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Study of Relaxation in Micellar Solution by the Numerical Experiment

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Abstract—A numerical simulation of the relaxation process of surfactant micellar solution to a new equilibrium state is performed using model analytical representations for the main characteristics of micellar aggregates. Relaxation stages of molecular aggregate size distribution in the typical regions of aggregation number variations predicted by the analytical theory in two-flux approximation are revealed. Good agreement between the predicted values of the relaxation times of micellar solution and those obtained in numerical simulation is disclosed within the domain of applicability of two-flux approximation. Numerical algorithm proposed in this work makes it possible to study the relaxation process of micellar solution even in the case when two-flux approximation becomes inapplicable. The realization of numerical algorithm can be considered as a kind of experiment for studying the relaxation process of a model micellar solution.

INTRODUCTION

The idea of applicability of the formalism of nucleation theory for describing the relaxation process in micellar solutions going back to the publications of [1–5] was logically continued in a series of works [6–10]. With the most general assumptions on the dependence of the work of the aggregate formation from the surfactant molecules in micellar solution, analytical expressions were derived for the main characteristics of the relaxation process in micellar solution [6–10].

The significant progress gained in [6–10] was the introduction of the concepts of direct and reverse fluxes of surfactant molecular aggregates in the space of their sizes. The direct flux specifies the intensity of fluctuation overcoming of the region of the local maximum of the formation work for molecular aggregates located at the aggregation number axis to the left of this region. Direct flux corresponds to the formation of new micelles from surfactant monomers. The micelle decomposition is also the barrier process. Decomposition is characterized by the reverse flux specifying the intensity of fluctuation overcoming of the region of local maximum of the formation work by the molecular aggregates in a micellar well during the micelle decomposition. With the constraints on the parameters of the dependence of the work of molecular aggregate formation on the aggregation number formulated in [7, 8] and the fulfillment of required hierarchy of the kinetic times of micellization, the direct and reverse fluxes of molecular aggregates are calculated in the stationary approximation. The knowledge of the direct and reverse fluxes as the functions of the current concentrations of surfactant monomers (direct flux) and the current concentrations of surfactant monomers and micelles (reverse flux) made it possible, in the combination with the bimodal approximation of the law of surfactant conservation in micellar solution, to derive and study [9] the kinetic equation for surfactant monomers at the stage of slow relaxation of micellar solution.

Hereafter, we call the analytical approach developed in [6–10] to the description of relaxation in micellar solution as two-flux approximation. Being rather productive, the two-flux approximation left unsolved a number of important problems concerning its foundation. Such an evident, at first glance, representation of the resultant flux of surfactant molecular aggregates in the space of their sizes as the difference between the direct and reverse fluxes, in fact, is not based on any physical feature, which can be used to specify (in the ensemble of aggregates) those aggregates that build up the direct and reverse fluxes. The aforementioned constraints on the parameters of the dependence of the work of molecular aggregate formation on the aggregation number have the form of strong inequalities. The strength of these inequalities (not so strong in practice) determines the errors of analytical expressions used to calculate the direct and reverse fluxes of molecular aggregates. As the micellar solution approaches the state of equilibrium when the direct and reverse fluxes are balanced, the weight of errors increases and they can affect the time of slow relaxation of a solution. The necessity of rather exact determination of surfactant monomer concentration at the stage of slow relaxation rises also the problem of the quality of the bimodal approximation of the conservation law for surfactant in solution under the comparability of the amounts of surfactant in micellar and monomer forms.

This work does not exhaustively answer all the questions listed above. In essence, it deals with a peculiar numerical experiment with the model micellar solu-

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tion. Results of numerical simulation presented in this work using the formalism of nucleation theory confirm all conclusions drawn on the relaxation process on the basis of two-flux approximation. The existence of the stage of the relaxation of molecular aggregate size distribution in the characteristic regions of the variations of aggregation numbers predicted by the analytical theory and good agreement between the predicted and measured (in numerical simulation) relaxation times of micellar solution are demonstrated for typical conditions. It is also shown how the time of slow relaxation of micellar solution observed in numerical experiment deviates from the corresponding value predicted by two-flux approximation as we go beyond the domain of applicability of this approximation. Numerical algorithm proposed in this work allows us to study the relaxation process of micellar solution even in the case when the two-flux approximation becomes inapplicable.

1. BASIC ELEMENTS OF NUMERICAL MODEL

The study is based on the finite-difference equation of the Volmer–Döring–Zel'dovich–Frenkel' kinetic theory of nucleation [11]

$$\frac{\partial c_n}{\partial t} = -(I_{n+1} - I_n) \quad (n = 2, 3, 4, \ldots), \tag{1.1}$$

where c_n is the concentration of molecular aggregates containing n surfactant molecules (correspondingly, c_1 is the monomer concentration); the flux I_n of aggregates in the space of sizes is determined by the expression

$$I_n = j^+_{n-1}c_{n-1} - j^-_n c_n \quad (n = 2, 3, 4, \ldots), \tag{1.2}$$

where j^+_n (j^-_n) is the average number of molecules absorbed (emitted) per unit time by the aggregate consisting of n molecules. Omitting argument t at concentrations c_n when writing equations, we remember that $c_n \equiv c_n(t)$.

