (7.80)$$

and the orthogonality and normalization relations,

$$\pi^{-1/2} \int_{-\infty}^{\infty} \exp(-\xi^2) H_i(\xi) H_{i'}(\xi) d\xi = i! 2^i \delta_{ii'} \quad \text{for} \quad i, i' = 0, 1, \dots, \quad (7.81)$$

where  $\delta_{ii'}$  is the Kronecker symbol and  $0! \equiv 1$ . With Eq. (7.80), we obtain

$$\frac{\partial}{\partial \xi} \left( 2\xi + \frac{\partial}{\partial \xi} \right) \exp(-\xi^2) H_i(\xi) = -2i \exp(-\xi^2) H_i(\xi) \quad (7.82)$$

for  $i = 0, 1, \dots$ . According to Eq. (7.79), the quasi-equilibrium concentrations  $c^{(e)}(u)$  satisfy the kinetic equation Eq. (7.77) and the relevant boundary conditions Eq. (7.78). It follows that the general solution of Eq. (7.77) with the boundary conditions Eq. (7.78) has (in the range  $-1 \lesssim u \lesssim 1$ ) the form

$$c(u, t) = c^{(e)}(u) + \sum_{i=1}^{\infty} k_i \exp \left[ -2ij_s^+ t / (\Delta n_s)^2 \right] \exp(-u^2) H_i(u). \quad (7.83)$$



The coefficients  $k_i$  are independent of  $u$  and  $t$ . They can be expressed with Eq. (7.81) via the initial concentrations  $c(u, t)|_{t=0}$  in the micellar region. The quasi-equilibrium concentrations  $c^{(e)}(u)$  can be included into Eq. (7.83) in the sum over  $i$ , adding the term with  $i = 0$  to the sum. This result indicates that the obtained solution Eq. (7.83) is indeed the general solution: it represents an expansion in complete system of functions.

Eq. (7.83) describes the establishment of the quasi-equilibrium concentrations of molecular aggregates in the micellar region. Its analysis shows that the quantities  $t_s^{(i)}$  can be determined as

$$t_s^{(i)} = \frac{(\Delta n_s)^2}{2ij_s^+} \quad \text{for } i = 1, 2, \dots \quad (7.84)$$

The quantities represent the spectrum of times required to establish these particular concentrations. For the largest of these times and, hence, the characteristic time,  $t_s$ , we have

$$t_s = \frac{(\Delta n_s)^2}{2j_s^+}. \quad (7.85)$$

According to Eq. (7.85), the larger  $\Delta n_s$  and the smaller  $j_s^+$ , the larger is the time  $t_s$ .

Now let us find out how the quasi-equilibrium concentrations of molecular aggregates are established with time in the pre-critical region  $n \lesssim n_c - \Delta n_c$ . We conclude that, since the same pre-critical region also exists in the case of nucleation, the quasi-equilibrium concentrations of molecular aggregates will be established in the pre-critical region in the same manner as in the course of nucleation. As was shown in [35, 36], it occurs due to the tendency of molecular aggregates with the initial aggregation number equal to unity to overcome (by fluctuations) the potential barrier of the work of their formation. Then, according to [35, 36, 24], we can estimate the characteristic time,  $t'$ , of establishing the quasi-equilibrium concentrations of molecular aggregates in the pre-critical region  $n \lesssim n_c - \Delta n_c$  as

$$t' \approx n_c \frac{\Delta n_c}{j_c^+}. \quad (7.86)$$

According to Eq. (7.86), the larger  $n_c$  and  $\Delta n_c$  and the lower  $j_c^+$ , the larger is the time  $t'$ .

Finally, it remains to be shown how the quasi-equilibrium concentrations of molecular aggregates are established with time in the range  $n_c + \Delta n_c \lesssim n \lesssim n_s - \Delta n_s$  of the super-critical region, which is located at the  $n$ -axis between the near-critical and micellar regions. Evidently, it occurs due to the tendency of molecular aggregates, which were originally located in the micellar region, to overcome (by fluctuations) the potential barrier of the work of their formation in the backward direction. Hence, there is a complete analogy between the establishment of the quasi-equilibrium concentrations of molecular aggregates in the  $n_c + \Delta n_c \lesssim n \lesssim n_s - \Delta n_s$  and  $n \lesssim n_c - \Delta n_c$  regions. The only difference is that the role  $n_c$  is now played by the difference  $n_s - n_c$ . Taking these facts into account, we estimate, by analogy with Eq. (7.86), the characteristic time,  $t''$ , of establishment of quasi-equilibrium concentrations of molecular aggregates in the range  $n_c + \Delta n_c \lesssim n \lesssim n_s - \Delta n_s$  as [24]

$$t'' \approx (n_s - n_c) \frac{\Delta n_c}{j_c^+}. \quad (7.87)$$

The larger  $n_s$  and  $\Delta n_c$  and the smaller  $n_c$  and  $j_c^+$ , then, according to Eq. (7.87), the larger is the time  $t''$ .

### 7.7.2 Near-critical Sizes

The assumption of quasi-steady concentrations of molecular aggregates in the near-critical region of their sizes is important in the kinetic theory of micellization. Let us consider how the quasi-steady state is established with time. The variation in concentrations  $c_n$  of molecular aggregates with time in the near-critical region is still determined by the continuity equation Eq. (7.46) where, however, the flux  $J_n(t)$  of molecular aggregates is determined, now, by Eq. (7.51). According to Eqs. (7.66) and (7.40), the boundary conditions to the kinetic equation Eqs. (7.46) and (7.51) can be rewritten in the near-critical region as

$$c_n(t) = c_n^{(e)} = \text{const} \cdot \exp[-(W_n - W_c)] \quad \text{for} \quad n \approx n_c \mp \Delta n_c, \quad (7.88)$$

where the factor *const* may be different on the left- and right-hand side from the near-critical region. Let us go over for the analysis of the behavior in the near-critical region from the variable  $n$  to the variable  $v$  via

$$v \equiv \frac{(n - n_c)}{\Delta n_c}, \quad -1 \lesssim v \lesssim 1. \quad (7.89)$$

Assuming

$$c(v, t) \equiv c_n(t) , \quad c^{(e)}(v) \equiv c_n^{(e)} \quad \text{for} \quad -1 \lesssim v \lesssim 1 , \quad (7.90)$$

we obtain from Eqs. (7.46) and (7.51) the following kinetic equation

$$\frac{\partial c(v, t)}{\partial t} = -\frac{j_c^+}{(\Delta n_c)^2} \frac{\partial}{\partial v} \left( 2v - \frac{\partial}{\partial v} \right) c(v, t) \quad \text{for} \quad -1 \lesssim v \lesssim 1 . \quad (7.91)$$

Then, substituting Eq. (7.89) into Eq. (7.88), we arrive at the boundary conditions

$$\frac{c(v, t)}{c^{(e)}(v)} \approx 1 \quad \text{for} \quad v \approx \mp 1 . \quad (7.92)$$

Employing Eq. (7.37) in Eq. (7.88) and using Eq. (7.89), we get

$$c^{(e)}(v) = \text{const} \cdot \exp(v^2) \quad \text{for} \quad -1 \lesssim v \lesssim 1 . \quad (7.93)$$

For the determination of the solution of Eq. (7.91) with the boundary condition Eq. (7.92), we cannot directly use the results obtained in the previous section. Eq. (7.91) and the conditions Eq. (7.92) differ from Eqs. (7.77) and (7.78). The quasi-steady concentrations of molecular aggregates,  $c^{(s)}(v)$ , which are established with time in the near-critical region satisfy the kinetic equation Eq. (7.91) with the boundary conditions Eq. (7.92). From Eq. (7.80), we get further

$$\frac{\partial}{\partial \xi} \left( 2\xi - \frac{\partial}{\partial \xi} \right) H_i(\xi) = 2(i+1) H_i(\xi) , \quad i = 0, 1, \dots \quad (7.94)$$

Then, taking into account that, according to Eq. (7.93), the quasi-steady concentrations  $c^{(e)}(v)$  increase with  $|v|$  quite rapidly, we can represent the general solution of Eq. (7.91) with the boundary conditions Eq. (7.92) as

$$c(v, t) = c^{(s)}(v) + \sum_{i=0}^{\infty} p_i \exp \left[ \frac{-2(i+1)j_c^+ t}{(\Delta n_c)^2} \right] H_i(v) \quad \text{for} \quad -1 \lesssim v \lesssim 1 . \quad (7.95)$$

The coefficients  $p_i$  are independent of  $v$  and  $t$ . They can be expressed, employing Eq. (7.81), via the initial concentrations  $c(v, t)|_{t=0}$  of aggregates in the near-critical region. The solution obtained is indeed the general solution: it represents the expansion of the difference  $c(v, t) - c^{(s)}(v)$  in the complete function system of the Hermitean polynomials  $H_i(v)$  ( $i = 0, 1, \dots$ ). Note that the rapid increase

in the quasi-equilibrium concentrations  $c^{(e)}(v)$  with  $|v|$  allows us to neglect the contribution from the polynomial sum over  $i$  in Eq. (7.95) at the boundaries of the near-critical region, and, hence, provides the fulfillment of the boundary conditions Eq. (7.92).

Eq. (7.95) describes the establishment of the quasi-steady concentrations of molecular aggregates in the near-critical region. As it is seen from Eq. (7.95), the quantities  $t_c^{(i)}$ ,

$$t_c^{(i)} = \frac{(\Delta n_c)^2}{2(i+1)j_c^+} \quad \text{for } i = 0, 1, \dots, \quad (7.96)$$

represent the spectrum of times required to establish these concentrations. For the largest of these times and, hence, the characteristic time,  $t_c$ , we have [24]

$$t_c = \frac{(\Delta n_c)^2}{2j_c^+}. \quad (7.97)$$

According to Eq. (7.97), the larger  $\Delta n_c$  and the smaller  $j_c^+$ , the larger is the time  $t_c$ .

## 7.8 Time of Fast Relaxation in Surfactant Solutions

Let us now elucidate the interrelation between the time  $t_s$  and the time of fast relaxation of micellar solutions. It is possible to clarify in this way the concept of the fast relaxation of a micellar solution introduced first in Refs. 13 - 16 and then widely used in the literature [37 - 40] as the concept corresponding to the process of local rearrangement of micelles without changing their numbers in the micellar region. Besides we will investigate the validity of the assumption of constancy of the monomer concentration at local rearrangement of the micelle size distribution in the micellar region. The assumption was important for the derivation of the results obtained in the two preceding sections.

We mark the values corresponding to the end of fast relaxation of micellar solutions with superscript zero. We introduce further with

$$\xi_n = \frac{(c_n - c_n^{(0)})}{c_n^{(0)}} \quad (7.98)$$

a measure of the relative deviation of current concentrations  $c_n$  of aggregates from the concentrations  $c_n^{(0)}$  at the end of the fast relaxation process. Assuming further that fast relaxation is realized only via the emission and absorption of monomers in the micellar region, we take into account in Eq. (7.98) exclusively the aggregates in the micellar region and the monomers at  $n = 1$ . For a description of the aggregates in the micellar region, we use, together with the aggregation number  $n$ , also the variable

$$w \equiv \frac{(n - n_s^{(0)})}{\Delta n_s^{(0)}} \quad (7.99)$$

varying within the range  $-1 \lesssim w \lesssim 1$ . Apparently, the variable  $w$  is similar to the variable  $u$  defined by Eq. (7.75). Taking into account Eqs. (7.45), (7.38) and (7.99), the micelle concentrations  $c_n^{(0)}$ , reached after completion of fast relaxation, can be written as

$$c_n^{(0)} = \left( \frac{c_M^{(0)}}{\pi^{1/2} \Delta n_s^{(0)}} \right) \exp(-w^2) \quad \text{for} \quad -1 \lesssim w \lesssim 1. \quad (7.100)$$

We considered the solution of the kinetic equation of aggregation in the micellar region already in Section 7.7. There the kinetic equation Eq. (7.77) was formulated under the assumption of constancy of the monomer concentration in surfactant solution. With sufficiently large micelle concentrations in the micellar region, the local rearrangement of the micelle distribution in sizes may be followed by considerable changes in the monomer concentration. Thus we cannot set a priori the monomer concentration as constant in the consideration of fast relaxation. Therefore we need to refine the form of the kinetic equation of aggregation in the micellar region. With Eq. (7.98), we have

$$c_n(t) = c_n^{(0)}(1 + \xi_n(t)) \quad \text{for} \quad n \geq 1, \quad j_n^+(t) = j_n^{+(0)}(1 + \xi_1(t)). \quad (7.101)$$

where  $j_n^{+(0)} = j_n^+(c_1^{(0)})$ . As follows from Eq. (7.21), the relations of detailed balance after completion of fast relaxation can be written in the micellar region as

$$j_n^{+(0)} c_n^{(0)} = j_{n+1}^- c_{n+1}^{(0)}. \quad (7.102)$$

According to the definition Eq. (7.21) and taking into account Eqs. (7.101)-(7.102), the flux  $J_n$  of aggregates can be expressed as

$$J_n = j_n^{+(0)} c_n^{(0)} (\xi_n - \xi_{n+1}) + j_n^{+(0)} c_n^{(0)} \xi_1 + j_n^{+(0)} c_n^{(0)} \xi_1 \xi_n . \quad (7.103)$$

Approaching the state of completion of fast relaxation, we have  $\xi_n \ll 1$ . This inequality allows us to neglect the last term on the right-hand side of Eq. (7.103) and to rewrite Eq. (7.103) at  $n \gg 1$  as

$$J_n \simeq -j_n^{+(0)} c_n^{(0)} \frac{\partial \xi_n}{\partial n} + j_n^{+(0)} c_n^{(0)} \xi_1 . \quad (7.104)$$

With Eqs. (7.46), (7.98) and (7.104) the desired kinetic equation of fast relaxation can be written as

$$c_n^{(0)} \frac{\partial \xi_n(t)}{\partial t} \simeq \frac{\partial}{\partial n} \left( j_n^{+(0)} c_n^{(0)} \frac{\partial \xi_n(t)}{\partial n} \right) - \xi_1(t) \frac{\partial}{\partial n} \left( j_n^{+(0)} c_n^{(0)} \right) . \quad (7.105)$$

As we did before, for a description of the evolution within the micellar region we can set  $j_n^{+(0)} \simeq j_s^{+(0)}$  on the right-hand side of Eq. (7.105). One important peculiarity of Eq. (7.105) is the presence of the last term on the right-hand side. The kinetic equation becomes inhomogeneous due to this term. Eq. (7.105) transforms at  $\xi_1(t) = 0$  into the homogeneous equation Eq. (7.77).

In addition to Eq. (7.105), we have to use Eq. (7.8) of mass balance of the surfactant per volume unit of the solution. Substituting the first expression in Eqs. (7.101) into the right-hand side of Eq. (7.8) and recognizing that the total surfactant concentration  $c$  remains the same after the completion of the fast relaxation process, we find

$$c_1^{(0)} \zeta_1(t) = - \sum_{n=2}^{\infty} n c_n^{(0)} \zeta_n(t) . \quad (7.106)$$

We will search for a solution of Eqs. (7.105) and (7.106) on the basis of the expansion

$$\xi_n(t) = \sum_{i=0}^{\infty} q_i(t) H_i(w) \quad \text{for} \quad -1 \lesssim w \lesssim 1 \quad (7.107)$$

in the full system of the Hermitean polynomials  $H_i(w)$ , where  $q_i(t)$  are  $w$ -independent coefficients of expansion, which are the desired functions of time

*t*. Substituting Eq. (7.107) into Eq. (7.106) and assuming that the main contribution to the sum on the right-hand side of Eq. (7.106) is given by the micellar region, passing from summation over  $n$  to integration over  $w$  with Eq. (7.99), taking into account Eq. (7.100) and the orthogonality relations Eqs. (7.81), we obtain

$$c_1^{(0)} \zeta_1(t) = -c_M^{(0)} \Delta n_s^{(0)} q_1(t) - c_M^{(0)} n_s^{(0)} q_0 . \quad (7.108)$$

Substituting further Eqs. (7.107) and (7.108) into Eq. (7.105) and using again Eqs. (7.99) and (7.100), computing the scalar products of both sides of Eq. (7.105) with the Hermitean polynomials  $H_k$ ,  $k = 0, 1, 2, \dots$  and taking into account Eq. (7.81), we get  $(\partial q_0(t)/\partial t) = 0$ , i.e.,  $q_0 = \text{const}$ , and

$$\frac{\partial q_1(t)}{\partial t} = -\frac{2j_s^{+(0)}}{(\Delta n_s^{(0)})^2} q_1(t) - j_s^{+(0)} \frac{c_M^{(0)}}{c_1^{(0)}} \left( q_1(t) + \frac{n_s^{(0)}}{\Delta n_s^{(0)}} q_0 \right) , \quad (7.109)$$

$$\frac{\partial q_k(t)}{\partial t} = -\frac{2j_s^{+(0)} k}{(\Delta n_s^{(0)})^2} q_k(t) \quad \text{for} \quad k = 2, 3, \dots . \quad (7.110)$$

We assume here further that

$$q_0(t) = 0 \quad (7.111)$$

holds. Condition Eq. (7.111) is required to guarantee that the final concentrations  $c_n^{(0)}$  are indeed achieved at the end of fast relaxation of the micellar solution. Eqs. (7.109)-(7.111) yield

$$q_1(t) = q_1(0) \exp\left(-\frac{t}{t_1}\right) , \quad q_k(t) = q_k(0) \exp\left(-\frac{kt}{t_s^{(0)}}\right) \quad (7.112)$$

for  $k = 2, 3, \dots$ . Here,  $q_1(0), q_2(0), \dots$  are the values of the coefficients  $q_1(t), q_2(t), \dots$  at the initial (for fast relaxation) time  $t = 0$ . The times  $t_1$  and  $t_s^{(0)}$  are defined by

$$t_1 = \frac{1}{j_s^{+(0)}} \left[ \frac{2}{(\Delta n_s^{(0)})^2} + \frac{c_M^{(0)}}{c_1^{(0)}} \right]^{-1} , \quad t_s^{(0)} = \frac{(\Delta n_s^{(0)})^2}{2j_s^{+(0)}} . \quad (7.113)$$

Note that the time  $t_s^{(0)}$  is an analogue of the characteristic time  $t_s$  given by Eq. (7.85). According to Eqs. (7.108) and (7.112), the relation

$$\xi_1(t) = -\frac{c_M^{(0)} \Delta n_s^{(0)}}{c_1^{(0)}} q_1(0) e^{-t/t_1} \quad (7.114)$$

holds as well provided that Eq. (7.111) is fulfilled.

Eqs. (7.43), (7.99), (7.100), (7.101), (7.107), (7.111) and (7.81) result in

$$c_M(t) = c_M^{(0)}, \quad (7.115)$$

i.e. the total number of micelles is constant during the fast relaxation process in a micellar solution. According to Eqs. (7.113), we have further

$$t_1 < t_s^{(0)}, \quad \text{and} \quad t_1 = t_s^{(0)} \quad \text{for} \quad \frac{c_M^{(0)}}{c_1^{(0)}} \ll \frac{2}{(\Delta n_s^{(0)})^2}. \quad (7.116)$$

For the micelles, we get from Eqs. (7.101), (7.107), (7.111)-(7.112) and (7.116) that

$$c_n(t)|_{t \gg t_s^{(0)}} = c_n^{(0)} \quad (7.117)$$

holds. For monomers, Eqs. (7.114) and (7.101) lead to

$$c_1(t)|_{t \gg t_1} = c_1^{(0)}. \quad (7.118)$$

Eqs. (7.117) and (7.118) indicate that the time-independent aggregate concentrations  $c_n^{(0)}$  in the micellar region and the monomer concentration  $c_1^{(0)}$  are actually established with time. If the contributions from the higher terms of the expansion Eq. (7.107) with  $i = 2, 3, \dots$  are ignored, then the condition of applicability  $t \gg t_s^{(0)}$  of Eq. (7.117) can be substituted by a weaker (as compared with Eq. (7.116)) condition  $t \gg t_1$ . Then, it is evident that the time  $t_1$  defined by the first expression in Eq. (7.113) is the time of fast relaxation of a micellar solution.