For the equilibrium solution of $c^{(0)}_n$, Eq. (1.2) results in the relation of detailed balance

$$j^+_{n-1}c^{(0)}_{n-1} - j^-_n c^{(0)}_n = 0 \quad (n = 2, 3, 4, \ldots),$$

which gives

$$j^-_n = j^+_{n-1}c^{(0)}_{n-1}/c^{(0)}_n \quad (n = 2, 3, 4, \ldots). \tag{1.3}$$

Let us take advantage of the representation for equilibrium distribution as

$$c^{(0)}_n = c^{(0)}_1 e^{-W_n}, \tag{1.4}$$

where W_n is the formation work (minimal) for the aggregate consisting of n molecules expressed in kT units (k is Boltzmann's constant, T is the absolute temperature). Then, expression (1.3) can be written as

$$j^-_n = j^+_{n-1}e^{W_n - W_{n-1}} \quad (n = 2, 3, 4, \ldots). \tag{1.5}$$

Yet one equation representing the law of matter conservation should be added to kinetic equation (1). In the closed system considered below, this equation has the form

$$\sum_{n=1}^{\infty} nc_n = c, \tag{1.6}$$

where c is the total number of surfactant molecules per solution unit volume.

The application of the formalism of nucleation theory suggests the knowledge of the work W_n of molecular aggregate formation and the average number of molecules j^+_n added to the aggregate per unit time as a function of aggregation number n and monomer concentration c_1. However, simplified model representations for the work W_n of molecular aggregate formation and the j^+_n value are sufficient for the purposes of this paper. Their use allows us to retain the heart of the matter in performing study and do not aggravate it with details.

Derivation of work W_n is based on model asymptotic representation [12, 13] for the quasi-droplet model of molecular aggregate, modifying it so as to fulfill equality $W_1 = 0$ needed by the meaning of the W_n value. Then, we write

$$W_n = \frac{b}{2}(n^2 - 1) - \frac{2a}{3}(n^{3/2} - 1) + \frac{a^2}{4b}(n-1) - (n-1)\ln\frac{c_1}{c_{10}}, \tag{1.7}$$

where c_{10} is the monomer concentration at which the plot of the dependence of formation work W_n on n has the horizontal tangent in the inflection point (by its meaning, concentration c_{10} is close to the critical micellization concentration). Parameter b in Eq. (1.7) is related to the hydrophilic interaction, parameter a characterizes the value of hydrophobic effect. According to [12, 13], numerical values of parameters a and b for aqueous surfactant solutions satisfy relations

$$a \sim 1, \quad b \ll 1. \tag{1.8}$$

Work W_n given by Eq. (1.7) possesses all required properties [6] of the work of spherical molecular aggregate formation in a real surfactant solution. At $c_1 < c_{10}$, work W_n increases monotonically with n. At $c_1 > c_{10}$, the local maximum W_c (activation barrier) and local minimum W_s with coordinates n_c and n_s, respectively

$$n_c = \left(\frac{a - 2\sqrt{b\ln(c_1/c_{10})}}{2b}\right)^2, \quad n_s = \left(\frac{a + 2\sqrt{b\ln(c_1/c_{10})}}{2b}\right)^2, \tag{1.9}$$

appear in the plot for work W_n. The region of local minimum at the aggregation number axis is called a micellar well. Molecular aggregates accumulated in the well are nothing other than micelles. Characteristic half-width Δn_c of the region of local maximum and half-width Δn_s of the micellar well are determined so that, upon deviation from point n_c by Δn_c, work W_n decreases by unity compared to its value in point n_c; upon deviation by Δn_s, work W_n increases by unity compared to its value in point n_s. According to Eq. (1.7), it follows for Δn_c and Δn_s:

$$\Delta n_c = \left(\frac{4}{an_c^{-1/2} - 2b}\right)^{1/2}, \quad \Delta n_s = \left(\frac{4}{2b - an_s^{-1/2}}\right)^{1/2}. \quad (1.10)$$

As is shown in [12], height difference ΔW between the values for the local maximum and minimum of work W_n

$$\Delta W = \frac{4}{3}\frac{a}{b^{3/2}}\ln^{3/2}\frac{c_1}{c_{10}}. \quad (1.11)$$

is determined in the analytical form from relation (1.7). The ΔW value acts as the height of activation barrier for the process of micelle decomposition.

Concentration c_{10} in Eq. (1.7) depends on parameters a and b according to

$$\ln c_{10} = \ln c_0 - \frac{a^2}{4b}, \quad (1.12)$$

where c_0 no longer explicitly depends on a and b. Hence, expression (1.7) can be conveniently written in the following form:

$$W_n = G_n - (n-1)\ln\frac{c_1}{c_0}, \quad (1.13)$$

where the first term G_n is independent of monomer concentration and determined only by parameters a and b

$$G_n = \frac{b}{2}(n^2 - 1) - \frac{2a}{3}(n^{3/2} - 1). \quad (1.14)$$

In view of Eq. (1.13), it is advisable to use concentration c_0 as a concentration unit for numerical calculations. When calculations are completed, all results can be represented in any convenient units, in particular, in units of concentration c_{10} that, as was already mentioned, is close by its meaning to the critical micellization concentration. As is seen from Eq. (1.12), the multiplier for the conversion of concentration in c_0 units into the concentration in c_{10} units is equal to $\exp(-a^2/4b)$.

Let us consider now the j_n^+ value. The average number of molecules j_n^+ absorbed per unit time by the spherical aggregate consisting of n molecules is proportional to concentration c_1. Because the theory of micellar solution contains no reliable approximations for the dependence of the j_n^+ value on aggregation number n, upon the modeling of the relaxation process of micellar solution, this dependence can be excluded at all by setting

$$j_n^+ = qc_1, \quad (1.15)$$

where q is the coefficient of proportionality. In this case, according to Eqs. (1.5), (1.7), and (1.15), the average number of molecules j_n^- emitted per unit time by the spherical aggregate consisting of n molecules will be a complex function of aggregation number n.

Note that the assumption of the independence of the j_n^+ value on the aggregation number n within the micellar well and determination of the j_n^- value from relation (1.3) using the Gaussian approximation for the distribution of molecular aggregates over the aggregation numbers in the micellar well was used in [2] when deriving the time of "fast" relaxation of micellar solution.

2. KINETIC EQUATION IN DIMENSIONLESS VARIABLES. RELAXATION TIMES

The state of model micellar solution and the main characteristics of molecular aggregates in this solution are determined by the numerical values of several parameters: the a and b parameters of work W_n of the molecular aggregate formation, total number c of surfactant molecules per solution unit volume, concentration c_0, and coefficient q in Eq. (1.15). The dependence of the last two parameters can be easily excluded from the consideration changing the units of concentration and time, respectively. Indeed, the measurement of all concentrations in the c_0 units allows us to set $c_0 = 1$ and the introduction of dimensionless time $\tau = qt$ excludes coefficient q from kinetic equation (1.1). Hereafter, we deal with dimensionless parameters, unless otherwise specified. Evidently, all results obtained are converted into customary units, if one sets c_0 (or c_{10}) and q.

On the contrary, parameters a, b, and c are the characteristic parameters. Their values determine not only the quantitative characteristic of the solution but also its qualitative behavior. The choice of representative values of parameters a, b, and c is significant for this study.

Substituting expressions (1.5) and (1.15) for coefficients $j_n^\pm$ into kinetic equation (1.1), using representation (1.13) for work W_n, and accounting for the introduction of new units, we arrive at the equation

$$\frac{\partial c_n}{\partial \tau} = c_1 c_{n-1} + c_{n+1}e^{G_{n+1} - G_n} - c_n(c_1 + e^{G_n - G_{n-1}}), \quad (2.1)$$
$$(n = 2, 3, 4, \ldots),$$

which forms, together with the law of matter conservation (1.6), the closed system of equations. Here, coefficients $\exp(G_{n+1} - G_n)$ are no longer dependent on the monomer concentration and, at fixed parameters a and

b, are constant. Note the nonlinearity of this system of equations that significantly complicates its analysis.

To solve Eq. (2.1), one should set the initial condition. As was already mentioned in Introduction, we are interested in the relaxation of micellar solution whose initial state in characterized by the equilibrium distribution $\bar{c}_n^{(0)}$ of molecular aggregates over the aggregation numbers to the new relaxation state corresponding to realized external action. The upper bar denotes the values referred to the initial state. As an initial condition to Eq. (2.1), it is natural to take the relation

$$c_n(0) = \bar{c}_n^{(0)}. \tag{2.2}$$

The external action can be different. The simplest form is the addition of new surfactant monomers to solution that causes the natural disturbance of equilibrium. However, we will concern about other disturbances when the thermodynamic state of micellar solution varies at constant total number *c* of surfactant molecules per solution unit volume. Physically, this can correspond, for example, to the variation of the solution temperature or pressure. Real action of such type affects to smaller or larger extent all parameters entering into relation (1.7) for work W_n. However, upon the numerical simulation of relaxation process, it is sufficient to assume that the external action changed the value of only one parameter, e.g., parameter *a*. The value of this parameter prior to action we denote by $\bar{a}$, after action, by $\tilde{a}$. Note that, if the concentration was expressed in c_{10} unit rather than in c_0 units, then, according to Eq. (1.12), the variation of parameter *a* automatically would vary the absolute values of concentration.

To find the equilibrium distribution at preset parameters *a*, *b*, and *c*, it is sufficient to determine, as is seen from Eqs. (1.4), (1.13), and (1.14), the value of concentration $c_1^{(0)}$ (in c_0 units) corresponding to these parameters. This can be done by the numerical solution of Eq. (1.6), which in this case can be represented with allowance for Eqs. (1.4) and (1.13) in the form

$$c = \sum_{n=1}^{\infty} nc_n^{(0)} = \sum_{n=1}^{\infty} n[c_1^{(0)}]^n e^{-G_n}. \tag{2.3}$$

As was shown in [14], if the G_n value is given by relation (1.14), the only solution $c_1^{(0)}$ of this equation always exists.

When solving the kinetic equation numerically, one should set the upper limit of the region of considered aggregation numbers. The simplest and most natural way is to assume that, beginning with a certain $n_{\max}$, the aggregate formation becomes impossible. Mathematically, this assumption is realized in the form of boundary condition

$$c_{n_{\max}}(t) = 0. \tag{2.4}$$

At the characteristic values of parameters *a*, *b*, and *c* used below, it is sufficient to choose the $n_{\max}$ value from condition $n_{\max} \geq 200$ at which concentrations $c_{n_{\max}}^{(0)}$ no longer exceed 10^{-150}; i.e., they are negligibly small.

According to Eq. (2.1), the evolution of the molecular aggregates distribution over the aggregation numbers from the initial equilibrium distribution $\bar{c}_n^{(0)}$ existed at the values of parameters $\bar{a}$, *b*, and *c* to the final equilibrium distribution $c_n^{(0)}$ corresponding to the former values of parameters *b*, and *c* and the new value of parameter $a = \tilde{a}$, is rather complex process. In this process, more characteristic stages are specified than it was suggested in [1–5].