Fast relaxation of a micellar solution, as described in Refs. 13 - 16, is directly observable in experiment [37 - 39, 41 - 44] and has been found in numerical modelling [45, 46]. This relaxation can be caused by the instantaneous external disturbance (for example, by temperature or pressure jumps) of the equilibrium



micellar solution at the initial moment  $t = 0$ . The external disturbance of the solution was not considered in the previous sections, where the evolution of the solution was due exclusively to internal processes beginning with the time when only monomers were present in a solution.

According to Eqs. (7.114) and (7.101), the monomer concentration  $c_1(t)$  varies in the period of fast relaxation of the solution; it increases at  $q_1(0) > 0$  and, on the contrary, decreases at  $q_1(0) < 0$ . The greater the initial solution disturbance, the greater is the variation of the concentration  $c_1(t)$ .

According to Eq. (7.115), the total micelle concentration  $c_M(t)$  does not vary in the course of fast relaxation of a micellar solution. However, the micelle concentration varies at the slower (final) stage of micellization as well as at the stage preceding its establishment. This variation is caused by the existence of direct  $J'$  ( $J' > 0$ ) and reverse  $J''$  ( $J'' < 0$ ) fluxes of molecular aggregates over the potential barrier of aggregation work and will be considered in the next section.

## 7.9 Time of Slow Relaxation in Surfactant Solutions

Direct  $J'$  and reverse  $J''$  fluxes of molecular aggregates over the potential barrier of the aggregation work result in the fluctuation transfer of the total number  $J' + J''$  ( $J'' < 0$ ) of molecular aggregates from the pre-critical to the micellar regions in a unit volume of micellar solution per unit time. As a result, we have

$$\frac{\partial c_M}{\partial t} = J' + J'' . \quad (7.119)$$

In the case (which is of interest for practice and the forthcoming analysis), where the surfactant concentration exceeds the critical micellization concentration (CMC), the strong inequalities Eq. (7.35) are valid. According to the second inequality in Eq. (7.35), the scattering  $\Delta n_s$  of the micellar aggregation numbers with respect to their average value  $n_s$  is quite small. Therefore, the number of surfactant monomers absorbed by micelles in a unit volume of a micellar solution is equal to  $n_s c_M$  with a high degree of accuracy. Then, due to the condition  $\exp(W_c) \gg 1$  and the resultant steep slope of the potential barrier of the aggregation work (at not too large values of  $n_c$ ), the inequality  $\sum_{n=2}^{n_c + \Delta n_c} n c_n \ll c_1$  is fulfilled. As a result we have (cf. Eq. (7.8)) the equation of a bimodal approximation for the total concentration of the surfactant in solution, i.e.,

$$c_1 + n_s c_M = c . \quad (7.120)$$

According to Eq. (7.44) the term  $n_s c_M$  is of significance in Eq. (7.120) if  $\exp(W_s)$  does not exceed  $n_s \Delta n_s$  too much. The stronger the inequality  $\exp(W_c) \gg \exp(W_s)$ , the more noticeable is the role of the term  $n_s c_M$ .

In the considered case of a closed micellar solution, the total concentration  $c$  has a preset value exceeding the CMC. Let us investigate the time evolution of such a solution, assuming that, in the initial moment when the surfactant is added to the solvent and mixed throughout its volume, almost the whole amount of dissolved surfactant is present in the system in form of monomers only. Hence, at the initial moment, the conditions  $c_1 = c$ ,  $c_M = 0$  and  $J'' = 0$  (only the direct flux  $J'$  exists) are valid. The concentration  $c_1$  decreases with time (at a given total concentration  $c$ ), while the micelle concentration  $c_M$  becomes different from zero and gradually increases. Correspondingly, the reverse flux  $J''$  of molecular aggregates develops, which progressively starts to compete with their direct flux  $J'$ . At fairly long times, the reverse flux  $J''$  begins to fully compensate the direct flux  $J'$ . In this case, the closed micellar solution comes to equilibrium.

With Eq. (7.120) and Eqs. (7.70) and (7.72) for the fluxes  $J'$  and  $J''$  at the known dependence of the aggregation work  $W_n$  on  $n$  and, hence, at the known dependences of  $n_c$ ,  $n_s$ ,  $\Delta n_c$ ,  $\Delta n_s$ ,  $W_c$ ,  $W_s$ , and  $j_c^+$  on concentration  $c_1$ , the relaxation equation Eq. (7.119) can be reduced to a nonlinear first-order differential equation with separable variables. The solution of this equation with respect to the monomer concentration  $c_1(t)$  can be written in a general form in quadratures over the entire time interval. However, the dependence of  $W_n$  on  $n$  is known only in some particular cases for specific models of micelles. Therefore, it is of interest to analytically solve the problem of the relaxation of the micellar solution at the final stage of micellization near the state of the complete equilibrium of a solution as well as the problem of the determination of the time of establishment of this final stage, using only the most representative general characteristics of the aggregation work  $W_n$  instead of the whole dependence of  $W_n$  on  $n$ .

Denoting the values characterizing the equilibrium state of the closed micellar solution by the upper tilde, we have

$$\tilde{J}' + \tilde{J}'' = 0. \quad (7.121)$$

Substituting Eqs. (7.70) and (7.72) into Eq. (7.121), we obtain

$$\tilde{c}_M = \pi^{1/2} \tilde{c}_1 \widetilde{\Delta n_s} \exp(-\widetilde{W_s}). \quad (7.122)$$

As follows from Eq. (7.122), (7.41) and (7.45) with respect to the concentrations  $c_n$  of molecular aggregates in the pre-critical and super-critical regions of their sizes, the complete equilibrium between all molecular aggregates of a micellar solution is established at the final stage. According to Eqs. (7.122) and (7.45), this state is characterized by the following concentrations of molecular aggregates

$$\tilde{c}_n^{(e)} = \tilde{c}_1 \exp\left(-\widetilde{W}_n\right). \quad (7.123)$$

Taking into account Eq. (7.122), Eq. (7.120) yields

$$\tilde{c}_1 + \pi^{1/2} \tilde{c}_1 \widetilde{n}_s \widetilde{\Delta n}_s \exp\left(-\widetilde{W}_s\right) = c. \quad (7.124)$$

At a given total concentration  $c$  and the known dependencies of  $\widetilde{n}_s$ ,  $\widetilde{\Delta n}_s$  and  $\widetilde{W}_s$  on monomer concentration  $\tilde{c}_1$ , Eq. (7.124) gives an equation for determination of the equilibrium concentration  $\tilde{c}_1$ . Once the equilibrium concentration  $\tilde{c}_1$  of surfactant monomers is found, the equilibrium concentration  $\tilde{c}_M$  can be determined using the relation

$$\tilde{c}_M = \frac{(c - \tilde{c}_1)}{\widetilde{n}_s}, \quad (7.125)$$

which follows from Eq. (7.120). If the equilibrium concentration  $\tilde{c}_1$  of surfactant monomers is known from the experiment, the total concentration  $c$  and the equilibrium concentration  $\tilde{c}_M$  are determined by Eqs. (7.124) and (7.125). If the equilibrium micelle concentration  $\tilde{c}_M$  is known experimentally, the equilibrium concentration  $\tilde{c}_1$  can be calculated solving Eq. (7.122) with respect to  $\tilde{c}_1$ , and the total concentration  $c$  can be determined using Eq. (7.125). Hence, for the nonequilibrium micellar solution, two concentrations out of three characteristic concentrations,  $c_1$ ,  $c_M$ , and  $c$ , are independent parameters (cf. Eq. (7.120)), while for the equilibrium solution, only one concentration will be an independent parameter (due to the Eq. (7.121)). It follows from Eq. (7.19) that

$$\frac{\partial W_n}{\partial c_1} = -\frac{(n-1)}{c_1} \quad (7.126)$$

holds. Taking into account the definition  $W_s \equiv W_n|_{n=n_s}$  of the minimum  $W_s$  of aggregation work  $W_n$ , we have

$$\frac{\partial W_s}{\partial c_1} = \frac{\partial W_n}{\partial c_1} \Big|_{n=n_s} + \frac{\partial W_n}{\partial n} \Big|_{n=n_s} \frac{\partial n_s}{\partial c_1}. \quad (7.127)$$

The work  $W_n$  is minimal at  $n = n_s$ . Taking into account the necessary condition  $(\partial W_n / \partial n)|_{n=n_s} = 0$ , Eqs. (7.127) and (7.126) yield

$$\frac{\partial W_s}{\partial c_1} = -\frac{(n_s - 1)}{c_1} < 0. \quad (7.128)$$

Similar considerations result in

$$\frac{\partial W_c}{\partial c_1} = -\frac{(n_c - 1)}{c_1} < 0. \quad (7.129)$$

According to Eq. (7.35), the inequality  $n_s \gg 1$  is valid. In this case, the dependence of the second term on the left-hand side of Eq. (7.124) on  $\tilde{c}_1$  is very strong (cf. Eq. (7.128)). As the result, we can make the following conclusion. As the total concentration  $c$  exceeds the CMC, the monomer concentration  $\tilde{c}_1$  also begins to exceed gradually (albeit rather slowly) the CMC, still remaining near the CMC. According to Eq. (7.128), the value in the left-hand side of Eq. (7.124) monotonically increases with concentration  $\tilde{c}_1$ . This result indicates that the solution of Eq. (7.124) with respect to concentration  $\tilde{c}_1$  at a given concentration  $c$  is the unique solution. According to Eq. (7.128), the solution of Eq. (7.122) with respect to concentration  $\tilde{c}_1$  at a given concentration  $\tilde{c}_M$  will also be the unique solution.

The solution of the system of equations Eqs. (7.119) and (7.120), describing slow relaxation in micellar solution after the initial addition of surfactant to the solvent and mixing throughout the entire volume, we begin with the times, when the concentrations  $c_1$  and  $c_M$  are already close to their values  $\tilde{c}_1$  and  $\tilde{c}_M$  at the equilibrium state of a solution and the reverse flux  $J''$  almost completely compensates the direct flux  $J'$ . These times correspond to the final stage of micellization. The smallness of the deviations of the solution characteristics from their equilibrium values at the final stage allows us to linearize Eqs. (7.119) and (7.120) at this stage and hereby to significantly simplify the problem.

Let us denote the deviations of the parameters from their values at the equilibrium state of micellar solution by  $\delta$ . Then, we have

$$c_1 = \tilde{c}_1 + \delta c_1, \quad c_M = \tilde{c}_M + \delta c_M. \quad (7.130)$$

Linearizing Eqs. (7.119) and (7.120) with Eqs. (7.130), taking into account Eqs. (7.70), (7.72) and (7.121) and the constancy of the total concentration  $c$  in the closed solution, we obtain

$$\frac{\partial \delta c_M}{\partial t} = \tilde{J}' \left[ (1 + \gamma + \eta) \frac{\delta c_1}{\tilde{c}_1} - \frac{\delta c_M}{\tilde{c}_M} \right], \quad (1 + \lambda) \delta c_1 + \tilde{n}_s \delta c_M = 0. \quad (7.131)$$

Here  $\gamma, \eta$  and  $\lambda$  are dimensionless parameters defined by

$$\begin{aligned} \gamma &\equiv -\tilde{c}_1 \left( \frac{\partial W_s}{\partial c_1} \right) \Big|_{c_1=\tilde{c}_1}, & \eta &\equiv \tilde{c}_1 \left( \frac{\partial \ln \Delta n_s}{\partial c_1} \right) \Big|_{c_1=\tilde{c}_1}, \\ \lambda &\equiv \tilde{c}_M \left( \frac{\partial n_s}{\partial c_1} \right) \Big|_{c_1=\tilde{c}_1}. \end{aligned} \quad (7.132)$$

These parameters characterize the influence of the monomer concentration  $c_1$  in the vicinity of its equilibrium value  $\tilde{c}_1$  on the values  $W_s$ ,  $\Delta n_s$  and  $n_s$ . A similar effect of the concentration  $c_1$  on the values  $j_c^+$ ,  $W_c$  and  $\Delta n_c$  in Eqs. (7.70) and (7.72) does not appear in Eq. (7.131) because the dependencies on  $j_c^+$ ,  $W_c$  and  $\Delta n_c$  in Eqs. (7.70) and (7.72) are identical. Eqs. (7.132) and (7.128) yield

$$\gamma = \tilde{n}_s - 1. \quad (7.133)$$

The flux  $\tilde{J}'$  in Eq. (7.131) can be written according to Eq. (7.70) as

$$\tilde{J}' = \tilde{c}_1 \tilde{j}_c^+ \exp(-\tilde{W}_c) / \pi^{1/2} \tilde{\Delta n}_c. \quad (7.134)$$

According to Eq. (7.121), the reverse flux  $\tilde{J}''$  differs from  $\tilde{J}'$  only in sign. The solution of the system of Eqs. (7.131) results in

$$\delta c_1 = -\tilde{n}_s \frac{\delta c_M}{(1 + \lambda)}, \quad \delta c_M = \text{const} \cdot \exp\left(-\frac{t}{t_r}\right), \quad (7.135)$$

where the time  $t_r$  is defined by [25]

$$\frac{1}{t_r} = \tilde{J}' \left[ \frac{\tilde{n}_s (1 + \gamma + \eta)}{\tilde{c}_1 (1 + \lambda)} + \frac{1}{\tilde{c}_M} \right]. \quad (7.136)$$

Let us perform, now, an estimate of the role of the parameters  $\eta$  and  $\lambda$  in Eq. (7.136). Eqs. (7.132) and (7.133) result in

$$\frac{\eta}{1 + \gamma} = \frac{\tilde{c}_1}{\tilde{n}_s} \left( \frac{\partial \ln \Delta n_s}{\partial c_1} \right) \Big|_{c_1=\tilde{c}_1}. \quad (7.137)$$

The value of  $\Delta n_s$  varies quite slowly with the variation of  $c_1$ . According to the first of the inequalities in Eq. (7.35),  $\ln \Delta n_s$  varies with concentration  $c_1$  even considerably slower than  $\Delta n_s$ . Further, taking into account the inequalities Eq. (7.35),

the inequality  $n_s \gg 1$  is valid. Then it follows from Eq. (7.137) that the inequality  $|\eta/(1+\gamma)| \ll 1$  holds. According to this inequality, the parameter  $\eta$  in Eq. (7.136) can be ignored. Likewise, in view of the weak dependence of the average micelle aggregation number  $n_s$  on concentration  $c_1$ , it follows from Eq. (7.132) that the inequality  $|\lambda| \ll 1$  holds. It follows that the parameter  $\lambda$  in Eq. (7.136) can also be ignored.

Omitting the parameters  $\eta$  and  $\lambda$  in Eq. (7.136), taking into account Eqs. (7.133) and (7.134), we have

$$t_r = \frac{\pi^{1/2} \tilde{c}_M \widetilde{\Delta n_c} \exp(\widetilde{W}_c)}{\tilde{c}_1 \tilde{j}_c^+} \left( 1 + \frac{\tilde{n}_s^2 \tilde{c}_M}{\tilde{c}_1} \right)^{-1}. \quad (7.138)$$

According to Eq. (7.138), the time  $t_r$  is positive. Thus, Eqs. (7.135) describe the irreversible tendency of the closed micellar solution to equilibrium. The same expressions indicate that the time  $t_r$ , given by Eq. (7.138), is the relaxation time of a solution at the final stage of micellization. According to Eq. (7.138), the relaxation time of the micellar solution does not depend on its volume.

As it is seen from Eq. (7.120), the quantity  $\tilde{n}_s \tilde{c}_M / \tilde{c}_1$  is the ratio of the amount of substance accumulated by the micelles at the final state of solution equilibrium to that part of the substance remaining in the form of monomers. In terms of the degree of micellization [5]  $\alpha$ ,

$$\alpha \equiv \frac{\tilde{n}_s \tilde{c}_M}{c}, \quad (7.139)$$

this ratio is equal to  $\alpha/(1-\alpha)$ . In a typical case, the critical degree of micellization (corresponding to the CMC) has a value of the order of 0.1. Thus, at  $\tilde{n}_s \gg 1$ , the strong inequality

$$\frac{\tilde{n}_s^2 \tilde{c}_M}{\tilde{c}_1} \gg 1 \quad (7.140)$$

holds. Since  $\tilde{n}_s \gg 1$ , this case surely is realized when  $\tilde{n}_s \tilde{c}_M / \tilde{c}_1 > 1$ , i.e., when micelles in the final state of solution equilibrium accumulate noticeable or even the main part of the whole amount of a surfactant is contained in them. With Eq. (7.140), we obtain from Eq. (7.138) that

$$t_r = (\pi^{1/2} \widetilde{\Delta n_c} / \tilde{n}_s^2 \tilde{j}_c^+) \exp(\widetilde{W}_c) \quad \text{for} \quad \tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 \gg 1. \quad (7.141)$$

Let us establish the relation between the time  $t_r$  and the micelle concentration in the final equilibrium state of the solution at a slow variation of the monomer concentration, when  $\tilde{n}_s$ ,  $\tilde{n}_c$ ,  $\tilde{\Delta n}_s$  and  $\tilde{\Delta n}_c$  remain practically constant. We consider two micellar solutions with almost identical monomer concentrations at the final equilibrium states. Specifying the values for these solutions by the superscripts (1) and (2), we then have  $(\tilde{c}_1^{(1)}/\tilde{c}_1^{(2)}) \approx 1$ , and, with Eqs. (7.128) and (7.129), we also have

$$\exp(\tilde{W}_s^{(1)})/\exp(\tilde{W}_s^{(2)}) = \left(\tilde{c}_1^{(2)}/\tilde{c}_1^{(1)}\right)^{\tilde{n}_s-1}, \quad (7.142)$$

$$\exp(\tilde{W}_c^{(1)})/\exp(\tilde{W}_c^{(2)}) = \left(\tilde{c}_1^{(2)}/\tilde{c}_1^{(1)}\right)^{\tilde{n}_c-1}. \quad (7.143)$$

Eqs. (7.122) and (7.142) yield

$$\tilde{c}_M^{(1)}/\tilde{c}_M^{(2)} = \left(\tilde{c}_1^{(1)}/\tilde{c}_1^{(2)}\right)^{\tilde{n}_s}. \quad (7.144)$$

Since  $\tilde{n}_s \gg 1$ , Eq. (7.144) demonstrates that, at almost identical monomer concentrations in the equilibrium solutions, the micelle concentrations can be quite different. According to Eqs. (7.143) and (7.144), we have

$$\exp(\tilde{W}_c^{(1)})/\exp(\tilde{W}_c^{(2)}) = \left(\tilde{c}_M^{(2)}/\tilde{c}_M^{(1)}\right)^{(\tilde{n}_c-1)/\tilde{n}_s}. \quad (7.145)$$

Taking into account Eqs. (7.144) and (7.145) and the fact that the rate  $\tilde{j}_c^+$  of monomer absorption by the critical molecular aggregate is proportional to the monomer concentration in the solution, with Eq. (7.141) we have

$$t_r^{(1)}/t_r^{(2)} = \left(\tilde{c}_M^{(2)}/\tilde{c}_M^{(1)}\right)^{\tilde{n}_c/\tilde{n}_s} \quad \text{for} \quad \tilde{n}_s^2 \tilde{c}_M^{(1)}/\tilde{c}_1^{(1)} \gg 1, \quad \tilde{n}_s^2 \tilde{c}_M^{(2)}/\tilde{c}_1^{(2)} \gg 1. \quad (7.146)$$

According to Eq. (7.146), the relaxation time  $t_r$  of a solution to a final equilibrium state decreases with an increase in micelle concentration  $\tilde{c}_M$  inversely proportional to  $\tilde{c}_M^{\tilde{n}_c/\tilde{n}_s}$ . The higher the micelle concentration at the final state of solution equilibrium is, the higher is the total surfactant concentration of this solution. Then we get from Eq. (7.146) that, at a rather large degree of micellization at the final state of solution equilibrium, the relaxation time of a solution decreases with an increase in the total surfactant concentration of this solution. This conclusion of the theory is supported by experimental data reported in Refs. 37 and 41 and by data of numerical modelling [45, 46].

Analyzing the time  $t_r$  of slow relaxation, we followed widely Ref. 25. The concept and a first derivation of this time was introduced by Aniansson and Wall [13].