In this numerical experiment, the attention will be focused on three stages. The fastest of these stages (that was not discussed in [1–5]) is the establishment of quasi-equilibrium distribution in the region of small aggregation numbers such that $2 \leq n < n_c - \Delta n_c$. For the theoretical estimate of duration $\tau^{(1)}$ of this stage, we use conclusions drawn in [15]. As lower $\tau_{\min}^{(1)}(n)$ and upper $\tau_{\max}^{(1)}(n)$ estimates for the time of the establishment of quasi-equilibrium distribution in the region of aggregation numbers lower than given *n*, according to [15], we can write, respectively

$$\tau_{\min}^{(1)}(n) = 1/\bar{j}_n, \quad \tau_{\max}^{(1)}(n) = n/\bar{j}_n. \tag{2.5}$$

The next (by the duration) stage is the stage of "fast" (according to accepted terminology) relaxation. At this stage, there occurs the rearrangement of the distribution of molecular aggregates over the aggregation numbers caused by the shift of micellar well along the aggregation number axis (at practically constant number of micelles) under the external action. The time of fast relaxation $\tau_{\text{th}}^{(2)}$ predicted by the theory (see [9, 10]) is equal to

$$\tau_{\text{th}}^{(2)} = \frac{1}{c_1}\left(\frac{2}{\Delta n_s^2} + \frac{c_M}{c_1}\right)^{-1}. \tag{2.6}$$

The slow relaxation is caused by the variation of the depth of micellar well. At this stage, the number of micelles in the micellar well achieves a new equilibrium value. The duration of slow relaxation under the conditions of performed numerical experiment, according to [9, 10], is estimated in the two-flux approximation by time $\tau_{\text{th}}^{(3)}$ equals

$$\tau_{\text{th}}^{(3)} = \frac{\sqrt{\pi}c_M \Delta n_c e^{W_c}}{c_1^2}\left(1 + \frac{n_s^2 c_M}{c_1}\right)^{-1}, \tag{2.7}$$

where micelle concentration c_M is found as

$$c_M = \sqrt{\pi}\Delta n_s c_1 \exp(-W_s). \tag{2.8}$$

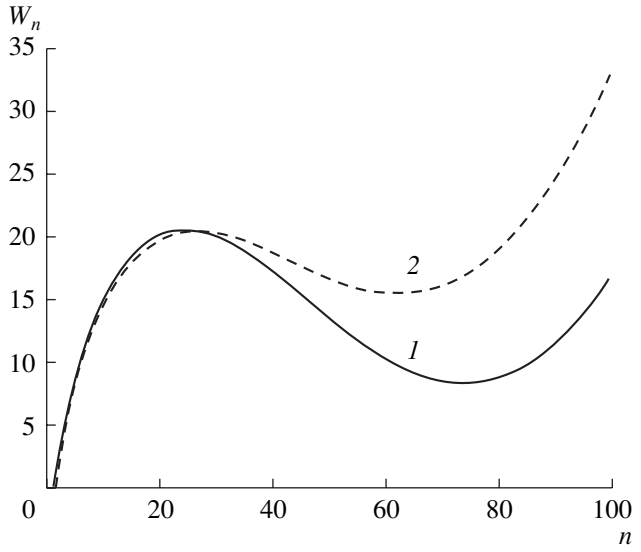

Fig. 1. Dependences of work W_n of the molecular aggregate formation on aggregation number n in the (*1*) initial and (*2*) final equilibrium states of micellar solution. $\bar{a}$: (*1*) 1.35 and (*2*) 1.30; $b = 0.1$.

All values in formulas (2.6)–(2.8) refer to the final equilibrium state.

Upon the numerical solution of the kinetic equation, the micelle concentration is determined using the relation

$$c_M = \sum_{n = n_s - 2\Delta n_s}^{n_s + 2\Delta n_s} c_n. \qquad (2.9)$$

The limits of summation in Eq. (2.9) are established from the consideration of a sufficient calculation accuracy. At the state of final equilibrium, the results of calculations by Eqs. (2.8) and (2.9) are virtually identical, provided that the micellar well is deep enough, $\Delta W \gtrsim 3$.

Table 1. The values of the characteristics of initial ($\bar{a} = 1.35$) and final ($\tilde{a} = 1.30$) equilibrium states of micellar solution

Elements of numerical model	$\bar{a} = 1.35$	$\tilde{a} = 1.30$
n_c; n_s	23.7; 74.5	26.0; 62.4
Δn_c; Δn_s	7.2; 9.6	8.5; 10.6
W_c	20.50	20.43
W_s	8.54	15.66
$c_1 \times 10^{-2}$	1.495	1.780
c_1/c_{10}	1.424	1.217
$c_M \times 10^{-5}$	5.00	0.00547
$C_M \times 10^{-3}$	3.695	0.00334

3. ALGORITHM OF THE NUMERICAL SOLUTION OF KINETIC EQUATION

Numerical solution of Eq. (2.1), together with the mass conservation law (1.6), makes it possible to obtain both the qualitative picture of the relaxation of micellar solution to the new equilibrium state and the characteristic times of this process. The values of parameters $\bar{a}$, b, and c determining initial equilibrium distribution $\bar{c}_n^{(0)}$ of molecular aggregates and the value of parameter $\tilde{a}$ established after the external action on micellar solution are chosen from the considerations of sufficient representation of the solution relaxation and equal to:

$$\bar{a} = 1.35, \quad b = 0.1, \quad c = 2.1 \times 10^{-2}, \quad \tilde{a} = 1.30. \qquad (3.1)$$

Note also that, at these values, the region of the local maximum of formation work on the aggregation number axis and the region of micellar well (Fig. 1) fit the range of aggregation numbers admitted for the applicability of the quasi-droplet model of molecular aggregate (relation (1.14) in [14]), provided that the number of hydrocarbon groups in the hydrophobic part of surfactant molecule n_c is no smaller than 18. The numerical values of parameters a and b agree qualitatively with the possible values of similar parameters of the quasi-droplet model of molecular aggregate [12, 13] characterizing the values of hydrophobic effect and hydrophilic interaction, respectively. Remind that parameters b and c are supposed to be invariant upon the external action. Concentration c (the total number of surfactant molecules per solution unit volume) in Eq. (3.1) is given in the c_0 units. In concentration c_{10} units (for the initial state), concentration c is equal to two units.