## 7.10 Time of Approach of the Final Micellization Stage

Let us now go over to the solution of the system of kinetic equations of aggregation in a micellar solution at the times preceding the final stage of micellization. Assuming the condition  $n_s = \tilde{n}_s$ , which will be justified somewhat later, we can rewrite Eqs. (7.120) and (7.119) at a given total concentration  $c$  of the solution as

$$c_1 + \tilde{n}_s c_M = c, \quad \frac{\partial c_1}{\partial t} = -\tilde{n}_s (J' + J''). \quad (7.147)$$

To obtain Eq. (7.131), we used the linearization of  $\exp(W_s)$  with respect to the deviation  $\delta c_1$ . Expanding  $\exp(W_s)$  in a Taylor series in powers of  $\delta c_1$  and taking Eq. (7.128) into account, we see that this linearization is valid at

$$\frac{\delta c_1}{\tilde{c}_1} < \frac{1}{\tilde{n}_s}. \quad (7.148)$$

Eq. (7.148) specifies the region at the  $c_1$ -axis, where the final stage of micellization occurs. Although this region is quite narrow at  $\tilde{n}_s \gg 1$ , the relative variation of the exponent  $\exp(W_s)$  can be rather significant as evident from Eq. (7.128).

Assuming the condition  $\Delta n_s = \widetilde{\Delta n}_s$ , which will be substantiated somewhat later, Eqs. (7.70), (7.72) and Eq. (7.121) yield

$$J' = \tilde{J}' \left( \frac{c_1 j_c^+ \widetilde{\Delta n}_c}{\tilde{c}_1 \tilde{j}_c^+ \Delta n_c} \right) \exp(-W_c + \widetilde{W}_c), \quad (7.149)$$

$$J'' = -\tilde{J}'' \left( \frac{c_M j_c^+ \widetilde{\Delta n}_c}{\tilde{c}_M \tilde{j}_c^+ \Delta n_c} \right) \exp(W_s - \widetilde{W}_s - W_c + \widetilde{W}_c).$$

Eqs. (7.149) result in

$$\frac{J''}{J'} = \left( \frac{c_M}{\tilde{c}_M} \right) \left( \frac{\tilde{c}_1}{c_1} \right) \exp(W_s - \widetilde{W}_s). \quad (7.150)$$

At the assumed equality  $n_s = \tilde{n}_s$ , Eq. (7.128) gives

$$\exp(W_s - \widetilde{W}_s) = \left( \frac{\tilde{c}_1}{c_1} \right)^{\tilde{n}_s - 1}. \quad (7.151)$$



Employing Eq. (7.151) and the evident inequality  $c_M \leq \tilde{c}_M$ , we obtain from Eqs. (7.150) and (7.130)

$$\frac{|J''|}{J'} \leq \exp \left[ -\tilde{n}_s \ln \left( 1 + \frac{\delta c_1}{\tilde{c}_1} \right) \right]. \quad (7.152)$$

According to Eq. (7.152), the inequality

$$|J''|/J' \ll 1 \quad (7.153)$$

will be actually valid at

$$\delta c_1 / \tilde{c}_1 > 1 / \tilde{n}_s. \quad (7.154)$$

Taking into account Eq. (7.154), we can transform the second equation in Eqs. (7.147) into

$$\frac{\partial c_1}{\partial t} = -\tilde{n}_s J' \quad \text{for} \quad \frac{\delta c_1}{\tilde{c}_1} > \frac{1}{\tilde{n}_s}. \quad (7.155)$$

Let us emphasize the different relative role of the reverse flux  $J''$  compared with the direct flux  $J'$  when passing from the concentration range  $c_1$  admitted by Eq. (7.154) to the concentration range  $c_1$  admitted by Eq. (7.148). In the concentration range  $c_1$  admitted by Eq. (7.154), the reverse flux  $J''$  does not play any significant role (cf. Eq. (7.153)). However, the reverse flux  $J''$  is already quite noticeable in the concentration range  $c_1$  admitted by Eq. (7.148) and even determines the condition Eq. (7.148) due to the term  $\exp(W_s)$  entering Eq. (7.72).

We assume the conditions  $\Delta n_c = \widetilde{\Delta n}_c$  and  $n_c = \tilde{n}_c$  which will be substantiated below. Then, from Eqs. (7.70) and (7.129), we have

$$J' = \tilde{J}' \left( \frac{c_1 j_c^+}{\tilde{c}_1 \tilde{j}_c^+} \right) \exp(-W_c + \widetilde{W}_c), \quad \exp(W_c - \widetilde{W}_c) = \left( \frac{\tilde{c}_1}{c_1} \right)^{\tilde{n}_c - 1}. \quad (7.156)$$

The number of monomers  $j_c^+$  absorbed by the critical molecular aggregate from a solution per unit time is proportional to the monomer concentration  $c_1$  in the solution. Taking this fact into account, we arrive with Eq. (7.156) at

$$J' = \tilde{J}' \left( \frac{c_1}{\tilde{c}_1} \right)^{\tilde{n}_c + 1}. \quad (7.157)$$

Substituting Eq. (7.157) into Eq. (7.155) yields

$$\frac{\partial c_1}{\partial t} = -\tilde{n}_s \tilde{J}' \left( \frac{c_1}{\tilde{c}_1} \right)^{\tilde{n}_c+1} \quad \text{for} \quad \frac{\delta c_1}{\tilde{n}_s} > \frac{1}{\tilde{n}_s}. \quad (7.158)$$

In order to fit the region specified by Eq. (7.154), the monomer concentration  $(1 + 1/\tilde{n}_s) \tilde{c}_1$ , corresponding, according to Eqs. (7.130) and (7.148), to the onset of the final stage of micellization, has to be lower than the monomer concentration  $c_1 = c$  corresponding to the onset of the whole process of micellization. Thus, we should have

$$\left( 1 + \frac{1}{\tilde{n}_s} \right) \frac{\tilde{c}_1}{c} < 1. \quad (7.159)$$

Otherwise, the condition Eq. (7.148) should be valid within the entire concentration region  $c \geq c_1 \geq \tilde{c}_1$  of the micellization process. Then, the final stage would occur from the very beginning of this process, and the relaxation time  $t_r$  at this stage would determine the total time of the establishment of the equilibrium in a micellar solution.

We assume hereafter that the inequality Eq. (7.159) is fulfilled. It is possible only at  $\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 > 1$ , as it is shown by

$$\frac{(1 + 1/\tilde{n}_s) \tilde{c}_1}{c} = \frac{\tilde{n}_s + 1}{\tilde{n}_s + \tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1}, \quad (7.160)$$

resulting from Eq. (7.147). Integrating Eq. (7.158) over  $c_1$  from the value  $c_1 = (1 + 1/\tilde{n}_s) \tilde{c}_1$  to  $c_1 = c$  and, taking into account Eq. (7.134), we obtain [25]

$$t_0 = \frac{\pi^{1/2} \Delta \tilde{n}_c \exp(\tilde{W}_c)}{\tilde{n}_s \tilde{n}_c \tilde{J}_c^+ (1 + 1/\tilde{n}_s)^{\tilde{n}_c}} \left\{ 1 - \left[ \frac{(1 + 1/\tilde{n}_s) \tilde{c}_1}{c} \right]^{\tilde{n}_c} \right\} \quad (7.161)$$

for

$$\left( 1 + \frac{1}{\tilde{n}_s} \right) \frac{\tilde{c}_1}{c} < 1. \quad (7.162)$$

The time  $t_0$  is the desired time of approach of the final stage of micellization. The accumulation of surfactants in micelles occurs just during the time  $t_0$  (accumulation at the final stage is negligible).

Let us establish the interrelation between the time  $t_0$  and the micelle concentration  $\tilde{c}_M$  at the final state of the solution equilibrium at a small variation in the equilibrium monomer concentration at which  $\tilde{n}_s$ ,  $\tilde{n}_c$ ,  $\widetilde{\Delta n_s}$  and  $\widetilde{\Delta n_c}$  remain practically constant. Ignoring in Eq. (7.161) the small at  $\tilde{n}_c \gg 1$  value  $[(1 + 1/\tilde{n}_s) \tilde{c}_1/c]^{\tilde{n}_c}$  (cf. Eq. (7.159)), taking into account Eqs. (7.144) and (7.145) and the fact that  $\tilde{j}_c^+$  is proportional to the concentration  $\tilde{c}_1$ , we have

$$t_0^{(1)} / t_0^{(2)} = \left( \tilde{c}_M^{(2)} / \tilde{c}_M^{(1)} \right)^{\tilde{n}_c / \tilde{n}_s} \quad (7.163)$$

for

$$(1 + 1/\tilde{n}_s) \tilde{c}_1^{(1)} / c^{(1)} < 1, \quad (1 + 1/\tilde{n}_s) \tilde{c}_1^{(2)} / c^{(2)} < 1. \quad (7.164)$$

Similar to the behavior of the time  $t_r$ , as described by Eq. (7.146), the time  $t_0$  decreases with an increase in micelle concentration  $\tilde{c}_M$  in inverse proportion to  $\tilde{n}_c / \tilde{n}_s$ .

Eq. (7.158) and  $\tilde{n}_c \gg 1$  lead to the conclusion that the rate of decrease in concentration  $c_1$  with time is relatively high in the region where  $c_1$  exceeds (at least negligibly)  $\tilde{c}_1$ , i.e., in the region where  $(c_1/\tilde{c}_1)^{\tilde{n}_c} \gg 1$ . Consequently, this region does not contribute much in the integration of Eq. (7.158). All said above justifies the equalities  $n_s = \tilde{n}_s$ ,  $n_c = \tilde{n}_c$ ,  $\Delta n_s = \widetilde{\Delta n_s}$  and  $\Delta n_c = \widetilde{\Delta n_c}$  advanced above. In view of Eq. (7.156), this result also justifies the suggested practical independence of  $\exp(W_c)$  on time.

## 7.11 The Hierarchy of Micellization Times

Let us consider the hierarchy of the characteristic times of micellization. The existence of such hierarchy proves that the quasi-equilibrium concentrations of molecular aggregates in the pre-critical and super-critical regions of their sizes and the quasi-steady concentration of molecular aggregates in the near-critical region of their sizes are actually established. The hierarchy also sets estimates of the relative values of the times of the formation and decomposition of micelles and is a clear indication of the complex multi-stage process of approaching the final state of equilibrium in a micellar solution.

The average time between two successive acts of emission of a surfactant monomer by a micelle is an important parameter in micellization. We denote this time by

$\tau_1$ . As follows from Eqs. (7.25) and (7.50) at the condition (cf. Eq. (7.35)) of the applicability of the macroscopic description of the micellization kinetics, the approximate equality

$$j_n^- = j_s^+ \quad \text{for} \quad n_s - \Delta n_s \lesssim n \lesssim n_s + \Delta n_s \quad (7.165)$$

is fulfilled in the micellar region with a high degree of accuracy. Thus the average time between two successive acts of emission of a surfactant monomer by the micelle containing  $n_s$  molecules is determined by the time

$$\tau_1 = 1/j_s^+ . \quad (7.166)$$

It is evident that, simultaneously,  $\tau_1$  is the average time of emission of any of  $n_s$  surfactant monomers, contained in a micelle, from a micelle. Because the probability of the emission of some of these monomers from a micelle is larger by  $n_s$  times than that of the isolated (labeled) surfactant monomer, the quantity  $n_s\tau_1$  determines the average time for an emission of the labeled surfactant monomer from a micelle, i.e., the average value of the resident time of a surfactant monomer in a micelle.

The average micelle lifetime is also an important parameter of micellization. We found in Section 7.6 the direct flux  $J'$  and the reverse flux  $J''$  of molecular aggregates overcoming by fluctuations the potential barrier of the aggregation work. The existence of the reverse flux  $J''$  results in the fluctuational transfer of  $-J''$  molecular aggregates from the micellar to the pre-critical region in a unit volume of the micellar solution per unit time (the outflow of molecular aggregates from the micellar region to the region  $n > n_s + \Delta n_s$  is not observed at the total surfactant concentrations below the second CMC due to a rather rapid increase in the aggregation work with an increase in  $n$  in this region).

The fluctuation transfer of molecular aggregates from the micellar to the pre-critical region results in a "decay" of micelles. This decay occurs by the multi-stage mechanism of the exchange of surfactant monomers between the molecular aggregates and the micellar solution. During the time  $\tau_M$ , determined by

$$\tau_M = c_M/|J''| , \quad (7.167)$$

the micellar region would be left by all micelles due to their fluctuational transfer to the pre-critical region. Hence, it is the time  $\tau_M$  that represents the average

value of the lifetime of a micelle. Using Eq. (7.72) for the flux  $J''$ , we rewrite Eq. (7.167) as

$$\tau_M = \pi \Delta n_c \Delta n_s \exp(W_c - W_s) / j_c^+ . \quad (7.168)$$

According to Eq. (7.168), the time  $\tau_M$  is independent of the volume of the micellar solution.

Let us collect the data on the characteristic kinetic times obtained in this and the previous sections. We are interested in the times  $t_s$  and  $t'$  of establishment of quasi-steady concentrations of molecular aggregates in the micellar and pre-critical regions, respectively; the time  $t''$  of establishing the quasi-steady concentrations of molecular aggregates in the part of the super-critical region located to the left of the micellar region at the  $n$ -axis; the time  $t_c$  of establishing the quasi-steady concentrations of molecular aggregates in the near-critical region; the time  $t_1$  of fast relaxation; the time  $t_0$  of approaching the final stage of micellization and the time  $t_r$  of relaxation of the micellar solution at the final stage of micellization; the average monomer lifetime  $\tau_1$  in a micelle and the average lifetime of a micelle  $\tau_M$ . While the times  $t_s$ ,  $t'$ ,  $t''$  and  $t_c$  describe the evolution of the ensemble of molecular aggregates within the characteristic ranges of aggregation numbers and the times  $t_1$ ,  $t_0$  and  $t_r$  are related to the relaxation behavior of the whole micellar solution (micelles and monomers), the times  $\tau_1$  and  $\tau_M$  characterize a single micelle.

According to Eqs. (7.86), (7.87) and (7.97), we have

$$\frac{t'}{t_c} \approx \frac{2n_c}{\Delta n_c}, \quad \frac{t''}{t_c} \approx \frac{2(n_s - n_c)}{\Delta n_c} . \quad (7.169)$$

Taking into account Eqs. (7.34) and employing the estimate  $n_s - n_c \gtrsim n_c$  (which allows for the equality of the orders of magnitudes for  $n_s - n_c$  and  $n_c$ ), we obtain from Eq. (7.169) the inequalities

$$\frac{t''}{t_c} \gtrsim \frac{t'}{t_c} \gg 1 . \quad (7.170)$$

According to Eqs. (7.85) and (7.97), we have

$$\frac{t_c}{t_s} = \left( \frac{\Delta n_c}{\Delta n_s} \right)^2 \left( \frac{j_s^+}{j_c^+} \right) . \quad (7.171)$$

Analytical models for the aggregation work  $W_n$  in surfactant solutions do not result in large differences between the values of  $\Delta n_c$  and  $\Delta n_s$ . Assuming that a large difference in the values of  $j_c^+$  and  $j_s^+$  is also improbable, we can see from Eq. (7.171) that

$$t_c/t_s \sim 1. \quad (7.172)$$

According to Eqs. (7.85) and (7.166), we have

$$t_s/\tau_1 = (\Delta n_s)^2/2. \quad (7.173)$$

A substitution of the first condition from Eq. (7.35) into Eq. (7.173) yields

$$t_s/\tau_1 \gg 1. \quad (7.174)$$

Comparing Eq. (7.161) for the time  $t_0$  with Eq. (7.138) for the time  $t_r$  and taking into account Eq. (7.160), we obtain

$$\frac{t_0}{t_r} = \frac{\tilde{n}_s}{\tilde{n}_c (1 + 1/\tilde{n}_s)^{\tilde{n}_c}} \left[ 1 - \left( \frac{\tilde{n}_s + 1}{\tilde{n}_s + \tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1} \right)^{\tilde{n}_c} \right] \quad \text{for} \quad \frac{\tilde{n}_s^2 \tilde{c}_M}{\tilde{c}_1} \gg 1. \quad (7.175)$$

Let us discuss the results for the realistic estimates  $\tilde{n}_s \sim 10^2$  and  $\tilde{n}_c \sim 30$ . At  $\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1 = 3$ , when Eq. (7.140) is fulfilled at the breaking point, we have from Eq. (7.175) the result  $t_0/t_r \simeq 1.5$ . When the ratio  $\tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1$  becomes larger than 3, and correspondingly, the inequality Eq. (7.140) becomes stronger, the ratio  $t_0/t_r$  slightly increases but still remains smaller than 2.5. Hence, it is clear that the time  $t_r$  is an estimate not only of the duration of the very final stage of micellization, but of the total time  $t_0 + t_r$  of the establishment of equilibrium in a micellar solution as well [26].

Hereafter we will use the estimates for all kinetic times as applied to the final stage of micellization (taken at values of parameters corresponding to the final equilibrium). According to Eqs. (7.141) and (7.87), we have

$$\frac{t_r}{t''} \approx \pi^{1/2} \exp(\tilde{W}_c) / [(\tilde{n}_s - \tilde{n}_c) \tilde{n}_s^2] \quad \text{for} \quad \frac{\tilde{n}_s^2 \tilde{c}_M}{\tilde{c}_1} \gg 1. \quad (7.176)$$

Taking into account that the first inequality in Eq. (7.36) is extremely strong due to its exponential character, we derive from Eq. (7.176) the strong inequality,

$$\frac{t_r}{t''} \gg 1 \quad \text{for} \quad \frac{\tilde{n}_s^2 \tilde{c}_M}{\tilde{c}_1} \gg 1. \quad (7.177)$$

According to Eqs. (7.141) and (7.168) accounting for Eq. (7.122), we have  $\tau_M/t_r = \tilde{n}_s^2 \tilde{c}_M / \tilde{c}_1$  and thus

$$\tau_M/t_r \gg 1 \quad \text{for} \quad \frac{\tilde{n}_s^2 \tilde{c}_M}{\tilde{c}_1} \gg 1. \quad (7.178)$$

Eqs. (7.85) and (7.113) yield then

$$t_1 \lesssim t_s \quad \text{for} \quad \frac{\tilde{n}_s^2 \tilde{c}_M}{\tilde{c}_1} \gg 1. \quad (7.179)$$

As a whole, the set of Eqs. (7.170), (7.172), (7.174), (7.175), (7.177), (7.178) and (7.179) discloses the following hierarchy of the times of micellization kinetics [26]

$$\tau_M \gg t_0 \sim t_r \gg t'' \gtrsim t' \gg t_c \sim t_s \gtrsim t_1 \gg \tau_1 \quad \text{for} \quad \frac{\tilde{n}_s^2 \tilde{c}_M}{\tilde{c}_1} \gg 1. \quad (7.180)$$

The last six relations in the hierarchical sequence Eq. (7.180) are not related with the limitation as expressed in Eq. (7.140).

According to Eq. (7.180), the times  $t_s$ ,  $t'$ ,  $t''$ ,  $t_c$  and  $t_1$  are much shorter than the time  $t_r$ . This result proves that quasi-steady concentrations of molecular aggregates in the pre-critical and super-critical regions and the quasi-steady concentrations of molecular aggregates in the near-critical region are actually established. Being the consequence of the proportionality between the time  $t_r$  and  $\exp(\tilde{W}_c)$ , the statement of the smallness of the times  $t_s$ ,  $t'$ ,  $t''$ ,  $t_c$  (compared with time  $t_r$ ) is valid in the general case, i.e., it is not related with the limitation as given via Eq. (7.140). The time  $\tau_M$  ranks first and the time  $\tau_1$  is the smallest among the characteristic times of the micellization kinetics in the hierarchical sequence Eq. (7.180). This result demonstrates that the micelles are stable molecular formations, which are quite capable of renewing the composition of constituting molecules.

The established here hierarchy of the kinetic times has recently been confirmed by the numerical solutions of the set of kinetic equations of micellization reported by Grinin and Grebenkov [46]. Some modern results on the experimental investigation of kinetic times in micellization are available in Refs. 41 - 44. Results of molecular dynamics simulations can be found in Ref. 47.

## 7.12 Chemical Potential of a Surfactant Monomer in a Micelle and the Aggregation Work in the Droplet Model of Spherical Micelles

Aggregates of surfactant molecules in micellar solutions, including the relatively stable micelles, are limited by the number of constituent molecules and have such a structure that they cannot be considered as small parts of a new macroscopic phase. This fact complicates the study of the thermodynamics of molecular aggregates as compared with the theory of nucleation and forces one to find a model representation of their structure and the contributions to the work of their formation or the chemical potential of the aggregates [6, 7, 48 - 50]. One of the widely recognized models of surfactant molecular aggregates is the droplet model of an aggregate with a liquid-like core formed by the hydrophobic fragments of surfactant molecules. This model was proposed by Tanford [6] and developed later in Refs. 5, 7 - 11, 17, 27, 28, 51 - 56.

For definiteness, we deal here with a typical case of an aqueous solution of molecules of nonionic or zwitterionic surfactants having dipole hydrophilic parts and hydrophobic fragments in the form of linear hydrocarbon radicals. Let us denote by  $n_C$  the number of carbon atoms in a hydrocarbon chain of a surfactant molecule. The end methyl group has the characteristic volume  $v_0$  while the volume of the methylene group is  $v$ . According to published data [6], we have  $v_0 \approx 54.3\text{\AA}^3$  and  $v \approx 26.9\text{\AA}^3$  at an absolute temperature  $T = 298$  K. Hereafter we assume that the equality  $v_0/v \simeq 2$  holds.

It is accepted in the droplet model of a spherical molecular aggregate that the total number  $nn_C$  of hydrocarbon segments of all  $n$  surfactant molecules constituting the molecular aggregate is located inside a spherical surface in a compact manner (with no voids). Then, considering volume balance, we have for the radius  $r$  of the aggregate surface

$$r = \left( \frac{3v_C}{4\pi} \right)^{1/3} n^{1/3}, \quad (7.181)$$

where the approximate equality

$$v_C = v_0 + v(n_C - 1) \approx v(n_C + 1) \quad (7.182)$$



is taken into account in view of  $v_0/v \simeq 2$ . At  $n_C \gg 1$ , Eq. (7.181) remains valid also in the case of a slight deviation of hydrocarbon chains from their complete insertion inside the sphere of radius  $r$ .

The inner contents of a sphere of radius  $r$ , occupied completely by the hydrocarbon groups of all surfactant molecules in a molecular aggregate, can be considered as a "hydrocarbon core". Let us emphasize that the hydrocarbon core does not include protruding hydrophilic parts of surfactant molecules. According to Eq. (7.181), as the aggregation number  $n$  increases, the radius  $r$  increases also. Since the hydrophilic parts of surfactant molecules in an aggregate are located outside the sphere of radius  $r$  and the droplet model does not suggest the existence of cavities inside the molecular aggregate, the hydrocarbon chains of surfactant molecules in the aggregate become less convolute with an increase in  $n$ . Denoting the length of the completely unfolded hydrocarbon chain of the surfactant molecule by  $l_C$ , for which according to [6] we have  $l_C = (1,5 + 1,265n_C) \text{ \AA}$ , we obtain the following packing condition,

$$r \leq l_C . \quad (7.183)$$

Rewriting  $l_C$  as  $l_C = l_1(n_C + 1)$ , where  $l_1 \equiv 1.265 \text{ \AA}$  is the average length of the hydrocarbon group, using Eq. (7.181) and taking into account the aforementioned equality  $v \approx 26,9 \text{ \AA}^3$ , we present Eq. (7.183) in the form of the constraint

$$n < 0.3(n_C + 1)^2 , \quad (7.184)$$

which is imposed from above on the aggregation number  $n$  in the droplet model of surfactant spherical molecular aggregates. The stronger the inequality  $n_C \gg 1$ , the weaker is the constraint Eq. (7.184). At a sufficiently large value of  $n_C$ , the constraint Eq. (7.184) is quite comparable with the constraint  $n \gg 1$ , which is required for the applicability of the asymptotic (with respect to  $n$ ) thermodynamic and kinetic theories of micellization.

We denote by  $\bar{\mu}_{1n}$  and  $\bar{\mu}_1$  the dimensionless chemical potential of surfactant molecules in the aggregate and, correspondingly, the dimensionless chemical potential of surfactant monomers in the micellar solution. Both chemical potentials are expressed in thermal energy units  $k_B T$ . The following general thermodynamic relationship [57]

$$\frac{\partial W_n}{\partial n} = \bar{\mu}_{1n} - \bar{\mu}_1 \quad (7.185)$$

is valid at thermal and mechanical equilibrium between the molecular aggregate and solution. From Eqs. (7.6) and Eq. (7.185), we immediately obtain

$$W_n = \int_1^n (\bar{\mu}_{1n} - \bar{\mu}_1) dn . \quad (7.186)$$

We also use the standard expression for the dimensionless chemical potential of a molecule in an arbitrary medium

$$\bar{\mu} = \bar{\mu}^0 + w + \ln(c_v \Lambda^3) , \quad (7.187)$$

where  $\bar{\mu}^0$  is the dimensionless chemical potential of a molecule with a fixed center of mass in vacuum,  $w$  is the work of transfer of a molecule from a fixed position in vacuum to a fixed position in a medium with concentration  $c_v$  (the number of molecules per unit volume),  $\Lambda$  is the de Broglie mean wavelength of a molecule. Eq. (7.187) is applicable to both  $\bar{\mu}_{1n}$  and  $\bar{\mu}_1$ , with identical  $\bar{\mu}^0$  and  $\Lambda$  in both expressions. The term  $v_1 p$ , where  $p$  is the pressure and  $v_1$  is the partial molar volume of a substance in a given phase, is usually separated in the expressions for the chemical potential of a substance in the condensed state. Therefore, for the chemical potential of a surfactant in solution (let it be the  $\beta$ -phase) with concentration  $c_1$ , we can write

$$\bar{\mu}_1 = \bar{\mu}^0 + w_1 + v_1 p^\beta / k_B T + \ln(c_1 \Lambda^3) , \quad (7.188)$$

where the work of transfer  $w_1$  is referred to zero-value pressure. In view of the low compressibility of condensed media, the partial molar volume of a substance can be considered as constant and coinciding with the molecular volume. The dependence of  $\bar{\mu}_1$  on  $c_1$  is given for the dilute solution by the  $\ln(c_1 \Lambda^3)$  term, thus, according to Eq. (7.188),  $w_1$  is independent of  $c_1$ .

The situation is more complicated when one is dealing with the chemical potential of a surfactant molecule in a molecular aggregate. Let us consider the inner part of a molecular aggregate, the hydrophobic core, as the  $\alpha$ -phase. We set a dividing surface between the  $\alpha$ - and  $\beta$ -phases and use the concepts of interfacial thermodynamics. In particular, if both phases are considered to be mechanically uniform up to the dividing surface, we should ascribe a certain surface tension  $\gamma$  to the latter. The position of a surfactant molecule in the molecular aggregate is such that the dividing surface splits it into two parts with volumes  $v^\alpha$  and  $v^\beta$ ,

$$v_1 = v^\alpha + v^\beta . \quad (7.189)$$

Moreover, these parts turned out to be at different pressures ( $p^\alpha$  and  $p^\beta$ ). In addition, the molecule intersects the dividing surface (producing cross section  $a$ ) and appeared under the action of surface tension  $\gamma$ . Therefore we arrive at the expression,

$$\bar{\mu}_{1n} = \bar{\mu}^0 + w_{1n} + \frac{(v^\alpha p^\alpha + v^\beta p^\beta - \gamma a)}{k_B T} + \ln(c_{1n} \Lambda^3) , \quad (7.190)$$

for the chemical potential  $\bar{\mu}_{1n}$  of a surfactant molecule in an aggregate. Here  $c_{1n}$  is the concentration of surfactant monomers in the molecular aggregate, the work  $w_{1n}$  of the molecular transfer to the aggregate is referred to zero-valued pressure, and the term  $-\gamma a$  is substantiated in the thermodynamics of interfacial phenomena [57]. In view of Eq. (7.189), Eq. (7.188) can be rewritten as

$$\bar{\mu}_1 = \bar{\mu}^0 + w_1 + \frac{(v^\alpha p^\beta + v^\beta p^\beta)}{k_B T} + \ln(c_1 \Lambda^3) . \quad (7.191)$$

The pressures in the  $\alpha$ - and  $\beta$ -phases are interrelated by the condition of mechanical equilibrium (Laplace's equation)

$$p^\alpha - p^\beta = \frac{2\gamma}{r'} , \quad (7.192)$$

where  $r'$  is the radius of the dividing surface. From Eqs. (7.190)-(7.192) we have

$$\bar{\mu}_{1n} - \bar{\mu}_1 = w_{1n} - w_1 + \frac{2\gamma v^\alpha}{r' k_B T} - \frac{\gamma a}{k_B T} + \ln\left(\frac{c_{1n}}{c_1}\right) . \quad (7.193)$$

Substitution of Eq. (7.193) into Eq. (7.186) yields

$$W_n = \int_1^n (w_{1n} - w_1) dn + \int_1^n \frac{2\gamma v^\alpha}{r' k_B T} dn - \int_1^n \frac{\gamma a}{k_B T} dn + \int_1^n \ln\left(\frac{c_{1n}}{c_1}\right) dn . \quad (7.194)$$

A difficulty arises in the direct calculation of the integrals in Eq. (7.194) if one takes into account the interactions of polar groups. These interactions result in the contribution  $W_n^p$  to the aggregation work  $W_n$ . It is more simple to calculate the contribution of the interactions separately, taking all other integrals in Eq. (7.194) as if the interaction of polar groups is nonexistent. Then, the surface tension  $\gamma$ , the radius of the dividing surface  $r'$ , and the limiting area  $a$  can be referred to the surface of the hydrocarbon core ( $\gamma = \gamma_0$ ,  $r' = r$ ,  $a = (4\pi)^{1/3} (3v)^{2/3}$ ) and the

volume  $v^\alpha$  is identified with the volume  $v_C$  of the hydrocarbon chain entering the hydrocarbon core. Within such an approach, Eq. (7.194) can be written as

$$W_n = \int_1^n (w_{1n} - w_1) dn + \int_1^n \frac{2\gamma_0 v_C}{r k_B T} dn - \int_1^n \frac{a\gamma_0}{k_B T} dn + \int_1^n \ln \left( \frac{c_{1n}}{c_1} \right) dn + W_n^p. \quad (7.195)$$

Evidently, the difference  $w_{1n} - w_1$  is the work of transfer of a surfactant molecule from the solution (the  $\beta$ -phase) to the molecular aggregate in the absence of pressure and surface tension. Considering the hydrocarbon core as the  $\alpha$ -phase, we express this work of transfer as  $w^{\beta\alpha}$  (the order of indices indicates the direction of transfer). For the dilute solution, the work  $w^{\beta\alpha}$  does not depend on the concentration of the solution. This result follows already from the aforementioned absence of the dependence of the work  $w_1$  on  $c_1$  for the dilute solution and also from the fact that the work  $w_{1n}$  is generally independent of  $c_1$ . If we denote the concentration of the hydrocarbon tails in the  $\beta$ - and  $\alpha$ -phases by  $c^\beta$  and  $c^\alpha$ , respectively, then it is evident that  $c^\beta = c_1$ ; however, strictly speaking,  $c^\alpha \neq c_{1n}$  (the concentration of hydrocarbon chains in the hydrocarbon core is not equal to that of the molecules in the aggregate). However, according to Eq. (7.181), at  $n_C \gg 1$  and  $n \gg 1$ , the radius  $r$  is so large that it considerably exceeds the thickness of the hydrophilic layer of an aggregate and the distance from the layer to the surface of the hydrocarbon core. Denoting by  $R$  the radius of a spherical molecular aggregate, we have then  $R \approx r$ , and it follows from  $c_{1n} = 3n/4\pi R^3$  and  $c^\alpha = 3n/4\pi r^3$  that  $c_{1n} \approx c^\alpha$ . Since for a dilute solution  $c_{1n}/c_1 \sim 10^4 \div 10^5$  and  $c^\alpha/c_1 \sim 10^4 \div 10^5$  hold, the equality  $\ln(c_{1n}/c_1) \approx \ln(c^\alpha/c_1)$  will be fulfilled with even higher accuracy. Taking into account this equality and  $c^\alpha = \text{const}$ , we write Eq. (7.195), after calculating the integral in the penultimate term at  $n \gg 1$ , as

$$W_n = \int_1^n w^{\beta\alpha} dn + \int_1^n \frac{2\gamma_0 v_C}{r k_B T} dn - \int_1^n \frac{a\gamma_0}{k_B T} dn + n \ln \left( \frac{c^\alpha}{c_1} \right) + W_n^p. \quad (7.196)$$

There are other, in addition to  $W_n^p$ , contributions to  $W_n$  due to the work of transfer. Some of them are already known in the integral form, the others will be calculated by integrating (during the integration, it is admissible to ignore the lower limit, similarly as it was done in the penultimate term in Eq. (7.196)).

Let us begin with the hydrophobic contribution  $W_n^h$  to the work  $W_n$  given by the first term on the right-hand side of Eq. (7.196). For the work  $w^{\beta\alpha}$  of transfer of the entire hydrophobic part of a single surfactant molecule containing  $n_C$  hydrocarbon groups from the surfactant solution to the hydrocarbon bulk phase through the flat surface, we have the empirical expression

$$w^{\beta\alpha} = -Bn_C, \quad (7.197)$$

which is valid at  $n_C \gg 1$ . Here,  $B$  is a positive dimensionless parameter of hydrophobic interaction. Eq. (7.197) does not refer to the zero-valued but rather to atmospheric pressure (identical in both phases). However, this difference can be ignored due to the small compressibility of liquids. The positive value of the parameter  $B$  reflects the hydrophobicity of the hydrocarbon groups. According to empirical data,  $B \simeq 1.4$  at 20°C. The difference between the work of transfer of one or two segments of a hydrocarbon chain nearest to the polar group and that of the end methyl group from the work  $-B$  does not practically affect the applicability of Eq. (7.197) at  $n_C \gg 1$ . The fact that, in the accepted model of molecular aggregates, the hydrocarbon core is really not the infinite bulk phase but is surrounded by the surface with radius  $r$  will be taken into account somewhat later.

Eq. (7.197) shows that the desired hydrophobic contribution  $W_n^h$  to the aggregation work  $W_n$  is given by

$$W_n^h = -nBn_C. \quad (7.198)$$

A negative value of the hydrophobic contribution  $W_n^h$  to the work  $W_n$  facilitates the formation of molecular aggregates in a micellar solution.

The hydrophobic tail of a surfactant molecule is slightly deformed at packing into the spherical hydrocarbon core of the molecular aggregate and its conformation, on the average, differs from the conformation in the infinitely large hydrocarbon phase. The difference in conformations generates a positive contribution to the work of molecular aggregate formation. The corresponding so-called deformation contribution  $W_n^d$  is described in [10, 53] and, in the notation employed here, is given by

$$W_n^d = n \frac{3\pi^2}{80} \frac{r^2}{NL^2}, \quad (7.199)$$

where  $N$  is the number of rigid segments in the hydrophobic part of the surfactant molecule and  $L$  is the length of the rigid segment. Evidently, the product  $NL$  is

equal to the length  $l_C$  of the hydrophobic part of a surfactant molecule. According to Ref. 53, the rigid segment contains, on the average, 3.6 methylene groups in the case of the hydrophobic part composed of such groups, so that  $N = n_C/3.6$ . With this relation and Eq. (7.183) we obtain from Eq. (7.199) the estimate

$$W_n^d \leq 0.1nn_C . \quad (7.200)$$

Comparing Eqs. (7.198) and (7.200), we see that, at  $B \simeq 1.4$ , the  $W_n^d$  contribution gives a small correction to the hydrophobic contribution  $W_n^h$ . Thus, hereafter the contribution  $W_n^h$  is neglected [27, 28].

As was mentioned above, the hydrophobic core is actually not the infinite bulk phase with a flat interface. According to Eq. (7.192), the curvature of latter leads to the appearance of the Laplace pressure, and a contribution  $W_n^L$  to the work of transfer which is represented by the second term on the right-hand side of Eq. (7.196). Using Eqs. (7.181) and (7.182), we rewrite the integrand in the second term on the right-hand side of Eq. (7.196) as

$$\frac{2\gamma_0 v_C}{rk_B T} = \frac{8\pi\gamma_0}{3k_B T} \left[ \frac{3v(n_C + 1)}{4\pi} \right]^{2/3} \frac{1}{n^{1/3}} . \quad (7.201)$$

Only the dependence of  $\gamma_0$  on  $n$  still remains unspecified in Eq. (7.201) so far. For simplicity, we consider the surface tension  $\gamma_0$  as constant and equal to its value for the flat surface. The possible dependence of the total surface tension  $\gamma$  on the size of the molecular aggregate is further taken into account through the contribution of polar groups.

Integrating now Eq. (7.201) with respect to aggregation number  $n$  and ignoring the lower limit of integration at  $n \gg 1$ , we obtain the Laplace contribution  $W_n^L$  to the aggregation work in the form

$$W_n^L = \frac{4\pi\gamma_0}{k_B T} \left[ \frac{3v(n_C + 1)}{4\pi} \right]^{2/3} n^{2/3} . \quad (7.202)$$

Eqs. (7.202) and (7.181) indicate that this contribution is equal to the Gibbs surface energy ( $4\pi\gamma_0 r^2/k_B T$ ) of the hydrophobic core (in units of  $k_B T$ ). Introducing a positive dimensionless parameter  $b_3$  as

$$b_3 \equiv (4\pi)^{1/3} \gamma_0 [3v(n_C + 1)]^{2/3} / k_B T , \quad (7.203)$$

we may present Eq. (7.202) as

$$W_n^L = b_3 n^{2/3} . \quad (7.204)$$

Eq. (7.204) yields the inequality  $W_n^L > 0$ . Positive values of the Laplace contribution  $W_n^L$  to the work  $W_n$  impede the formation of molecular aggregates in a micellar solution.

Let us consider now the contribution  $W_n^p$  of polar groups. The forced approach of the polar groups due to the addition of the monomers into the molecular aggregate results in an interaction, whose most typical part is the mutual electrostatic repulsion of dipoles. We denote this electrical contribution to the work  $W_n$  by  $W_n^{el}$  and consider the case when the electrostatic component characterizes rather well the total interaction of polar groups:  $W_n^{el} \approx W_n^p$ . Because the molecular aggregates are formed in a solution at constant temperature and external pressure,  $W_n^{el}$  is nothing else than the Gibbs electric energy of a capacitor formed by the hydrophilic parts of the surfactant molecules in the molecular aggregate. Assuming that the capacitor formed by the hydrophilic parts of surfactant molecules in the molecular aggregate possesses spherical symmetry, we arrive in  $k_B T$  units at [7, 5]

$$W_n^{el} = \frac{(zen)^2 \delta}{8\pi k_B T \epsilon_0 \epsilon (r + \Delta l) (r + \Delta l + \delta)} . \quad (7.205)$$

Here,  $ze$  is the electric charge of a single hydrophilic part of a surfactant molecule in the dipole ( $e$  is the elementary charge);  $\delta$  is the length of the dipole of the hydrophilic part, i.e., the capacitor thickness;  $\epsilon$  is the effective permittivity of a capacitor medium;  $\epsilon_0$  is the dielectric constant; and  $\Delta l$  is the bond length connecting the hydrophobic part of a surfactant molecule with its polar hydrophilic part. We assume that the inequality  $r + \Delta l \gg \delta$  holds (which, according to Eqs. (7.181) and (7.182), is valid at  $n_C \gg 1$  and  $n \gg 1$ ). Suggesting further the inequalities  $r \gg \delta$  and  $r \gg \Delta l$  to be valid at  $n_C \gg 1$  and  $n \gg 1$ , we can rewrite Eq. (7.205) with Eqs. (7.181) and (7.182) as

$$W_n^{el} = b_1 n^{4/3} , \quad (7.206)$$

where

$$b_1 \equiv \frac{(ze)^2 \delta}{2(4\pi)^{1/3} k_B T \epsilon_0 \epsilon [3v(n_C + 1)]^{2/3}} \quad (7.207)$$

is a positive dimensionless parameter.

A positive value of the electric contribution  $W_n^{el}$  to the work  $W_n$  impedes the formation of molecular aggregates in a micellar solution. It should be mentioned that we calculated the total contribution of polar interactions from both the chemical potential and surface tension. For our purposes, there is no necessity to calculate separately the contribution of mutual repulsion of polar groups to the surface tension that results, as it is known, in a decrease of the surface tension with an increase in the micelle size. In addition to electric forces, yet more powerful forces of direct repulsion of polar groups arising at their contact, are possible under very close approach of the hydrophilic parts of surfactant molecules. Such picture is typical in the case when the molecular packing in micelles is governed by the size of polar groups. However, we focus our attention to the case when hydrocarbon chains determine the packing, and polar groups participate in the micellization only via the long-range forces of electric repulsion.