Table 1 lists the values of the main characteristics of the initial and final equilibrium states of micellar solution. The C_M value in the last line of Table 1 is the total number of surfactant molecules per unit volume and expressed in c_0 units; it was calculated by the formula:

$$C_M = \sum_{n = n_s - 2\Delta n_s}^{n_s + 2\Delta n_s} n c_n. \qquad (3.2)$$

As is seen from Table 1, the considered external action leads to the decomposition of the substantial part of a micelle. Figure 1 demonstrates the difference in the behavior of the work W_n of molecular aggregate formation as a function of aggregation number n in the initial and final states of solution. This difference is fairly large in the region of micellar wells, although the corresponding change in parameter a is relatively small.

Finite-difference scheme of the solution of the system of equations (1.1) chosen for numerical experiment is closely related to the basic principle of the construction of this system. Coefficients j_n^+ and j_n^- in the right-hand side of determination (1.2) are the average num-

bers of molecules absorbed (emitted) per unit time by the aggregate consisting of n molecules. Only under the condition that the average numbers of molecules absorbed $j_n^+ d\tau$ or emitted $j_n^- d\tau$ by the aggregates per each time span $d\tau$ of the computational procedure is much smaller than unity, we can guarantee that the system of equations (1.1) controls the variation of the number of aggregates with given aggregation number. Each aggregate absorbs or emits no more than one molecule; correspondingly, the total number of molecules absorbed or emitted by the aggregates with given aggregation number makes a certain contribution to the change in the number of aggregates with given aggregation number and with the aggregation numbers that are larger or smaller by unity than the given value. At the indicated in Eq. (3.1) values of the parameters of work W_n of the molecular aggregate formation set by relation (1.7), an adequate accuracy of computational procedure is provided by time span $d\tau = 5 \times 10^{-2}$. On the other hand, the characteristic time of the establishment of final equilibrium state at the parameter values shown in Eq. (3.1) is of the order of 10^6, while at the other parameter values it can be of the order of 10^{10}. Hence, for constructing solution, one should realize 10^8–10^{12} cycles of calculation procedure. Similar calculations take too much of computer time even for the high-performance computers.

Required smallness of time span and longer duration of the observed relaxation process are matched by the realization of "jumps" in time. At the first computational stage, usual span mode of the solution of Eq. (2.1) is realized, which is used to monitor the evolution of the ensemble of molecular aggregates before the establishment of quasi-equilibrium distribution over the aggregation numbers when the relative concentration variations for the aggregates of all sizes become small. Under these conditions, the velocities of concentration variation for the aggregates of all sizes are calculated. At the second computational stage, the jump in time is realized whose duration exceeds manifold the duration of the first stage. The values of aggregate concentration by the end of jump are calculated (using the linear extrapolation) by the velocities of concentration variations determined at the first stage. Such operation is justified, because the velocities of concentration variation vary slightly over quite large time intervals. Monomer concentration by the end of jump is determined from the mass conservation law. At the third computational stage, the span-by-span mode of the solution of Eq. (2.1) is used again in order to "bring system at rest" after the linear extrapolation.

The "quieting" of solution, after the jump realization, is done to put the distribution of molecular aggregates over the aggregation numbers obtained after the jump into correspondence with the altered (after the jump) trend of the dependence of the work of molecular aggregate formation on the aggregation number. At the natural course of relaxation process, such a correction proceeds continuously. Possibility and efficiency of the quieting stage is based on the smallness of the times of the establishment of quasi-equilibrium molecular aggregate distribution in the regions of small aggregation numbers and micellar well compared to the time of slow relaxation of micellar solution defined by the analytical theory and confirmed in this numerical experiment.

Described manipulations are repeated several times until the desired closeness to the final equilibrium distribution of molecular aggregates over the aggregation numbers is achieved. The stability of computational procedure is gained by varying the duration of the first stage and the value of jumps with time. The quality of computational procedure was also confirmed by comparing with the solution obtained using the finite-difference scheme under conditions when the time required to realize this scheme was not so long.

4. RESULTS OF NUMERICAL EXPERIMENT

Three aforementioned characteristic stages in the evolution of the distribution of molecular aggregates over the aggregation numbers are distinctly specified upon the realization of computational procedure. The establishment of the quasi-equilibrium distribution of molecular aggregates within a certain range of aggregation numbers signifies the completion of each stage.

At the first stage, there occurs the redistribution of aggregate concentrations within a small number ($n < n_c - \Delta n_c$) of surfactant molecules. Within this range of aggregation numbers, concentrations vary substantially, whereas the concentrations of other aggregates remain virtually constant. The observed temporal dependence of dimer concentration $c_2(t)$ shown in Fig. 2 is representative. It is distinctly seen that the dimer concentration rapidly approaches its quasi-equilibrium value at current monomer concentration $c_1(t)$. Using the exponential approximation of the law of approach of concentration $c_n(t)$ of aggregates with $n < n_c - \Delta n_c$ to their quasi-equilibrium $c_n^{(0)}(t)$ values at current monomer concentration $c_1(t)$, we calculated corresponding characteristic times $\tau^{(1)}(n)$ of this process. Quasi-equilibrium values of the $c_n^{(0)}(t)$ concentrations at current monomer concentration $c_1(t)$ are determined, according to Eqs. (1.4) and (1.13), as

$$c_n^{(0)}(t) = \exp[n \ln c_1(t) - G_n]. \qquad (4.1)$$

The $\tau^{(1)}(n)$ times increase with n. Therefore, time $\tau^{(1)}(n)$ at each given n can be considered as the observed time of the establishment of quasi-equilibrium distribution in the region of aggregation numbers smaller than given n. The values of $\tau^{(1)}(n)$ time calculated by the results of numerical simulation, as well as calculated by Eq. (2.5) theoretical estimates of lower $\tau_{\min}^{(1)}(n)$ and

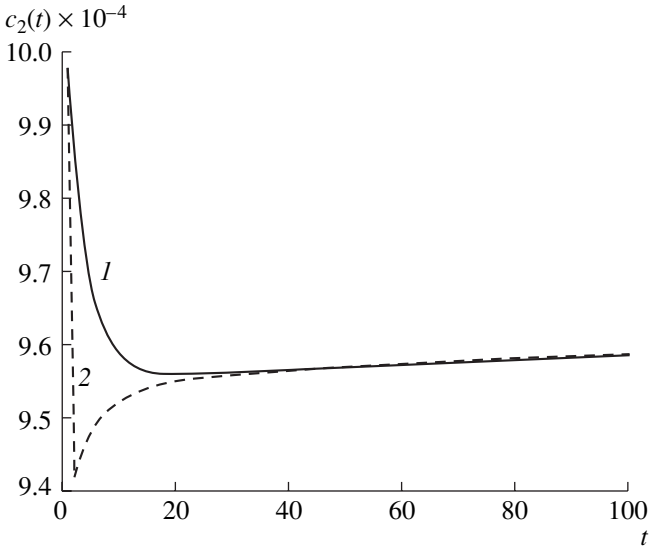

Fig. 2. Kinetics of the variation of dimer concentration at the first stage. Solid line represents the real variation; the dashed line, equilibrium distribution (4.1) with the current monomer concentration.

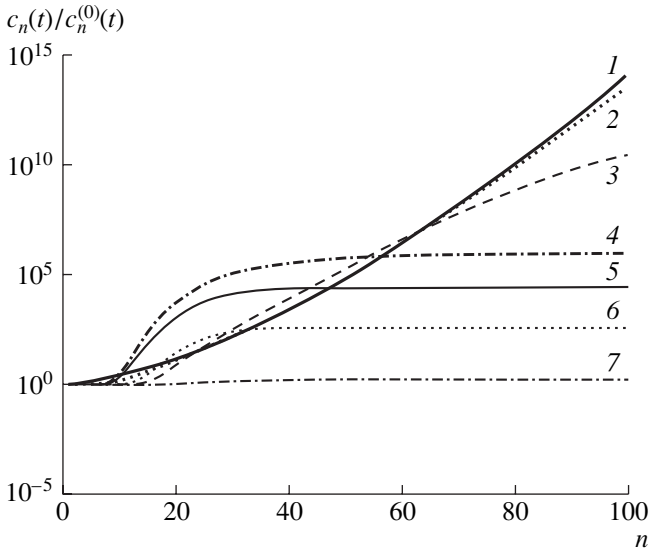

Fig. 3. Distribution of molecular aggregates over the aggregation numbers at time moments $t_k = 10^k$ normalized to the quasi-equilibrium distribution at monomer concentration $c_1(t_k)$ and various k: (*1*) 1, (*2*) 2, (*3*) 3, (*4*) 4, (*5*) 5, (*6*) 6, and (*7*) 7. The $n \approx 10$ value can be considered as the upper boundary of the region of small aggregation numbers within which the quasi-equilibrium distribution of molecular aggregates over the aggregation numbers is established.

upper $\tau_{max}^{(1)}(n)$ limits of these times, are listed in Table 2 for several n values. It is seen that the observed $\tau^{(1)}(n)$ value lies between the theoretical estimates but closer to the lower limit.

General picture of the observed distributions of molecular aggregates over the aggregation numbers represented in Fig. 3 allows us to indicate upper boundary ($n_1 \approx 10$) of the range of small aggregation numbers within which the quasi-equilibrium distribution (4.1) of molecular aggregates over the aggregation numbers is established by the end of first stage. According to Table 1, this n_1 value agrees with the $n_c - 2\Delta n_c$ value. The duration $\tau^{(1)}$ of the first stage of the relaxation process in micellar solution can naturally be taken as equal to

$$\tau^{(1)} = \tau^{(1)}(n_1). \quad (4.2)$$

Using data listed in Table 2, we conclude that, in the simulated process (at chosen parameters a, b, and c), time $\tau^{(1)}$ is equal to

$$\tau^{(1)} \sim 10^2. \quad (4.3)$$

Note that all curves in Fig. 3 lie above the unity level. If the $\tilde{a}$ value of parameter a in the final state was chosen larger than $\bar{a}$, all the curves would be arranged below this level.

As was already stated, the next (by the duration) stage of relaxation process in micellar solution is called, according to the accepted terminology, the stage of "fast" relaxation. At this stage, the quasi-equilibrium distribution of molecular aggregates over the aggregation numbers is established in the region of micellar well at the background of relatively slow variation of the total number of micelles. Current micelle concentration in solution acts as the parameter of this distribution. Once the stage of fast relaxation is completed, the distribution of molecular aggregates in the region of potential well normalized to quasi-equilibrium distribution at current monomer concentration $c_1(t)$ acquires the form of horizontal line. Distribution curves shown in Fig. 3 are characterized by the presence of such parts beginning with curve *4*. Here, the form of molecular