The penultimate term on the right-hand side of Eq. (7.196) can be called the concentration contribution. Combining this term with other contributions which are proportional to the aggregation number  $n$  and introducing the dimensional parameter  $b_2$ ,

$$b_2 \equiv Bn_C + \frac{a\gamma_0}{k_B T} + \ln\left(\frac{c_1}{c^\alpha}\right) = Bn_C + \frac{(4\pi)^{1/3} (3v)^{2/3} \gamma_0}{k_B T} + \ln\left(\frac{c_1}{c^\alpha}\right), \quad (7.208)$$

we rewrite the work of aggregate formation  $W_n$ , employing Eqs. (7.196), (7.198), (7.204) and (7.206) as [27]

$$W_n = b_1 n^{4/3} - b_2 n + b_3 n^{2/3}. \quad (7.209)$$

The terms in Eq. (7.209) are arranged in decreasing powers of  $n$ . Evidently Eq. (7.209) is valid at  $n \gg 1$ .

According to Eqs. (7.207), (7.208) and (7.203), the coefficients  $b_1$ ,  $b_2$  and  $b_3$  are dimensionless parameters independent of the aggregation number  $n$ . In addition, the coefficients  $b_1$  and  $b_3$  do not depend on the concentration  $c_1$  of surfactant monomers in solution. Eq. (7.209) is consistent with the expression reported in Refs. 6 and 56. However, the coefficient at  $n$  obtained in Refs. 6 and 56, does not explicitly include the dependence on the monomer concentration in the solution.



## 7.13 Critical Micelle Concentration and Thermodynamic Characteristics of Micellization

### 7.13.1 Results of Analysis of the Droplet Model

With the dependence of aggregation work  $W_n$ , given explicitly by Eq. (7.209), we are able to find all thermodynamic characteristics of micellization in the droplet model of molecular aggregates. Eq. (7.209), taking into account that the coefficients  $b_1$ ,  $b_2$ , and  $b_3$  are independent of  $n$ , yields

$$\frac{\partial W_n}{\partial n} = \frac{4}{3}b_1n^{1/3} - b_2 + \frac{2}{3}b_3n^{-1/3}, \quad \frac{\partial^2 W_n}{\partial n^2} = \frac{4}{9}b_1n^{-2/3} - \frac{2}{9}b_3n^{-4/3}. \quad (7.210)$$

With Eq. (7.210) we can derive the roots  $n = n_c$  and  $n = n_s$  of the equations

$$\left(\frac{\partial W_n}{\partial n}\right)_{n=n_c} = 0, \quad \left(\frac{\partial W_n}{\partial n}\right)_{n=n_s} = 0, \quad (7.211)$$

determining the aggregation numbers  $n_c$  and  $n_s$  of critical and stable molecular aggregates, respectively. The fact that the largest root  $n_s$  corresponds to the minimum and, respectively, the smallest root  $n_c$ , to the maximum of the work  $W_n$  follows from  $b_1 > 0$  and an asymptotic rise of the work  $W_n$  with an increase in aggregation number  $n$ . The root  $n = n_0$  of equation

$$\left(\frac{\partial^2 W_n}{\partial n^2}\right)_{n=n_0} = 0 \quad (7.212)$$

determines the inflection point  $n_0$  of the work  $W_n$ ,

$$n_0 = (b_3/2b_1)^{3/2}. \quad (7.213)$$

According to Eqs. (7.213), (7.207) and (7.203), the inflection point  $n_0$  of the work  $W_n$  does not depend on the monomer concentrations  $c_1$  in the surfactant solution. Eq. (7.213) allows one to reveal the constraint on the value of  $(b_3/2b_1)^{3/2}$ , at which  $n_0$  fits the region of aggregation numbers  $n$  that is realistic for spherical molecular aggregates.

The droplet model of the molecular aggregates reflects the existence of the potential maximum and potential well of the work  $W_n$  at a sufficiently high monomer

concentration  $c_1$  in the surfactant solution. We denote the monomer concentration in surfactant solutions, at which the potential maximum and potential well of the work  $W_n$  appear, by  $c_{10}$ . Since at  $c_1 = c_{10}$  the maximum and minimum of the work  $W_n$  merge in its inflection point  $n_0$ , Eq. (7.211) yields

$$\left(\frac{\partial W_n}{\partial n}\right)_{c_1=c_{10}, n=n_0} = 0. \quad (7.214)$$

Note that the concentration  $c_{10}$  is lower than the CMC, at which the potential well of the work  $W_n$  begins to play a significant role in the consumption of the total amount of surfactant from micellar solution.

Let us represent Eq. (7.208) as

$$b_2 = \ln\left(\frac{c_1}{c_{10}}\right) + \tilde{b}_2, \quad (7.215)$$

where  $\tilde{b}_2$  is no longer dependent on  $c_1$ . Using Eqs. (7.214), (7.213) and (7.210), we then arrive at

$$\tilde{b}_2 = \frac{4}{3}(2b_1b_3)^{1/2}, \quad (7.216)$$

which, together with Eq. (7.215), gives a dependence between the coefficient  $b_2$  and the coefficients  $b_1$  and  $b_3$  in Eq. (7.209). Finally, substituting Eqs. (7.215) and (7.216) into Eq. (7.209), we obtain

$$W_n = b_1 n^{4/3} - \left[ \ln\left(\frac{c_1}{c_{10}}\right) + \frac{4}{3}(2b_1b_3)^{1/2} \right] n + b_3 n^{2/3}. \quad (7.217)$$

Eq. (7.217) contains three parameters  $b_1$ ,  $b_3$  and  $c_{10}$  which are independent of  $n$  and  $c_1$ . The introduction of the parameter  $c_{10}$  allows us to eliminate the dependence on  $B$  and  $c^\alpha$  in Eq. (7.217). All three parameters  $b_1$ ,  $b_3$  and  $c_{10}$  have a clear physical meaning.

According to Eqs. (7.208), (7.215) and (7.216), the parameter  $c_{10}$  is related to the parameters  $B$  and  $c^\alpha$  by

$$\ln\left(\frac{c_{10}}{c^\alpha}\right) = -Bn_C - \frac{(4\pi)^{1/3}(3v)^{2/3}\gamma_0}{k_B T} + \frac{4}{3}(2b_1b_3)^{1/2}. \quad (7.218)$$

Taking into account  $c^\alpha = 1/v_C$  and Eq. (7.182), we rewrite Eq. (7.218) as

$$\ln(v c_{10}) = -B n_C - \frac{(4\pi)^{1/3} (3v)^{2/3} \gamma_0}{k_B T} - \ln(n_C + 1) + \frac{4}{3} (2b_1 b_3)^{1/2} . \quad (7.219)$$

Eqs. (7.217) and (7.211) show that the aggregation numbers of critical and stable molecular aggregates satisfy at  $c_1 > c_{10}$  the relations

$$n_c = (8b_1)^{-3} \left\{ 2^{5/2} (b_1 b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) - \sqrt{\left[ 2^{5/2} (b_1 b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) \right]^2 - 32b_1 b_3} \right\}^3 , \quad (7.220)$$

$$n_s = (8b_1)^{-3} \left\{ 2^{5/2} (b_1 b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) + \sqrt{\left[ 2^{5/2} (b_1 b_3)^{1/2} + 3 \ln \left( \frac{c_1}{c_{10}} \right) \right]^2 - 32b_1 b_3} \right\}^3 . \quad (7.221)$$

Let us calculate, now, the thermodynamic characteristics of the kinetics of micellization such as  $n_c$ ,  $n_s$ ,  $W_c$ ,  $W_s$ ,  $\Delta n_c$  and  $\Delta n_s$  in the droplet model of a surfactant spherical molecular aggregate. We use the following values of the initial parameters of the model

$$n_C = 18 , \quad \gamma_0 = 30 \frac{\text{mN}}{\text{m}} , \quad \varepsilon = 30 , \quad \delta = 3 \cdot 10^{-10} \text{ m} , \quad z = 1 , \quad T = 293 \text{ K} . \quad (7.222)$$

For the accepted value of the parameter  $n_C$  (it can be an octadecyl radical that can be completely packed into the hydrocarbon core or a fragment of a longer aliphatic hydrocarbon radical), Eq. (7.184) is reduced to  $n < 108$ . Results of calculations reported below are fairly sensitive to the values of the parameters  $\gamma_0$ ,  $\varepsilon$  and  $\delta$ .

From Eqs. (7.207), (7.203) and (7.213) with allowance for Eq. (7.222), we have

$$b_1 = 1.13 , \quad b_3 = 22.4 , \quad n_0 = 31.2 . \quad (7.223)$$

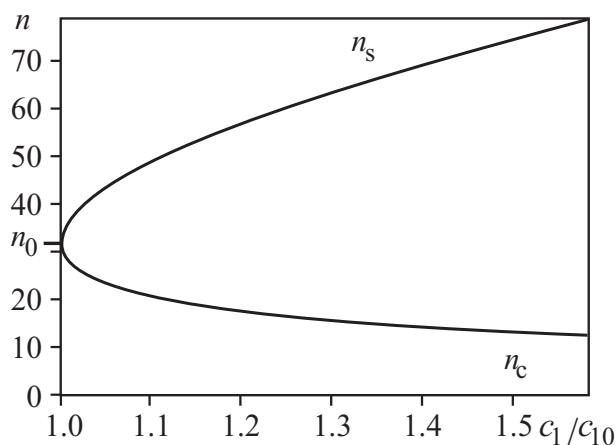


Fig. 7.2 Dependencies of  $n_c$  and  $n_s$  on the concentration ratio ( $c_1/c_{10}$ ).

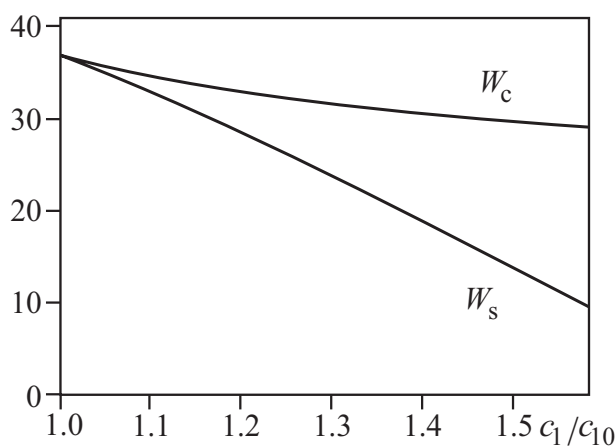


Fig. 7.3 Dependencies of  $W_c$  and  $W_s$  on the concentration ratio  $c_1/c_{10}$ .

Results of the calculation of the dependence of  $n_c$  and  $n_s$  on  $c_1/c_{10}$  obtained with Eqs. (7.220), (7.221) and (7.223) are shown in Fig. 7.2. At  $c_1/c_{10} = 1$ , the values  $n_c$  and  $n_s$  coincide and are equal to  $n_0$ . As the ratio  $c_1/c_{10}$  increases, the value  $n_c$  decreases monotonically and the value  $n_s$  increases monotonically; moreover,  $n_s$  increases faster than  $n_c$  decreases so that the curve has the form of an asymmetric loop. In this case, the constraints  $n_s < 108$  and  $n_c \gg 1$ , which are required as the conditions of the applicability of the droplet model of molecular aggregation at  $n_C = 18$ , are fulfilled to increasingly lower extent.

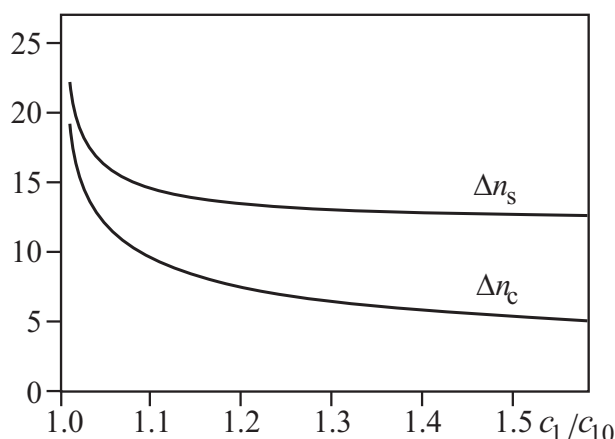


Fig. 7.4 Dependencies of  $\Delta n_c$  and  $\Delta n_s$  on the concentration ratio  $c_1/c_{10}$ .

Fig. 7.3 demonstrates the dependences of  $W_c$  and  $W_s$  on the concentration ratio  $c_1/c_{10}$  obtained using Eqs. (7.217), (7.220), (7.221) and (7.223). At  $c_1/c_{10} = 1$ , the values  $W_c$  and  $W_s$  coincide. As the ratio  $c_1/c_{10}$  increases, the values  $W_c$  and  $W_s$  decrease monotonically; moreover,  $W_c$  decreases much slower than  $W_s$ . Finally, the results of the calculations of the dependences of  $\Delta n_c$  and  $\Delta n_s$  on the ratio  $c_1/c_{10}$ , obtained using Eqs. (7.217), (7.220), (7.221), (7.33) and (7.223), are shown in Fig. 7.4. At  $c_1/c_{10} = 1$ , the values  $\Delta n_c$  and  $\Delta n_s$  tend to infinity. As the ratio  $c_1/c_{10}$  increases, the values  $\Delta n_c$  and  $\Delta n_s$  decrease monotonically; however, the inequality  $\Delta n_c < \Delta n_s$  is fulfilled (the peak of the aggregation work becomes noticeably narrower than the potential well). Figs. 7.2-7.4 agree with Fig. 7.1.

Let us consider further the CMC. The values at the CMC will be marked by a subscript  $m$ . Passing to the CMC in Eq. (7.122) for  $c_M$ , using the bimodal approximation Eq. (7.120) and the definition Eq. (7.139) of the degree of micellization  $\alpha$ , we obtain [27]

$$W_{sm} = \ln \left( \pi^{1/2} \frac{1 - \alpha_m}{\alpha_m} n_{sm} \Delta n_{sm} \right). \quad (7.224)$$

As earlier in Section 7.10, we take the critical degree of micellization as equal to  $\alpha_m \approx 0.1$ . Possible deviations of the value  $\alpha_m$  from 0.1 are slightly manifested in Eq. (7.224) due to weaker sensitivity of the logarithm to its argument.

The substitution of Eq. (7.221) into Eq. (7.217) at  $c_1 = c_{1m}$  makes it possible to express the value  $W_{sm}$  on the left-hand side of Eq. (7.224) as a known function

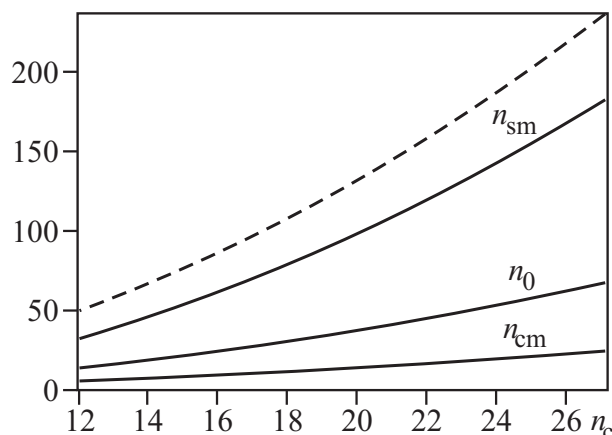


Fig. 7.5 Dependencies of  $n_{cm}$ ,  $n_0$  and  $n_{sm}$  on  $n_c$ . The dotted curve denotes the upper boundary of the values of aggregation number for the spherical model of molecular aggregate corresponding to the constraint Eq. (7.184).

of the ratio  $c_{1m}/c_{10}$ . Using Eqs. (7.220) and (7.217) and the second relation of Eq. (7.33) at  $c_1 = c_{1m}$ , we can also represent the right-hand side of Eq. (7.224) as a known function of the ratio  $c_{1m}/c_{10}$ . As a result, a transcendental equation for the determination of the ratio  $c_{1m}/c_{10}$  can be derived from Eq. (7.224) at  $\alpha_m \simeq 0.1$ . Solving this equation with Eq. (7.223), we have

$$c_{1m}/c_{10} = 1.58 . \quad (7.225)$$

Substituting Eqs. (7.225) and (7.223) into Eqs. (7.220) and (7.217) and into the second relation of Eq. (7.33), we find

$$n_{sm} = 79.0 , \quad W_{sm} = 9.67 , \quad \Delta n_{sm} = 12.6 . \quad (7.226)$$

Similarly, substituting Eqs. (7.225) and (7.223) into Eqs. (7.220) and (7.217) and into the first relation of Eq. (7.33), we obtain

$$n_{cm} = 12.3 , \quad W_{cm} = 29.1 , \quad \Delta n_{cm} = 4.97 . \quad (7.227)$$

As it is seen from Eqs. (7.226) and (7.227), the values  $n_{sm}$  and  $n_{cm}$  for the droplet model are located at the CMC in the realistic region of aggregation numbers admitted by the constraint  $n < 108$ . It is also seen that the inequality  $n_{sm} \gg$

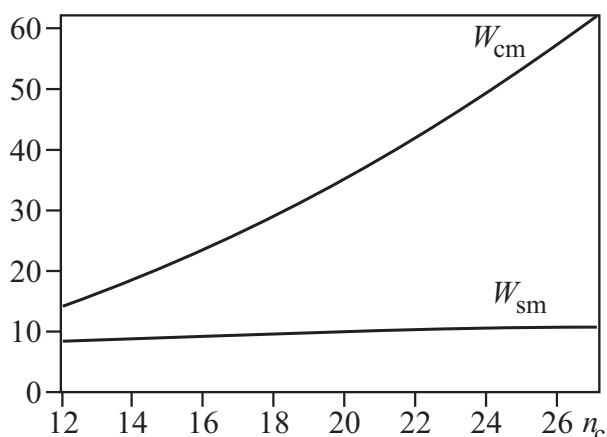


Fig. 7.6 Dependencies of  $W_{cm}$  and  $W_{sm}$  on  $n_C$ .

1 and even the inequality  $n_{cm} \gg 1$  are fulfilled, which are necessary for the applicability of the theory.

The dependence of the thermodynamic characteristics of micellization on the number  $n_C$  of hydrocarbon groups in the hydrophobic part of a surfactant molecule (the length of the hydrocarbon chain) is also important for any model of molecular aggregates. Figs. 7.5-7.7 show the behavior of the values  $n_{cm}$ ,  $n_0$  and  $n_{sm}$  as well as the values  $W_{cm}$ ,  $W_{sm}$  and  $c_{1m}/c_{10}$  as functions of  $n_C$  in the range  $12 \leq n_C \leq 27$ . Although the number  $n_C$  in Eq. (7.222) varies in this case, the other parameters in Eq. (7.222) are assumed, for definiteness, to be constant. As it is seen from Fig. 7.5, regardless of the rapid increase in the value  $n_{sm}$  with an increase in  $n_C$ , Eq. (7.184) is fulfilled at  $n = n_{sm}$  rather well. This result can be explained by a quadratic increase of the right-hand side of Eq. (7.184) with an increase in  $n_C$ .

According to the definitions Eqs. (7.207) and (7.203), the product  $b_1 b_3$  is independent of  $n_C$ . With Eqs. (7.223) and (7.219), we obtain

$$\ln(vc_{10}) = -Bn_C - \frac{(4\pi)^{1/3} (3v)^{2/3} \gamma_0}{k_B T} - \ln(n_C + 1) + 9.4. \quad (7.228)$$

Within the entire range  $12 \leq n_C \leq 27$ , the inequality  $\ln(vc_{10}) < -10$  follows from Eq. (7.228) and  $B = 1.4$ . As shown in Fig. 7.7, within the same range, the ratio  $c_{1m}/c_{10}$  is equal approximately to 1.6. We then have  $\ln(vc_{1m}) = \ln(vc_{10}) +$

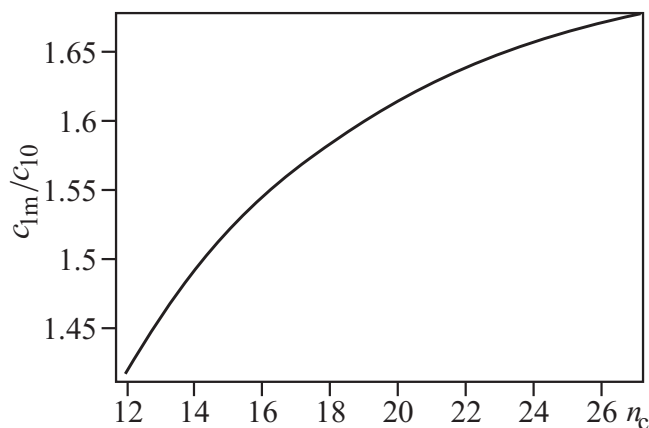


Fig. 7.7 Dependence of the concentration ratio  $c_{1m}/c_{10}$  on  $n_C$ .

$\ln(1.6)$  with a rather high accuracy. Therefore, in addition to Eq. (7.228), the relation [27]

$$\ln(vc_{1m}) = -Bn_C - \frac{(4\pi)^{1/3} (3v)^{2/3} \gamma_0}{k_B T} - \ln(n_C + 1) + 9.9 \quad (7.229)$$

is also valid. According to Eq. (7.229), the logarithm of the concentration  $c_{1m}$ , i.e., the logarithm of the CMC, decreases with an increase in  $n_C$  almost linearly at  $n_C \gg 1$ . This result is confirmed by known experimental data [6, 10, 53, 56].

### 7.13.2 The Quasi-droplet Model

As it is known from experiments [6] and the theory of the hydrophilic-hydrophobic balance [5], water molecules can partly penetrate into the depth of a micelle. In this sense, the droplet model considers the limiting version of the structure of a molecular aggregate that completely excludes water penetration into the hydrocarbon core. It is thus of interest to consider the model of a surfactant spherical molecular aggregate allowing for the maximal (in accordance with the packing rules) penetration of water molecules into the aggregate and, hence, realizing another limiting version of the structure of the hydrocarbon core. This



model is called the quasi-droplet model of surfactant molecular aggregates [29]. The formation of micelles from surfactant molecules begins with the appearance of molecular aggregates of two, three, etc. monomers. In this case, the part of the would-be micelle is occupied by water. As new surfactant molecules are added to the aggregate, water is displaced from the space between surfactant molecules in the aggregate; however, at small aggregation numbers, water can rather deeply penetrate into the molecular aggregate.

In the quasi-droplet model of molecular aggregates, shown schematically in Fig. 7.8, the hydrophobic part of each molecule constituting the aggregate is represented by two fragments. The first fragment counted from the hydrophilic part is still surrounded by water molecules. The second fragment is in the internal region of the molecular aggregate into which water molecules cannot penetrate. This region is similar to the hydrocarbon core in the droplet model of the molecular aggregate, and that explains the name "quasi-droplet model". Due to mutual repulsion of the hydrophilic parts, the first fragments of monomer hydrophobic parts are located, on the average, on the radii coming out from the aggregate center and are uniformly distributed over all directions in space. The angle  $\phi$  formed by two such radii corresponding to adjacent monomers in the aggregate is determined by the aggregation number  $n$  and, at fairly large values of  $n$ , is given by the simple formula

$$\varphi = (4\pi/n)^{1/2} \quad \text{for} \quad n \gg 1. \quad (7.230)$$

We bear here in mind that fairly large values are, in particular, such values of  $n$  which satisfy the inequality  $\varphi/2 \ll 1$  allowing to replace the function  $\sin(\varphi/2)$  by its argument. In this sense, a value  $n = 10$  is no longer small.

The radius  $r_\alpha$  of the internal (free of water molecules) region in the center of a molecular aggregate is determined by the possibility of arrangement of water molecules with the characteristic diameter  $d_{H_2O}$  between the first fragments of the hydrophobic parts of neighboring surfactant molecules in the aggregate with the characteristic cross-section diameter  $d$ . This internal region is filled with the second (in the aforementioned meaning) fragments of the hydrophobic parts of the monomers constituting the aggregate. With Eq. (7.230), we obtain

$$r_\alpha = (d + d_{H_2O})n^{1/2}/(2\pi^{1/2}), \quad (7.231)$$

where the approximation  $\sin(\varphi/2) \approx \varphi/2$  is used. We assume here, as in the droplet model, that the second fragments of the hydrophobic parts interact with

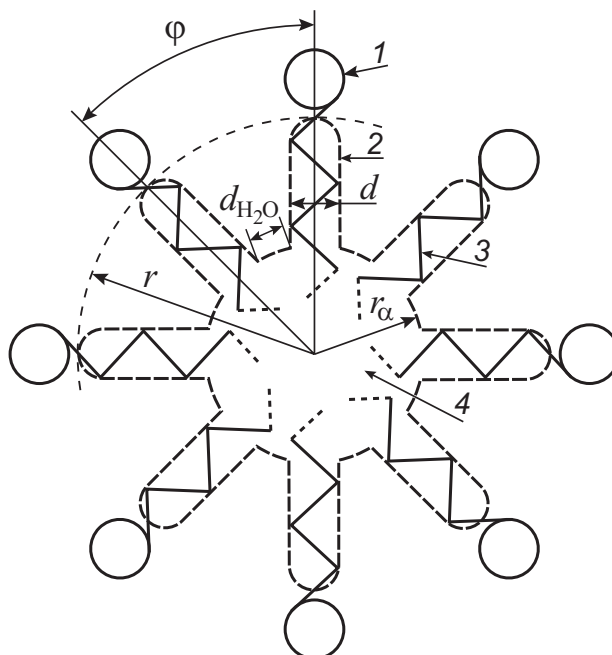


Fig. 7.8 Quasi-droplet model of molecular aggregates: (1) the hydrophilic part of a surfactant molecule, (2) the boundary of water penetration into the aggregate, (3) the hydrophobic part of a surfactant molecule, and (4) the hydrocarbon core of the molecular aggregate.

each other in such a way that they seemingly constitute the hydrocarbon phase. The internal region of molecular aggregate determined as described above we will call the hydrocarbon core similar to the case of droplet model. We use values  $d = 5.2\text{\AA}$  [5] and  $d_{H_2O} = 3.1\text{\AA}$  for the further numerical estimates.

Let us find the number  $\Delta n_C$  of hydrocarbon groups in the second fragments of the hydrophobic parts of molecules, constituting the hydrocarbon core. The volume  $\Delta v_C$  of each fragment can be represented in the form

$$\Delta v_C = v(\Delta n_C + 1) , \quad (7.232)$$

where the fact that the terminal methyl group has a characteristic volume  $v_0$

which is approximately twice as large as the volume  $v$  is taken into account. According to the packing rule, we have

$$\frac{4}{3}\pi r_\alpha^3 = n\Delta v_C . \quad (7.233)$$

Eqs. (7.232) and (7.233) result with Eq. (7.231) in

$$\Delta n_C = (d + d_{H_2O})^3 n^{1/2} / (6\pi^{1/2}v) - 1 . \quad (7.234)$$

The determination of the number  $\Delta n_C$  from Eq. (7.234) as a continuous quantity suggests that this number is already fairly large. Let us assume that this condition is fulfilled, if

$$\Delta n_C > 4 \div 5 . \quad (7.235)$$

In view of Eq. (7.234), Eq. (7.235) implies the existence of a lower bound  $n_1$ ,  $n > n_1$ , for the aggregation numbers in the quasi-droplet model. According to Eqs. (7.234) and (7.235), we obtain

$$n_1^{1/2} = (5 \div 6)6\pi^{1/2}v / (d + d_{H_2O})^3 . \quad (7.236)$$

In contrast, the condition  $\Delta n_C < n_C$  introduces the upper bound  $n_2$  of aggregation numbers permissible for the applicability of the proposed model. With Eq. (7.234), the value  $n_2$  is determined as

$$n_2^{1/2} = (n_C + 1)6\pi^{1/2}v / (d + d_{H_2O})^3 . \quad (7.237)$$

At the characteristic values of  $d$ ,  $d_{H_2O}$  and  $v$ , we have the estimate

$$6\pi^{1/2}v / (d + d_{H_2O})^3 \approx 1/2 . \quad (7.238)$$

We combine, now, the constraints on the aggregation number in the quasi-droplet model. Eqs. (7.236) - Eq. (7.238) allow to conclude that the permissible values of the aggregation number  $n$  should fit the range

$$(5 \div 6)^2 / 4 < n < (n_C + 1)^2 / 4 . \quad (7.239)$$

Note that the lower bound of  $n$  in Eq. (7.239) agrees with the constraint introduced in the note to Eq. (7.230).

Evidently, the first (surrounded by water molecules) fragments of the hydrophobic parts of surfactant molecules constituting the aggregate contain  $n_C - \Delta n_C$  hydrocarbon groups each and have the length  $(n_C - \Delta n_C)l_1$ . Adding this length to the radius  $r_\alpha$ , using Eqs. (7.231) and (7.234), we find the radius  $r$  of a sphere with the center in the middle of the molecular aggregate as

$$r = l_1(n_C + 1) + [(d + d_{\text{H}_2\text{O}})/(2\pi^{1/2}) - (d + d_{\text{H}_2\text{O}})^3 l_1 / (6\pi^{1/2} v)] n^{1/2}. \quad (7.240)$$

The hydrophobic parts of surfactant molecules enter this sphere completely. According to Eq. (7.235), we have  $r - r_\alpha \geq 0$ . Introducing the notation

$$\alpha_{qd} = [(d + d_{\text{H}_2\text{O}})/(2\pi^{1/2}) - (d + d_{\text{H}_2\text{O}})^3 l_1 / (6\pi^{1/2} v)] [l_1(n_C + 1)]^{-1}, \quad (7.241)$$

we rewrite Eq. (7.240) as

$$r = l_1(n_C + 1) \left(1 + \alpha_{qd} n^{1/2}\right). \quad (7.242)$$

Substituting the numerical values of the parameters into Eq. (7.241), we arrive at the estimate

$$\alpha_{qd} \approx -0.15/(n_C + 1). \quad (7.243)$$

With Eq. (7.239), this estimate demonstrates that the term  $\alpha_{qd} n^{1/2}$  in the second round brackets on the right-hand side of Eq. (7.242) is bounded in its absolute value as

$$\left|\alpha_{qd} n^{1/2}\right| \lesssim 0.08. \quad (7.244)$$

Note that, according to Eqs. (7.240) or (7.242), the radius  $r$  decreases with an increase in the aggregation number  $n$  due to the negative value of the parameter  $\alpha_{qd}$ . Nevertheless, the radius  $r$  is larger than the radius of the hydrocarbon core in the droplet model of surfactant molecular aggregates at each  $n$  satisfying Eq. (7.239). Eqs. (7.230), (7.231) and (7.242) determine the geometric parameters of the molecular aggregates in the quasi-droplet model. Let us assume that the molecular aggregate is in a mechanical equilibrium at these parameters.

Taking into account the fairly small number of molecules in the molecular aggregates that are of interest to us, their geometric and thermodynamic characteristics in the quasi-droplet model undergo noticeable changes on adding a new molecule to the aggregate. In particular, the hypothetical condensed phase for the

substance constituting the hydrocarbon core of the molecular aggregate consists only of the second (in the meaning indicated at the beginning of this section) fragment of hydrocarbon chains of surfactant molecules. The characteristics of such a phase are changed as the length of these fragments varies with aggregation numbers.

In any phase, the molecular chemical potential is given by the standard expression Eq. (7.187). If the phase characteristics of the molecular aggregate do not change with the attachment of a surfactant monomer, then Eq. (7.191) would follow from Eq. (7.187) allowing to determine the difference in the monomer chemical potentials in the aggregate and in the solution. We need just to take into account that, during this process, only the second fragment of the hydrophobic part of a molecule is transferred from the solution to the hydrocarbon core of the molecular aggregate.

If the surface of the hydrocarbon core is flat and the hydrophobic part of a surfactant molecule is completely transferred to the core, then the work of transfer of a single hydrophobic part from water to the bulk of the hydrocarbon phase would be equal to the value known from experiments. This value is a linear function of the number of carbon atoms constituting the hydrocarbon part with the coefficient of linear dependence  $-B$ , the positive dimensionless parameter of hydrophobic interaction, determined earlier. Since, in the quasi-droplet model, only the second fragment of the hydrophobic part of a surfactant molecule enters into the hydrocarbon core composed of  $\Delta n_C$  hydrocarbon groups, the relevant transfer work  $w^{\beta\alpha}$  can be evidently represented as

$$w^{\beta\alpha} = -B\Delta n_C . \quad (7.245)$$

With Eq. (7.234), we can write Eq. (7.245) also in the form

$$w^{\beta\alpha} = -a_3 n^{1/2} + B , \quad (7.246)$$

where

$$a_3 \equiv B (d + d_{H_2O})^3 / (6\pi^{1/2}v) . \quad (7.247)$$

The surface of a hydrocarbon core is curved and is characterized by the surface tension  $\gamma_0$ ; therefore, the work of surfactant molecule transfer from the solution to the molecular aggregate contains a contribution  $w_L$  expressing the work required to overcome the Laplace pressure difference on this surface (the surface of polar groups will be accounted for separately). For a spherical surface (with a radius

$r_\alpha$ ) of the hydrocarbon core composed of molecular fragments with a volume  $\Delta v_C$ , this contribution is (instead of the third term on the right-hand side of Eq. (7.193)) given by

$$w_L = \left( \frac{2\gamma_0}{r_\alpha k_B T} \right) \Delta v_C . \quad (7.248)$$

Substitution of Eqs. (7.231) and (7.232) for  $r_\alpha$  and  $\Delta v_C$  into Eq. (7.248) with account of Eq. (7.234) yields

$$w_L = \left( \frac{2\gamma_0}{3k_B T} \right) (d + d_{H_2O})^2 . \quad (7.249)$$

In addition, one should take into account that the surfactant molecule is not transferred as a whole into the bulk of the hydrocarbon phase but remains in a position when it intersects the aggregate dividing surface (to which the surface tension is referred) with the cross section  $a$ . Therefore, the monomer chemical potential in the aggregate contains also, as well as in the droplet model, the additional surface contribution  $(-\gamma_0 a_0 / k_B T)$ .

During the transfer of a surfactant molecule to the molecular aggregate, polar groups remain in the solvent medium; however, they approach each other and form the electrical double layer. The corresponding electrostatic contribution  $w_{el}$  can be estimated, as in the case of the droplet model, with the aid of the model of a spherical capacitor. We take advantage here of Eq. (7.205) for the electrostatic contribution  $W_n^{el}$ . According to Eq. (7.185), we can calculate the electrostatic contribution  $w_{el}$  by differentiating Eq. (7.205) with respect to aggregation number  $n$  and using Eq. (7.242) for the radius  $r$  of the surface confining the hydrocarbon parts of surfactant molecules in the quasi-droplet model of molecular aggregates. When writing the result and utilizing the inequalities  $r \gg \delta$  and  $r \gg \Delta l$  at  $n_C \gg 1$  and  $n \gg 1$ , we ignore the second-order terms due to the small (because of the constraint Eq. (7.244)) value of  $\alpha_{qd} n^{1/2}$ . With Eq. (7.242), we find

$$w_{el} = 2a_1 n \left[ 1 - \frac{5}{2} \alpha_{qd} n^{1/2} \right] , \quad (7.250)$$

where

$$a_1 \equiv \frac{(ez)^2 \delta}{8\pi\epsilon_0 \epsilon [l_1 (n_C + 1)]^2 k_B T} . \quad (7.251)$$

According to above given derivation, the contribution  $w_{el}$  takes into account the change in the characteristics of the molecular aggregate (more specific, its radius  $r$ ) on the attachment of new molecules to the aggregate. Let us take now into account the contributions  $w^{\beta\alpha}$  and  $w_L$ , as well as the concentration contribution  $w_{conc} = \ln(c_{1n}/c_1)$  given by the last term on the right-hand side of Eq. (7.193).

The chemical potentials of a surfactant monomer in an aggregate and the relevant contributions caused by the change in the characteristics of molecular aggregates we will specify with an accent. It follows from above considerations that

$$w'_{el} = w_{el} . \quad (7.252)$$

As it is seen from Eq. (7.234), when the next molecule is attached, the number  $\Delta n_C$  of hydrocarbon groups (entering into the aggregate core) of the hydrophobic part of each molecule constituting the aggregate increases. According to Eq. (7.232), the volume  $\Delta v_C$  (the volume of the fragments of the hydrophobic parts of surfactant molecules forming the hydrocarbon core) also increases. The increase in the number  $\Delta n_C$  gives rise to the energy gain from the transfer of the corresponding fragment of the hydrophobic part of surfactant molecules to the hydrocarbon core of the aggregate. Extending Eq. (7.245), we can write

$$w'^{\beta\alpha} = -B \left( \Delta n_C + n \frac{\partial \Delta n_C}{\partial n} \right) . \quad (7.253)$$

The factor  $n$  in front of the derivative with respect to  $n$  suggests that all  $n$  molecules in the molecular aggregate participate in the formation of the chemical potential in this aggregate. From Eq. (7.253) with Eqs. (7.234) and (7.247), we obtain

$$w'^{\beta\alpha} = -\frac{3}{2} a_3 n^{1/2} + B . \quad (7.254)$$

According to Eq. (7.197), the contribution  $w^{\beta\alpha}$  in the droplet model is independent of the aggregation number of the molecular aggregate; however, the similar contribution  $w'^{\beta\alpha}$  in the quasi-droplet model increases in its absolute value with  $n$  according to Eq. (7.254). In this case, it can be shown that the contribution Eq. (7.254) is smaller in its absolute value as compared with the similar contribution for the droplet model in the lower part of the range of permissible values of aggregation numbers determined by Eqs. (7.239); in contrast, it is larger in the upper part.

During the attachment of a new molecule to the aggregate, an increase in volume  $\Delta v_C$  of all second fragments of the hydrophobic parts of molecules constituting the hydrocarbon core of the aggregate tends to increase the work required for overcoming the Laplace pressure difference on the surface of the hydrocarbon core. We determine the contribution  $w'_L$ , that takes into account this effect, by

$$w'_L = \frac{2\gamma_0}{r_\alpha k_B T} \left( \Delta v_C + n \frac{\partial \Delta v_C}{\partial n} \right) \quad (7.255)$$

generalizing Eq. (7.248). Hence, combining Eqs. (7.231), (7.232) and (7.234), we arrive at

$$w'_L = \frac{\gamma_0}{k_B T} (d + d_{H_2O})^2 . \quad (7.256)$$

Eq. (7.256) shows that the contribution  $w'_L$  is independent of aggregation number. This circumstance distinguishes the quasi-droplet model from the droplet model where a similar contribution is inversely proportional to the cubic root of  $n$ .

The molecular concentration  $c^\alpha$  in the contribution  $w_{conc}$  is estimated in the case of the quasi-droplet model as the concentration of the second fragments of the hydrophobic parts of surfactant molecules constituting the hydrocarbon core of the molecular aggregate. According to Eqs. (7.232) and (7.234), at the suggested dense core packing, the concentration  $c^\alpha$  is then estimated by the relation

$$c^\alpha = [v_1 (\Delta n_C + 1)]^{-1} = \frac{6\pi^{1/2}}{n^{1/2}(d + d_{H_2O})^3} . \quad (7.257)$$

The dependence of the concentration  $c^\alpha$  on the aggregation number  $n$  (that was absent in the droplet model) requires the refinement of the contribution  $w_{conc}$ . Performing this refinement, using Eq. (7.257) and acting by analogy with Eqs. (7.253) and (7.255), we obtain

$$w'_{conc} = \ln \left( \frac{c^\alpha}{c_1} \right) + n \frac{\partial \ln(c^\alpha/c_1)}{\partial n} = \ln \left[ \frac{6\pi^{1/2}}{c_1 n^{1/2}(d + d_{H_2O})^3} \right] - \frac{1}{2} . \quad (7.258)$$

For dilute solutions, the ratio  $c^\alpha/c_1$  is fairly large ( $\sim 10^5$ ). Although Eq. (7.257) for  $c^\alpha$  is a rough estimate, these values lead to practically exact expressions for  $\ln(c^\alpha/c_1)$ , which have been actually used in Eq. (7.258).