Table 2. The $\tau^{(1)}(n)$ times of the relaxation of the concentration of aggregates consisting of small number of surfactant molecules at the first stage and the lower $\tau_{min}^{(1)}(n)$ and upper $\tau_{max}^{(1)}(n)$ estimates for these times

n	$\tau_{min}^{(1)}(n)$	$\tau^{(1)}(n)$	$\tau_{max}^{(1)}(n)$
2	4.2	3.4	8.4
3	6.1	7.6	18.2
4	8.0	12.9	32.0
5	10.0	18.6	50.2
6	12	29	72
7	14	35	100
8	16	45	133
9	19	57	170
10	21	74	213

aggregate distribution corresponds already to the equilibrium at the current monomer concentration; however, the total number of aggregates in the micellar well over the long time exceeds (under considered conditions) the corresponding equilibrium value. Theoretical estimate of the $\tau_{th}^{(2)}$ time of fast relaxation calculated by Eq. (2.6) gives

$$\tau_{th}^{(2)} = 3.2 \times 10^3. \quad (4.4)$$

The $\tau^{(2)}$ time of fast relaxation is determined in numerical experiment by the calculated temporal dependence of the total (in the c_0 units) amount $C_M(t)$ of surfactant molecules in micelles. This amount is found, according to Eq. (3.2), at the current distribution $c_n(t)$ of molecular aggregates. Operating equation for calculating the $\tau^{(2)}$ time

$$\tau^{(2)} = \left| \frac{t_2 - t_1}{\ln[C'_M(t_1)/C'_M(t_2)]} \right|, \quad (4.5)$$

is derived under the assumption of purely exponential law of the approach of $C_M(t)$ to its value in the quasi-equilibrium state. The superscript (dash) over the symbol in Eq. (4.5) denotes the derivative with respect to time, t_1 and t_2, as two consecutive time moments. If the exponential law of approach had fulfilled exactly, the calculation by formula (4.5) would produce the result independent of the choice of times t_1 and t_2. However, data represented in Table 3 for four time moments t_1 and $t_2 = t_1 + 1000$ testify the existence of such dependence.

A certain increase in time $\tau^{(2)}$ [calculated by Eq. (4.5)] with t_1 is due to the variation of the total number of micelles with time, which is the parameter of the quasi-equilibrium distribution of molecular aggregates over the aggregation numbers in the region of potential well. Fairly large rise of the lower point of micellar well after the external action on solution (see Fig. 1) denotes the large excess of micelles at the beginning of relaxation process. A decrease in height difference ΔW causes an increase in the reverse flux (decomposition) of micelles, which at the initial period of relaxation is not balanced by the direct flux of surfactant molecular aggregates in the space of their sizes. Both factors lead to fairly fast change in the total number of micelles that affects the stage of fast relaxation in the considered numerical experiment. It is evident at the same time, that the data of Table 3 are qualitatively consistent with theoretical estimate (4.4) of time $\tau^{(2)}$.

Theoretical value of time $\tau_{th}^{(3)}$ of slow relaxation calculated by Eq. (2.7), using data of Table 1, is equal to

$$\tau_{th}^{(3)} = 1.9 \times 10^6. \quad (4.6)$$

Note that theoretical $\tau_{th}^{(3)}$ value is the time of slow relaxation of monomer concentration $c_1(t)$. In the numerical experiment, such times can be determined for all aggregates.

Table 3. Calculation results for time $\tau^{(2)}$ of fast relaxation at various t_1 and $t_2 = t_1 + 1000$

t_1	1000	2000	3000	4000
$\tau^{(2)} \times 10^3$	2.4	2.9	3.4	3.9

Table 4. The values of time $\tau^{(3)}$ of slow relaxation calculated at various t_1 and $t_2 = t_1 + 10^6$

$t_1 \times 10^6$	2	3	4	5	6
$\tau^{(3)} \times 10^6$	1.64	1.80	1.89	1.94	1.97

At the stage of slow relaxation, the approach of concentration $c_1(t)$ to final equilibrium value $\tilde{c}_1(0)$ is described by the exponential law:

$$c_1(t) = \tilde{c}_1^{(0)} + A\exp[-t/\tau^{(3)}], \quad (4.7)$$

where A is the numerical coefficient, $\tau^{(3)}$ is the calculated time of slow relaxation of monomer concentration $c_1(t)$. Equilibrium concentration $\tilde{c}_1^{(0)}$ at chosen parameters $a = \tilde{a}$, b, and c is found in advance (before the solution of kinetic equations) from Eq. (2.3), as was being done upon the calculation of initial aggregate distribution $\bar{c}_n^{(0)}$. According to Eq. (4.7), the time of slow relaxation $\tau^{(3)}$ can be determined by the values of monomer concentration $c_1(t_1)$ and $c_1(t_2)$ in two consecutive time moments t_1 and t_2

$$\tau^{(3)} = \frac{t_2 - t_1}{\ln[(c_1(t_1) - \tilde{c}_1^{(0)})/(c_1(t_2) - \tilde{c}_1^{(0)})]}. \quad (4.8)$$

If the real behavior of concentration $c_1(t)$ had obey law (4.7), time $\tau^{(3)}$ calculated by Eq. (4.8) would be independent of the choice of t_1 and t_2. The values of $\tau^{(3)}$ calculated at various t_1 and t_2 are listed in Table 4. Note that the values obtained are similar to each other and to the theoretical estimate given by Eq. (4.6). The sequence of the $\tau^{(3)}$ values obtained at further increase in t_1 (at $t_2 = t_1 + 10^6$) tends to its limiting value:

$$\tau^{(3)} \cong 2.01 \times 10^6, \quad (4.9)$$

which should precisely be considered as the value of the time of slow relaxation in the numerical experiment. In contrast to the stage of fast relaxation, the third stage deals with the approach to the total equilibrium that allows one to calculate the time of slow relaxation with a high accuracy.