Similarly to Eq. (7.193), we can represent the desired chemical potential  $\bar{\mu}'_{1n}$  of surfactant molecules in the molecular aggregate in the quasi-droplet model as

$$\bar{\mu}'_{1n} = \bar{\mu}_1 - w'^{\beta\alpha} + w'_L - \frac{\gamma_0 a}{k_B T} + w'_{el} + w'_{conc}. \quad (7.259)$$

Substituting Eq. (7.259) into Eq. (7.186) and taking into account Eqs. (7.250), (7.252), (7.254), (7.256) and (7.258), we can write the expression for the aggregation work  $W_n$  in the case of the quasi-droplet model at  $n \gg 1$  as [29]

$$W_n = -a_3 n^{3/2} + a_1 n^2 \left(1 - 2\alpha_{qd} n^{1/2}\right) - \frac{1}{2} n \ln n + \left\{ B + \left(\frac{\gamma_0}{k_B T}\right) \left[(d + d_{H_2O})^2 - a\right] - \ln \left[\frac{c_1 (d + d_{H_2O})^3}{6\pi^{1/2}}\right] \right\} n. \quad (7.260)$$

According to Eq. (7.260), there is a point  $n = n_0$  of inflection of the work  $W_n$  in the case of the quasi-droplet model. This point is independent of the concentration of the solution and satisfies Eq. (7.212) with substitution of Eq. (7.260). There is also a monomer concentration  $c_{10}$  that satisfies Eq. (7.214) with substitution of Eq. (7.260). The work  $W_n$  rises monotonically with  $n$  at  $c_1 < c_{10}$ . This result leads to the absence of relatively stable aggregates in the solutions at such surfactant concentrations. At  $c_1 > c_{10}$ , the work  $W_n$  is characterized by a local maximum at  $n_c$  and a local minimum at  $n_s$  corresponding to micelles. As  $c_1$  increases, the points  $n_c$  and  $n_s$  move correspondingly to the left and right from the inflection point  $n_0$ . Thus, the qualitative behavior of the aggregation work  $W_n$  in the case of the quasi-droplet model is similar to that in the droplet model.

Let us consider an approximation for the work  $W_n$  allowing for an analytical study. For such purposes, we omit in Eq. (7.260), according to Eq. (7.244), the terms proportional to the parameter  $\alpha_{qd}$  and set  $\ln n = \ln n_0$  (assuming that the relative deviations of  $n$  from  $n_0$  are not so large in the near-critical and micellar regions of aggregation numbers). Then we can rewrite Eq. (7.260) as

$$W_n = -a_3 n^{3/2} + a_1 n^2 + \left(\frac{9a_3^2}{32a_1} - \ln \frac{c_1}{c_{10}}\right) n, \quad (7.261)$$

where Eqs. (7.260), (7.212) and (7.214) yield

$$n_0 = (3a_3/8a_1)^2, \quad (7.262)$$

$$\ln \frac{c_{10} (d + d_{\text{H}_2\text{O}})^3}{6\pi^{1/2}} = -\frac{9}{32} \frac{a_3^2}{a_1} + B \quad (7.263)$$

$$+ \frac{\gamma_0 \left[ (d + d_{\text{H}_2\text{O}})^2 - a \right]}{k_B T} - \ln \frac{3a_3}{8a_1}.$$

Note in conclusion that the significant formal difference in the dependence of the work  $W_n$  on the aggregation number  $n$  according to Eq. (7.261) for the quasi-droplet model and according to Eq. (7.217) for the droplet model is in fact that the work  $W_n$  is represented in Eq. (7.217) as the expansion in powers of the cubic root of  $n$ , whereas in Eq. (7.261) the expansion is performed in powers of the quadratic root of  $n$ . Latter result can be considered as a reflection of an almost two-dimensional structure of the surfactant molecular aggregate in the quasi-droplet model with a structure similar to the rolled surfactant monolayer. A comparison of the predictions of both models in application to experimental data should demonstrate which of these models and in which cases more fully accounts for the properties of real micellar solutions.

### 7.13.3 Comparison of Droplet and Quasi-droplet Models

We have seen in the preceding sections that both the droplet and the quasi-droplet models of molecular aggregates result in different (albeit qualitatively similar) dependencies of the aggregation work on the aggregation number and the concentration of surfactant monomers. At the same time, simplified assumptions concerning both the structure of the molecular aggregates and the way how the basic interactions of the surfactant molecules constituting the aggregate are taken into account introduce some uncertainty into the quantitative data obtained by using these models. It seems natural to interpret this uncertainty as the result of the insufficiently correct determination of the initial parameters of the models of the aggregates. The predictive power of the models can be increased by introducing representative experimental characteristics of micellization, provided that formulas linking the initial parameters of the models with the observable values are understood as rigorous relations.

By now, relatively reliable experimental data on the position of the potential well of the work of surfactant molecular aggregate formation on the aggregation number axis (on the mean micelle size,  $n_s$ ), as well as on the half-width of this well (the average statistical scattering of micelle sizes,  $\Delta n_s$ ) are available in literature for various micellar solutions. These data can be refined in the course of further

experimental study of the equilibrium distribution with respect to the micelle aggregation numbers. Note that the value  $\Delta n_s$  can experimentally be found by measuring the time  $t_1$  of fast relaxation of the micellar solution.

According to their physical meaning, the initial parameters of the droplet and quasi-droplet models of molecular aggregates (represented by the coefficients in Eqs. (7.217) and (7.261)) cannot be determined directly from experiment or by molecular simulations. At the high sensitivity of the thermodynamic characteristics of micellization to these parameters, it is more convenient to initially take into account in the theory the position and half-width of the potential well of aggregation work. As a result, this procedure allows us to relate the theory to experiment, moreover, in application to specific micellar solutions. Therefore the main aim of this section is to demonstrate how, knowing the experimental position and half-width of the potential well of the aggregation work, one can find all other thermodynamic characteristics of micellization, in particular, those referring to molecular aggregates in the pre-micellar (pre-critical and near-critical) regions of their sizes and which are not easily accessible in experiment. We will follow here the approach proposed in Ref. 22. Another approach based on deriving and solving the differential equations for the initial parameters of the model aggregation work was considered in Ref. 58.

It follows from Figs. 7.2 and 7.4 that the values  $n_s$  and  $\Delta n_s$  undergo in the droplet model only relatively small changes with concentration  $c_1$ , beginning with the CMC where the surfactant starts to be accumulated in micelles and ending with the concentrations at which almost the whole surfactant is accumulated in micelles. As we will see below, the same is true in the quasi-droplet model. Along with that, taking into account Eq. (7.128) and  $n_s \gg 1$ , the function  $\exp(-W_s)$  rapidly increases as  $c_1$  increases from  $c_{1m}$  at the CMC. This property makes the concentrations  $c_n^{(e)}$  in Eq. (7.45) to be sensitive to the values  $n_s$  and  $\Delta n_s$ , thereby decreasing the error of experimental determination of these values via Eq. (7.45). The total concentration  $c_M$  of micelles in the micellar region is determined at solution equilibrium by Eq. (7.122). Dropping the sign  $\sim$  and neglecting the weak dependence of the half-width  $\Delta n_s$  on  $c_1$ , we get from Eqs. (7.122) and (7.128) the useful relation  $\partial \ln c_M / \partial c_1 = n_s / c_1$ , which makes it possible to determine experimentally the value  $n_s$ , provided that the dependence of  $c_M$  on  $c_1$  is known. Eq. (7.224) relates the value  $W_{sm}$  of the aggregation work at CMC, i.e. at  $c_1 = c_{1m}$ , with the value  $n_{sm}$  of the aggregation number, the value  $\Delta n_{sm}$  of the average statistical scattering of micelle sizes and the value  $\alpha_m$  of the degree of micellization at  $c_1 = c_{1m}$ . The critical degree of micellization  $\alpha_m$  is estimated as  $\alpha_m \approx 0.1$ . Then, according to Eq. (7.139), we have  $n_{sm} c_{Mm} / c_{1m} \approx 1/9$  so that the relative

amount of substance in the micelles at the CMC is still small, although it is already noticeable. In order to increase the ratio  $n_s c_M / c_1$  approximately tenfold and, hence the relative amount of surfactant in micelles to exceed unity, we need to increase the concentration  $c_1$  from  $c_{1m}$  by the value  $\Delta c_1$  small compared with  $c_{1m}$ . Eqs. (7.122) and (7.128) result in  $\Delta c_1 / c_{1m} \approx \ln(10) / (n_{sm} - 1)$ . Note that, as we will see below, the value  $\Delta c_1$  turns out also to be small as compared with the increase of  $c_{1m} - c_{10}$  at the concentration  $c_1$  required to achieve the CMC after the appearance of the potential barrier and the potential well of the work  $W_n$ . This result supports the correctness of the approximate value  $\alpha_m \approx 0.1$  of the critical degree of micellization accepted and the corresponding approximate value of CMC. Possible small deviations of the value  $\alpha_m$  from  $\alpha_m \approx 0.1$  can be only slightly manifested in Eq. (7.224) due to the low sensitivity of the logarithm in Eq. (7.224) to its argument at  $n_{sm} \Delta n_{sm} \gg 1$ .

Let us go over now to an analysis of other thermodynamic characteristics of micellization at the CMC which may depend on the choice of the specific model of the molecular aggregates. We start with the droplet model. The second relations in Eqs. (7.211) and (7.33) at  $c_1 = c_{1m}$ ,  $n_s = n_{sm}$ ,  $\Delta n_s = \Delta n_{sm}$ , Eqs. (7.224), (7.217) and the definition  $W_{sm} \equiv W_n|_{c_1=c_{1m}, n=n_{sm}}$  give three transcendental equations that allow us to analytically express three parameters  $b_1$ ,  $b_3$  and  $\ln(c_{1m}/c_{10})$  via  $n_{sm}$ ,  $\Delta n_{sm}$  and  $\alpha_m$ . Solving these equations, we obtain

$$b_1 = \frac{9n_{sm}^{2/3}}{(\Delta n_{sm})^2} (1 + \epsilon) , \quad b_3 = \frac{9n_{sm}^{4/3}}{(\Delta n_{sm})^2} (1 + 2\epsilon) , \quad (7.264)$$

$$\ln\left(\frac{c_{1m}}{c_{10}}\right) = \frac{1.1n_{sm}}{(\Delta n_{sm})^2} (1 - 1.3\epsilon) , \quad (7.265)$$

where the quantity  $\epsilon$  depends on  $n_{sm}$ ,  $\Delta n_{sm}$ , and  $\alpha_m$  and is determined by

$$\epsilon = \frac{1}{3} \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2 \ln \left( \pi^{1/2} \frac{1 - \alpha_m}{\alpha_m} n_{sm} \Delta n_{sm} \right) . \quad (7.266)$$

At  $\alpha_m \approx 0.1$  and typical (by the order of magnitude) estimates  $n_{sm} \sim 10^2$  and  $\Delta n_{sm} \sim 10$ , we get from Eq. (7.266) the result  $\epsilon \sim 0.03$  so that the value of  $\epsilon$  can be considered as small as compared with one. Therefore we keep only the principal (linear with respect to  $\epsilon$ ) correction, ignoring quadratic and higher-order corrections with respect to  $\epsilon$ . We emphasize that the existence of a fairly

small parameter  $(\Delta n_{sm}/n_{sm})^2$  is responsible for the strong inequality  $\epsilon \ll 1$ . Note that Eqs. (7.264) are not restricted in its validity by the constraint  $\epsilon \ll 1$ .

Employing Eqs. (7.217) and (7.264)-(7.265), we find the analytical dependence of the values  $n_{cm}$ ,  $\Delta n_{cm}$  and  $W_{cm}$  on  $n_{sm}$ ,  $\Delta n_{sm}$  and  $\alpha_m$ . Taking into account only the first equations in Eqs. (7.211) and (7.33) at  $c_1 = c_{1m}$ ,  $n_c = n_{cm}$ ,  $\Delta n_c = \Delta n_{cm}$ , as well as the definition  $W_{cm} \equiv W_n|_{c_1=c_{1m}, n=n_{cm}}$ , we arrive at

$$\begin{aligned} n_{cm} &= \frac{n_{sm}}{8} (1 + 3\epsilon) , & \Delta n_{cm} &= \frac{\Delta n_{sm}}{2^{3/2}} \left(1 + \frac{3}{2}\epsilon\right) , \\ W_{cm} &= \frac{9}{16} \left(\frac{n_{sm}}{\Delta n_{sm}}\right)^2 \left(1 + \frac{11}{3}\epsilon\right) . \end{aligned} \quad (7.267)$$

Eqs. (7.224) and (7.265)-(7.267) express thermodynamic characteristics of micellization at the CMC via  $n_{sm}$ ,  $\Delta n_{sm}$  and  $\alpha_m$  in the droplet model of molecular aggregates. Eq. (7.265), together with Eq. (7.219) for the concentration  $c_{10}$ , allows us to find the experimentally measurable CMC.

According to Eqs. (7.267), the inequalities  $\Delta n_{cm} < \Delta n_{sm}$  and  $\Delta n_{cm}/n_{cm} > \Delta n_{sm}/n_{sm}$  are valid. Hence, the scattering of aggregation numbers in the region of the potential barrier of work  $W_n$  is smaller than that of aggregation numbers in the region of the potential well of the work  $W_n$ . However, the relative scattering of the aggregation numbers in the region of the potential barrier is larger than that of the aggregation numbers in the region of the potential well.

Let us illustrate the preceding statements by simple numerical calculations. For comparison, we cover two typical cases with  $n_{sm} = 100$ ,  $\Delta n_{sm} = 15$  and  $\Delta n_{sm} = 20$  (for simplicity, we vary only  $\Delta n_{sm}$  out of two parameters,  $n_{sm}$  and  $\Delta n_{sm}$ ). From Eqs. (7.224) and (7.264)-(7.266), at  $\alpha_m \approx 0.1$ ,  $n_{sm} = 100$  and  $\Delta n_{sm} = 15$  we can easily find

$$W_{sm} = 10.1 , \quad b_1 = 0.926 , \quad b_3 = 21.4 , \quad \frac{c_{1m}}{c_{10}} = 1.61 , \quad (7.268)$$

and for  $n_{sm} = 100$  and  $\Delta n_{sm} = 20$

$$W_{sm} = 10.4 , \quad b_1 = 0.552 , \quad b_3 = 13.3 , \quad \frac{c_{1m}}{c_{10}} = 1.30 . \quad (7.269)$$

Further, from Eqs. (7.266)-(7.267) at  $\alpha_m \approx 0.1$ ,  $n_{sm} = 100$  and  $\Delta n_{sm} = 15$ , we can easily obtain

$$n_{cm} = 15.3 , \quad \Delta n_{cm} = 5.90 , \quad W_{cm} = 31.9 , \quad (7.270)$$

and for  $n_{sm} = 100$  and  $\Delta n_{sm} = 20$

$$n_{cm} = 17.7, \quad \Delta n_{cm} = 8.54, \quad W_{cm} = 21.2. \quad (7.271)$$

Let us now recover the dependence (at the CMC) of the thermodynamic characteristics of micellization on the initial parameters  $b_1$  and  $b_3$  of the droplet model of molecular aggregates. Now it can be easily done, expressing in Eqs. (7.264) and (7.266) the parameters  $n_{sm}$  and  $\Delta n_{sm}$  by perturbation theory at  $\epsilon \ll 1$  via the initial parameters  $b_1$  and  $b_3$ . As a result we obtain

$$n_{sm} = \left(\frac{b_3}{b_1}\right)^{3/2} \left(1 - \frac{3}{2}\epsilon\right), \quad \Delta n_{sm} = \frac{3b_3^{1/2}}{b_1}, \quad (7.272)$$

$$\epsilon = \frac{3b_1}{b_3^2} \ln \left(3\pi^{1/2} \frac{1 - \alpha_m}{\alpha_m} \frac{b_3^2}{b_1^{5/2}}\right). \quad (7.273)$$

The high sensitivity of the parameter  $n_{sm}$  and a lower sensitivity of the parameter  $\Delta n_{sm}$  to the values of the parameters  $b_1$  and  $b_3$  are evident. In order for Eqs. (7.272) to secure realistic estimates of  $n_{sm} \sim 10^2$  and  $\Delta n_{sm} \sim 10$ , and correspondingly, in order for Eq. (7.273) to secure the inequality  $\epsilon \ll 1$ , the values of the initial parameters  $b_1$  and  $b_3$  of the droplet model should satisfy rather severe constraints. Eqs. (7.272)-(7.273), with Eqs. (7.224), (7.265) and (7.267), determine in an analytical form the desired dependence (at the CMC) of all thermodynamic characteristics of micellization on the parameters  $b_1$  and  $b_3$  of the droplet model of molecular aggregates. In particular, the approximations for the values  $n_{sm}$  and  $n_{cm}$ ,

$$n_{sm} \approx \left(\frac{b_3}{b_1}\right)^{3/2}, \quad n_{cm} \approx \frac{1}{8} \left(\frac{b_3}{b_1}\right)^{3/2} \quad (7.274)$$

follow from Eqs. (7.272) and (7.267) when correction terms containing the small parameter  $\epsilon$  are ignored. From Eqs. (7.213) and (7.274), we have  $n_{cm}/n_0 \approx 1/2^{3/2}$  and  $n_{sm}/n_0 \approx 2^{3/2}$ . These relations indicate that the relative positions of maximum, inflection point and minimum of work  $W_n$  on the aggregation number axis are independent of the parameters  $b_1$  and  $b_3$  in the droplet model of molecular aggregates.

Let us turn, now, to the quasi-droplet model of molecular aggregates. The second equations in Eqs. (7.211) and (7.33) at  $c_1 = c_{1m}$ ,  $n_s = n_{sm}$ ,  $\Delta n_s = \Delta n_{sm}$ ,

Eqs. (7.224) and (7.261) and the definition  $W_{sm} \equiv W_n|_{c_1=c_{1m}, n=n_{sm}}$  give again three transcendental equations that allow us to analytically express the three parameters  $a_1$ ,  $a_3$  and  $\ln(c_{1m}/c_{10})$  via  $n_{sm}$ ,  $\Delta n_{sm}$  and  $\alpha_m$ . Solving these equations, we obtain

$$a_1 = \frac{4}{(\Delta n_{sm})^2} (1 + \epsilon) , \quad a_3 = \frac{8n_{sm}^{1/2}}{(\Delta n_{sm})^2} \left( 1 + \frac{4}{3} \epsilon \right) , \quad (7.275)$$

$$\ln \frac{c_{1m}}{c_{10}} = \frac{1}{2} \frac{n_{sm}}{(\Delta n_{sm})^2} (1 - \epsilon) , \quad (7.276)$$

where the quantity  $\epsilon$  depends on  $n_{sm}$ ,  $\Delta n_{sm}$ , and  $\alpha_m$  and is given by

$$\epsilon = \frac{3}{4} \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2 \ln \left( \pi^{1/2} \frac{1 - \alpha_m}{\alpha_m} n_{sm} \Delta n_{sm} \right) . \quad (7.277)$$

At  $\alpha_m \approx 0.1$  and typical (by the order of magnitude) estimates  $n_{sm} \sim 10^2$  and  $\Delta n_{sm} \sim 10$ , we have from Eq. (7.277) the result  $\epsilon \sim 0.07$ . Thus the value of  $\epsilon$  can be considered as small as compared with one also in the quasi-droplet model. This result allows us to keep only the principal (linear with respect to  $\epsilon$ ) correction, ignoring quadratic and higher-order corrections with respect to  $\epsilon$ . Similarly to the droplet model, the existence of a fairly small parameter  $(\Delta n_{sm}/n_{sm})^2$  is responsible for the strong inequality  $\epsilon \ll 1$ . Note that Eqs. (7.275) are not restricted in its validity to the constraint  $\epsilon \ll 1$ .

Using Eqs. (7.261) and (7.275)-(7.276), we find the analytical dependence of the values  $n_{cm}$ ,  $\Delta n_{cm}$ , and  $W_{cm}$  on  $n_{sm}$ ,  $\Delta n_{sm}$  and  $\alpha_m$ . Taking into account only the first equations in Eqs. (7.211) and (7.33) at  $c_1 = c_{1m}$ ,  $n_c = n_{cm}$ ,  $\Delta n_c = \Delta n_{cm}$ , as well as the definition  $W_{cm} \equiv W_n|_{c_1=c_{1m}, n=n_{cm}}$ , we arrive at

$$n_{cm} = \frac{n_{sm}}{4} (1 + 2\epsilon) , \quad \Delta n_{cm} = \frac{\Delta n_{sm}}{2^{1/2}} \left( 1 + \frac{1}{2} \epsilon \right) , \quad (7.278)$$

$$W_{cm} = \frac{1}{4} \left( \frac{n_{sm}}{\Delta n_{sm}} \right)^2 \left( 1 + \frac{11}{3} \epsilon \right) . \quad (7.279)$$

Eqs. (7.224), (7.276)-(7.279) express the thermodynamic characteristics of micellization at the CMC via  $n_{sm}$ ,  $\Delta n_{sm}$  and  $\alpha_m$  in the quasi-droplet model of

molecular aggregates. Eq. (7.276), together with Eq. (7.263) for the concentration  $c_{10}$ , allows us to find the experimentally measurable CMC.