We can conclude that theoretical estimate (4.6) turned out to be fairly good. Moreover, the difference between $\tau^{(3)}$ and $\tau_{th}^{(3)}$ is much smaller than it could be expected. As is seen from Table 1, the surfactant mono-

Table 5. Characteristics of minimal formation work W_n and the times of slow relaxation at five values of total concentration c of surfactant molecules in solution (at five ΔW values)

c	0.030	0.029	0.028	0.027	0.026
c_1/c_{10}	1.1989	1.1679	1.1336	1.1025	1.0689
c_1	0.0241	0.0235	0.0228	0.0222	0.0215
n_c; n_s	24.0; 57.7	25.0; 56.2	26.2; 54.4	27.7; 52.4	29.5; 49.9
Δn_c; Δn_s	8.5; 10.6	9.0; 11.0	9.5; 11.4	10.3; 12.1	11.5; 13.2
W_c; W_s	17.27; 13.20	17.89; 14.67	18.58; 16.20	19.35; 17.74	20.20; 19.30
ΔW	4.07	3.22	2.38	1.61	0.90
$\tau_{\text{th}}^{(3)} \times 10^5$	6.9	3.3	1.6	0.9	0.54
$\tau^{(3)} \times 10^5$	7.0	3.6	1.8	1.0	0.50

mer concentration, together with total amount C_M of surfactant molecules in micelles, does not yield total concentration c of surfactant molecules in solution indicated in Eq. (3.1). In the discussed numerical experiment and, possibly, under the real conditions, the noticeable amount of surfactant molecules seems to be concentrated in the aggregates consisting of small number of molecules (dimers, trimers, etc.). Consequently, the error introduced by the bimodal approximation of the law of matter conservation to the theoretical estimate should also be noticeable. Let us estimate this error.

The rate of the approach to quasi-equilibrium aggregate distribution in the region of small aggregation numbers enables us to fundamentally refine the bimodal approximation at the stage of slow relaxation. When describing this stage, we can assume that the bimodal approximation determines not the monomer concentration $c_1(t)$ but certain concentration $c_{\text{eff}}(t)$ equals

$$c_{\text{eff}}(t) = c_1(t) + \sum_{n=2}^{n_c - 2\Delta n_c} n c_n^{(0)}(t), \qquad (4.10)$$

where quasi-equilibrium distribution $c_n^{(0)}(t)$ is related to the current monomer concentration by Eq. (4.1). Hence, when deriving the kinetic equation for monomer concentration $c_1(t)$ in the two-flux approximation, one should deal with the derivative of $c_{\text{eff}}(t)$ with respect to time rather than with the derivative of $c_1(t)$. Based on Eqs. (4.1) and (4.10), the relation

$$\frac{dc_{\text{eff}}(t)}{dt} = \frac{dc_1(t)}{dt} \times \left\{1 + \sum_{n=2}^{n_2 - 2\Delta n_c} n^2 \exp[(n-1)\ln c_1(t) - G_n]\right\} \qquad (4.11)$$

is valid for $c_{\text{eff}}(t)$. The numerical value of expression in braces in the state of final equilibrium under the considered conditions is equal approximately to 1.4. It is precisely by this factor that theoretical estimate $\tau_{\text{th}}^{(3)}$ would be smaller than calculated time $\tau^{(3)}$, if the bimodal approximation of the law of matter conservation had been the only source for the error of two-flux approximation. The fact that the difference between times $\tau_{\text{th}}^{(3)}$ and $\tau^{(3)}$ turned out to be not too large resulted from the presence of other sources of the errors of theoretical approach, which was discussed in the introduction. These sources are not subjected to simple control. However, it is seen that the error introduced by these sources is opposite (in sign) to the error of bimodal approximation. Being commensurable, these errors partly compensate each other, thus improving the agreement between times $\tau^{(3)}$ and $\tau_{\text{th}}^{(3)}$.

5. CONCLUSIONS

The performed numerical experiment confirms the validity of theoretical concepts underlying the two-flux approximation and demonstrates (within the domain of their applicability) a fairly high quality of the results obtained using this approximation. Numerical experiment makes it also possible to estimate the quality of predictions of two-flux approximation under the conditions when its application (by formal features) should not lead to the realistic results. This is illustrated by the calculations of the time of slow relaxation for various values of height difference ΔW of the local maximum and minimum of work W_n in the state of micellar solution after the external action. Remind that one of the conditions of the applicability of two-flux approximation [6–10] is the constraint

$$\Delta W \gg 1, \qquad (5.1)$$

which is the better fulfilled, the more concentration c_1 exceeds concentration c_{10}.

Data of calculations of the time of slow relaxation $\tau^{(3)}$ upon the transition from the state with parameters $\bar{a} = 1.30$ and $b = 0.1$ to the state of final equilibrium characterized by $\tilde{a} = 1.25$ and $b = 0.1$ for five ΔW val-

ues are listed in Table 5. The ΔW value varied by setting the various values of total concentration c of surfactant molecules in solution. It is seen that, up to $W = 1.61$, a good agreement between the $\tau^{(3)}$ and $\tau_{th}^{(3)}$ times is retained when, as in Section 4, $\tau^{(3)}$ exceeds slightly the $\tau_{th}^{(3)}$ value. A surprising and, probably, occasional event is the closeness of the $\tau^{(3)}$ and $\tau_{th}^{(3)}$ times at $\Delta W = 0.9$, when the error of calculation of micelle concentration c_M using relation (2.8) becomes extremely large. Note that, in this last case, time $\tau_{th}^{(3)}$ exceeds $\tau^{(3)}$.

Hence, the numerical simulation makes it possible to refine and, accordingly, to extend the domain of applicability of the two-flux approximation, in any case, with respect to constraint (5.1).

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