Let us perform a comparison of the droplet and quasi-droplet models. According to Eqs. (7.278), the inequalities  $\Delta n_{cm} < \Delta n_{sm}$  and  $\Delta n_{cm}/n_{cm} > \Delta n_{sm}/n_{sm}$  are still valid in the quasi-droplet model. According to Eq. (7.279), a fairly strong dependence of the value  $W_{cm}$  on the large parameter  $(n_{sm}/\Delta n_{sm})^2$  still exists. However, as it is now seen from a comparison of Eqs. (7.279) and (7.267), this dependence is approximately by 9/4 times weaker than in the droplet model of molecular aggregates. Correspondingly, the extremely strong dependence of  $\exp(W_{cm})$  on the large parameter  $(n_{sm}/\Delta n_{sm})^2$  becomes now weaker approximately by  $\exp\left[(5/16)(n_{sm}/\Delta n_{sm})^2\right]$  times. Because  $\exp(W_{cm})$  determines the time of slow relaxation of the micellar solution, it can be expected that, for micellar solutions where this time is not so long and, hence,  $\exp(W_{cm})$  is not very large, the quasi-droplet model of molecular aggregates provides the estimate  $\exp(W_{cm}) \sim \exp\left[(1/4)(n_{sm}/\Delta n_{sm})^2\right]$  which seems to be preferable. On the contrary, for micellar solutions where this time is very large and, hence,  $\exp(W_{cm})$  is also very large, the droplet model of molecular aggregates provides the estimate  $\exp(W_{cm}) \sim \exp\left[(9/16)(n_{sm}/\Delta n_{sm})^2\right]$  which seems to be preferable in this alternative case. Note also that, in the quasi-droplet model at the same values  $n_{sm}$  and  $\Delta n_{sm}$ , the values  $n_{cm}$  and  $\Delta n_{cm}$  will be approximately twice as large (as is seen from a comparison of Eqs. (7.278) with Eqs. (7.267)) and, on the contrary, the value  $\ln(c_{1m}/c_{10})$  will be approximately twice as small as in the droplet model (as evident from a comparison of Eqs. (7.276) and (7.265)).

Let us illustrate the preceding considerations by simple numerical calculations, again. For comparison, we cover two typical cases with  $n_{sm} = 100$ ,  $\Delta n_{sm} = 10$  and  $\Delta n_{sm} = 15$  (for simplicity, we vary only  $\Delta n_{sm}$  out of two parameters,  $n_{sm}$  and  $\Delta n_{sm}$ ). From Eqs. (7.224) and (7.275)-(7.277), at  $\alpha_m \approx 0.1$ ,  $n_{sm} = 100$  and  $\Delta n_{sm} = 15$  we can easily find

$$W_{sm} = 9.68, \quad a_1 = 0.0429, \quad a_3 = 0.877, \quad \frac{c_{1m}}{c_{10}} = 1.59, \quad (7.280)$$

and for  $n_{sm} = 100$  and  $\Delta n_{sm} = 15$

$$W_{sm} = 10.1, \quad a_1 = 0.0208, \quad a_3 = 0.436, \quad \frac{c_{1m}}{c_{10}} = 1.20. \quad (7.281)$$



Further, from Eqs. (7.277)-(7.279) at  $\alpha_m \approx 0.1$ ,  $n_{sm} = 100$  and  $\Delta n_{sm} = 10$ , we can easily obtain

$$n_{cm} = 28.6, \quad \Delta n_{cm} = 7.33, \quad W_{cm} = 31.7, \quad (7.282)$$

and for  $n_{sm} = 100$  and  $\Delta n_{sm} = 15$

$$n_{cm} = 33.5, \quad \Delta n_{cm} = 11.5, \quad W_{cm} = 18.0. \quad (7.283)$$

Let us now recover the dependence on the initial parameters  $a_1$  and  $a_3$  in the quasi-droplet model. From Eqs. (7.275) and (7.277), by the perturbation method at  $\epsilon \ll 1$ , we obtain

$$n_{sm} = \left( \frac{a_3}{2a_1} \right)^2 \left( 1 - \frac{2}{3} \epsilon \right), \quad \Delta n_{sm} = \frac{2}{a_1^{1/2}} \left( 1 + \frac{1}{2} \epsilon \right), \quad (7.284)$$

$$\epsilon = \frac{48a_1^3}{a_3^4} \ln \left( \pi^{1/2} \frac{1 - \alpha_m}{\alpha_m} \frac{a_3^2}{2a_1^{5/2}} \right). \quad (7.285)$$

The high sensitivity of the parameter  $n_{sm}$  to the parameters  $a_1$  and  $a_3$  and lower sensitivity of the parameter  $\Delta n_{sm}$  to the parameter  $a_1$  is evident. In order for Eqs. (7.284) to provide realistic estimates of  $n_{sm} \sim 10^2$  and  $\Delta n_{sm} \sim 10$ , and correspondingly, in order for Eq. (7.285) to provide the inequality  $\epsilon \ll 1$ , the values of the initial parameters  $a_1$  and  $a_3$  of the quasi-droplet model should satisfy rather severe constraints. Eqs. (7.284)-(7.285), with Eqs. (7.224), (7.276) and (7.278)-(7.279), determine in an analytical form the desired dependence (at the CMC) of all thermodynamic characteristics of micellization on the parameters  $a_1$  and  $a_3$  of the quasi-droplet model of molecular aggregates. In particular, the approximations for values  $n_{sm}$  and  $n_{cm}$ ,

$$n_{sm} \approx \left( \frac{a_3}{2a_1} \right)^2, \quad n_{cm} \approx \left( \frac{a_3}{4a_1} \right)^2 \quad (7.286)$$

follow from Eqs. (7.284) and (7.278) when corrections due to terms containing the small parameter  $\epsilon$  are ignored. From Eqs. (7.262) and (7.286), we have  $n_{cm}/n_0 \approx (2/3)^2$ ,  $n_{sm}/n_0 \approx (4/3)^2$ . These relations indicate that the relative positions of maximum, point of inflection and minimum of the work  $W_n$  on the aggregation number axis are independent of the parameters  $a_1$  and  $a_3$  in the quasi-droplet model of molecular aggregates.

Let us now derive formulas for the thermodynamic characteristics of micellization in the droplet and quasi-droplet models of molecular aggregates that are valid in the region  $c_1 > c_{1m}$  of monomer concentration  $c_1$ . It is natural that, within the framework of the models, all conclusions will be referred only to the region of concentrations where micelles still retain their spherical shape. As will be shown below, this concentration region can be considered, even upon the accumulation (in micelles) of almost the entire surfactant in micellar solution (when the degree of micellization is close to unity and the total surfactant concentration is much higher than the CMC), as so narrow that the relations

$$n_c \approx n_{cm}, \quad n_s \approx n_{sm}, \quad \Delta n_c \approx \Delta n_{cm}, \quad \Delta n_s \approx \Delta n_{sm} \quad (7.287)$$

hold in this region with a high accuracy with an error that does not exceed several percent. It follows from Eq. (7.144) that, even at

$$c_M/c_{Mm} \lesssim 10^3, \quad (7.288)$$

the inequality

$$c_1/c_{1m} < 1 + (6.91/n_{sm}) \quad (7.289)$$

is valid. According to Eq. (7.139) and  $\alpha_m \simeq 0.1$ , we have  $\alpha \simeq 0.99$  at the upper limit of inequalities Eqs. (7.288) and (7.289). This result implies that micelles already accumulate the main part of the entire surfactant in micellar solution. Hereafter, we assume that Eqs. (7.288) and (7.289), which indicate the narrowness of the concentration region  $c_1 > c_{1m}$ , are fulfilled.

For the droplet model of molecular aggregates we can find with Eqs. (7.210), (7.33) and (7.217) the dependence of the values  $n_c$ ,  $n_s$ ,  $\Delta n_c$  and  $\Delta n_s$  on concentration  $c_1$  via  $\ln(c_1/c_{10})$  even in an analytical form. Eqs. (7.289) and (7.265) show that, at the upper limit of the constraint Eq. (7.289), we have

$$\frac{\ln(c_1/c_{10}) - \ln(c_{1m}/c_{10})}{\ln(c_{1m}/c_{10})} \simeq 6.28 \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2. \quad (7.290)$$

For simplicity, we ignore here and below the correction terms of order  $\epsilon$ . Thus we see that the deviation of the value of  $\ln(c_1/c_{10})$  from its magnitude at the CMC is relatively small at  $(\Delta n_{sm}/n_{sm})^2 \sim 10^{-2}$ . Then, retaining the principal (with respect to this deviation) contributions to the dependencies of  $n_c$ ,  $n_s$ ,  $\Delta n_c$

and  $\Delta n_s$  on  $\ln(c_1/c_{10})$  and taking into account Eqs. (7.264)-(7.265), (7.267) and (7.290), we obtain

$$\begin{aligned} n_c &\simeq n_{cm} \left[ 1 - 3.45 \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2 \right], & n_s &\simeq n_{sm} \left[ 1 + 3.45 \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2 \right], \\ \Delta n_c &\simeq \Delta n_{cm} \left[ 1 - 3.45 (\Delta n_{sm}/n_{sm})^2 \right] \end{aligned} \quad (7.291)$$

$$\begin{aligned} \Delta n_s &\simeq \Delta n_{sm} \left\{ 1 - \left[ 0.77 \ln \left( \frac{\pi^{1/2}(1-\alpha_m)}{\alpha_m} n_{sm} \Delta n_{sm} \right) - 2.65 \right] \times \right. \\ &\quad \left. \times \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^4 \right\}. \end{aligned} \quad (7.292)$$

The same approach can be used for the quasi-droplet model. Here Eqs. (7.210), (7.33) and (7.261) allow to determine the dependence of  $n_c$ ,  $n_s$ ,  $\Delta n_c$  and  $\Delta n_s$  on concentration  $c_1$  via  $\ln(c_1/c_{10})$  (again, in an analytical form). As follows from Eqs. (7.289) and (7.276), we have at the upper limit of the constraint Eq. (7.289) in the quasi-droplet model the result

$$\frac{\ln(c_1/c_{10}) - \ln(c_{1m}/c_{10})}{\ln(c_{1m}/c_{10})} \simeq 13.8 \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2. \quad (7.293)$$

We see that the deviation of  $\ln(c_1/c_{10})$  from its value at the CMC is still relatively small. Then, retaining principal (with respect to this deviation) contributions to the dependencies of  $n_c$ ,  $n_s$ ,  $\Delta n_c$ , and  $\Delta n_s$  on  $\ln(c_1/c_{10})$  and taking into account Eqs. (7.275)-(7.276), (7.278) and (7.293), we obtain in the quasi-droplet model

$$n_c \simeq n_{cm} \left[ 1 - 6.91 \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2 \right], \quad n_s \simeq n_{sm} \left[ 1 + 3.45 \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2 \right], \quad (7.294)$$

$$\Delta n_c \simeq \Delta n_{cm} \left[ 1 - 5.18 \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2 \right], \quad (7.295)$$

$$\Delta n_s \simeq \Delta n_{sm} \left[ 1 - 2.59 \left( \frac{\Delta n_{sm}}{n_{sm}} \right)^2 \right].$$

It follows from Eqs. (7.291)-(7.292) and Eqs. (7.294)-(7.295) at  $(\Delta n_{sm}/n_{sm})^2 \sim 10^{-2}$  that Eqs. (7.287) are fulfilled with high accuracy at the upper limit of the constraint Eq. (7.289). Evidently, this statement is valid throughout the concentration region  $c_1 > c_{1m}$  admitted by the constraint Eq. (7.289). The existence of the small parameter  $(\Delta n_{sm}/n_{sm})^2$  is responsible for the fulfillment of Eqs. (7.287) in the droplet and quasi-droplet models of molecular aggregates.

Note also the following circumstance. According to Eq. (7.289), a relative increase in monomer concentration  $c_1$  that is needed to accumulate almost the whole surfactants in micelles after reaching the CMC turned out to be still markedly lower than the relative increase in monomer concentration  $c_1$  estimated by Eqs. (7.268), (7.269) and (7.280), (7.281) that is necessary to reach the CMC after the appearance of the potential barrier and potential well of work  $W_n$  at  $c_1 = c_{10}$ . This results confirm all statements which have been made concerning the physical meaning of the CMC.

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### References

1. Becker R.: *Theorie der Wärme*. Springer-Verlag, Berlin, 1955.
2. Kashchiev D.: *Nucleation: Basic Theory with Applications*. Butterworth-Heinemann, Oxford, 2000.
3. Shinoda, K., Hutchinson, E. J., Phys. Chem. **66**, 577 (1962).
4. Hall, D. G., Faraday Trans. Royal Soc. II **68**, 668 (1972).
5. Rusanov, A. I.: *Micellization in Surfactant Solutions*. Harwood Academic Publ., Reading, 1997.
6. Tanford, C.: *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*. J. Wiley and Sons Inc., 2nd ed., Toronto, 1980; J. Phys. Chem. **78**, 2469 (1974).
7. Israelachvili, J. N., Mitchell, D. J., Ninham, B. W., J. Chem. Soc. Faraday Trans. II **72**, 1525 (1976).
8. Ruckenstein, E., Nagarajan, R.: *Thermodynamics of Amphiphilar Aggregation into Micelles and Vesicles*. In: *Micellization, Solubilization and Microemulsions*, Mittal, K. L., (Ed.), Plenum Press, New-York, pgs. 133-149 (1977).

9. Nagarajan, R., Ruckenstein, E., *J. Coll. Interface Sci.* **71**, 580 (1979).
10. Nagarajan, R., Ruckenstein E., *Langmuir* **7**, 2934 (1991).
11. Nagarajan, R., Ruckenstein, E.: *Self-Assembled Systems*. In: *Equations of State for Fluids and Fluid Mixtures*. Eds. J. V. Sengers et al., pgs. 589-749, IUPAC, 2000.
12. Fodi, B., Hetschke R., *Langmuir* **16**, 1626 (2000).
13. Aniansson, E. A. G., Wall, S. N., *J. Phys. Chem.* **78**, 1024 (1974).
14. Almgren, M., Aniansson, E. A. G., Holmaker, K., *Chem. Phys.* **19**, 1 (1977).
15. Aniansson, E. A. G., *Ber. Bunsenges. Phys. Chem.* **82**, 981 (1978).
16. Aniansson, E. A. G.: *A Treatment of the Kinetics of Micelles*. In: *Techniques and Applications of Fast Reactions in Solution*. Ed. by W. J. Gettins and E. Wyn-Jones. D. Reidel Publ. Co., Dordrecht, pgs. 249 - 258 (1979).
17. Nagarajan, R., Ruckenstein, E., *J. Coll. Interface Sci.* **60**, 221 (1977).
18. Rusanov, A. I., Kuni, F. M., Shchekin, A. K., *Colloids and Surfaces A* **128**, 13 (1997).
19. Kuni, F. M., Shchekin, A. K., Grinin, A. P., Rusanov A. I., *Colloid J.* **62**, 172 (2000).
20. Kuni, F. M., Grinin, A. P., *Vestn. Leningr. Univ.* **22**, 10 (1982).
21. Kuni, F. M., Shchekin, A. K., Grinin, A. P., *Physics Uspekhi* **44**, 331 (2001).
22. Kuni, F. M., Shchekin, A. K., Grinin, A. P., Rusanov, A. I., *Colloid J.* **65**, 459 (2003).
23. Rusanov, A. I., Kuni, F. M., Shchekin, A. K., *Colloid J.* **62**, 167 (2000).
24. Kuni, F. M., Grinin, A. P., Shchekin, A. K., Rusanov, A. I., *Colloid J.* **62**, 451 (2000).
25. Kuni, F. M., Grinin, A. P., Shchekin, A. K., Rusanov, A. I., *Colloid J.* **63**, 197 (2001).
26. Kuni, F. M., Shchekin, A. K., Grinin, A. P., Rusanov, A. I., *Colloid J.* 2001. **63**, 723 (2001).
27. Rusanov, A. I., Kuni, F. M., Grinin, A. P., Shchekin, A. K., *Colloid J.* **64**, 605 (2002).
28. Rusanov, A. I., Grinin, A. P., Kuni, F. M., Shchekin, A. K., *J. General Chemistry* **72**, 607 (2002).
29. Grinin, A. P., Rusanov, A. I., Kuni, F. M., Shchekin, A. K., *Colloid J.* **65**, 145 (2003).
30. Bilingham, J., Coveney, P. V., *J. Chem. Soc. Faraday Trans.* **90**, 1953 (1994).
31. Coveney, P. V., Wattis, J. A. D., *Proc. R. Soc. London A* **452**, 2079 (1996).
32. Waton, G., *J. Phys. Chem.* **B 101**, 9727 (1997).
33. Coveney, P. V., Wattis, J. A. D., *J. Chem. Soc., Faraday Trans.* **94**, 233 (1998).
34. Mukerjee, P., *J. Phys. Chem.* **76**, 565 (1972).

35. Binder, K., Phys. Rev. **B 15**, 4425 (1977).
36. Kuni, F. M., Grinin, A. P., Kolloid. Zh. **46**, 23 (1984).
37. Aniansson, E. A. G., Wall, S. N., Almgren, M., Hoffman, H., Kielmann, I., Ulbricht, W., Zana, R., Lang, J., Tondre C., J. Phys. Chem. **80**, 905 (1976).
38. Hoffmann, H., Nagel, R., Platz, G., Ulbricht, W., Colloid and Polymer Sci. **254**, 812 (1976).
39. Hoffmann, H., Progr. Colloid and Polymer Sci. **65**, 148 (1978).
40. Wall, S., Elvingson, C., J. Phys. Chem. **89**, 2695 (1985).
41. Gormally, J., Gettins, W. J., Wyn-Jones, E.: *Micellization in Surfactants*. In: *Molecular Interactions*, Ratajczak, H., Orvil-Thomas, N. I. (Eds.), vol. 2, Wiley-Interscience, 1981.
42. Telgmann, T., Kaatze, U., J. Phys. Chem. **B 101**, 7758 (1997).
43. Telgmann, T., Kaatze, U., J. Phys. Chem. **B 101**, 7766 (1997).
44. Chertkov, E. V., Saidov, A. A., Khabibullaev, P. K., Colloids and Surfaces **A 168**, 185 (2000).
45. Wall, S. N., Aniansson, E. A. G., J. Phys. Chem. **84**, 727 (1980).
46. Grinin, A. P., Grebenkov, D. S., Colloid Journal **65**, 603 (2003).
47. Marrink, S. J., Tieleman, D. P., Mark, A. E., J. Phys. Chem. **104**, 12165 (2000).
48. van Os, N. M., Smit, B., Karaborni, S., Recl. Trav. Chim. Pays-Bas **101**, 181 (1994).
49. Wennerstrom, H., Current Opinion in Colloid and Interface Science **1**, 370 (1996).
50. Blankschtein, D., Shiloach, A., Zoeller, N., Current Opinion in Colloid and Interface Science **2**, 294 (1997).
51. Nagarajan, R., Colloids and Surfaces **A 71**, 39 (1993).
52. Nagarajan, R., Langmuir **10**, 2028 (1994).
53. Nagarajan, R.: *Theory of Micelle Formation. Quantitative Approach to Predicting the Micellar Properties from Surfactant Molecular Structure*. In: *Structure-Performance Relationships in Surfactants*. Eds. K. Esumi and M. Ueno, Marcel Dekker, New York, pgs. 1-81 (1997).
54. Ruckenstein, E., Nagarajan, R., J. Phys. Chem. **79**, 2622 (1975).
55. Ruckenstein, E., Nagarajan, R., J. Colloid Interface Sci. **57**, 388 (1976).
56. Nagarajan, R., Ruckenstein, E., J. Colloid Interface Sci. **91**, 500 (1983).
57. Rusanov, A. I.: *Phasengleichgewichte und Grenzflächenerscheinungen*. Akademie-Verlag, Berlin, 1978.
58. Grebenkov, D.S., J. Colloid Interface Sci. **249**, 162 (2002).