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STUDY OF RELAXATION IN
A MODEL MICELLAR SOLUTION

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Scientific secretary of
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GENERAL CHARACTERISTICS

Actuality of the work. The kinetics of the relaxation processes in micellar solutions composed of surfactant molecules the study of which had been initiated thirty years ago continues to be the central subject of numerous theoretical and experimental researches. The relaxation times of different dynamical characteristics of a micellar solution as a function of the chemical structure of surfactant molecules and thermodynamic parameters of the solution present an important source of the information about the behavior of the micellar solution and the internal structure of molecular aggregates in it. The scientific interest to the problems of kinetics has noticeable grown in last years. A series of papers written at Saint Petersburg State University [1-5], or general review [6], can be mentioned.

The solution of kinetic problems is closely related to the development of theoretical models of molecular aggregates, their thermodynamic description and efficient formalism allowing to describe the temporal evolution of these aggregates in a micellar solution. All these aspects have been advanced in [1-5]. Under rather general assumptions about the dependence of the aggregation work (required to form a molecular aggregate in a micellar solution) on the aggregation number, analytical expressions have been obtained for the main characteristics of the relaxation process. In particular, the two-flux approximation has been developed to describe the slow relaxation stage.

The present PhD thesis concerns a specific numerical experiment with a model micellar solution. The obtained results confirm the main theoretical conclusions of the thermodynamic and kinetic theory of micellization [1-5] and justify the two-flux approximation. Under characteristic conditions, the existence of predicted stages of the relaxation of molecular aggregate distribution into subcritical, critical and micellar domains is demonstrated. The corresponding relaxation times are shown to be in good agreement with theoretical estimations. The role of basic assumptions is studied in order to extend the range of applicability of the theory. The developed numerical algorithm allows to investigate the relaxation of a micellar solution even in the case when the two-flux approximation becomes invalid.

The goal of the work is to study equilibrium and non-equilibrium properties of a micellar solution with the help of analytical and numerical methods and consists of:

- verification of the applicability of the two-flux approximation used to describe the relaxation process in a micellar solution; in particular, the estimation of the true relative error of the classical approximation for the stationary flux (nucleation rate);

- determination in a general form of the dependence of the equilibrium concentrations of monomers and molecular aggregates on thermodynamic parameters of a micellar solution (method of parametric equations);
- elucidation of different stages of the relaxation process, numerical calculation of characteristic relaxation times, and verification of the thermodynamic and kinetic theory of micellization [1-5] in a numerical experiment with a model micellar solution.

Scientific novelty of the work. During the PhD thesis work, the new analytical method has been developed for determination of the dependence of the equilibrium concentrations of monomers and molecular aggregates on thermodynamic parameters of a micellar solution (method of parametric equations). In particular, this method has been applied to determine such dependencies in the case of two practically important models of spherical micelles [7-10]. The deduced functional dependencies have been obtained for the first time.

A numerical algorithm has been developed to study the relaxation processes in a micellar solution which allows to use the finite difference scheme for solution of non-linear differential equations (describing the kinetics in a micellar solution) in the case of very high relaxation times.

Three stages of the relaxation process have been revealed, the corresponding relaxation times have been computed. This analysis can be considered as a first verification of the thermodynamic and kinetic theory of micellization [1-5]. The first stage of the relaxation process has been numerically studied for the first time.

Scientific and practical value of the work consists of the elucidation of predicted stages of the relaxation process in the numerical experiment. The verification of the analytical theory [1-5] in the case of particular models of spherical micelles seems to be practically important. On the one hand, it allows to extend the applicability of the theory by better understanding which conditions are pertinent. On the other hand, the numerical simulation provides a possibility to study the behavior of a micellar solution even in the case when the theory cannot be applied formally. Analytical determination of the dependence of the equilibrium concentrations of monomers and molecular aggregates on thermodynamic parameters of a micellar solution seems to be practically important for comparison of different models of spherical micelles.

Presentation of the work. The main results of the PhD thesis have been presented at two conferences:

- Student conference at Saint Petersburg, 2000:
I.S. Siparov, D.S. Grebenkov *Numerical simulation of the relaxation process of micellar solution*;
- VII Research Workshop “Nucleation Theory and Applications”, Dubna, 2003:
A.P. Grinin, D.S. Grebenkov *Time Evolution of Ensembles of Molecular Aggregates in a Micellar Solution after an Instantaneous Change of the Thermodynamic Parameters*.

These researches have been supported by Russian Foundation for Basic Research (RFFI) (grants 98-03-32009a, 01-03-32334).

Publications. The main results of the PhD thesis have been published in 5 papers.

Structure of the manuscript. The PhD thesis manuscript is divided into Introduction, four Chapters, Conclusion, Appendix and References (61 items). The whole volume of the manuscript is 145 pages including 13 figures and 14 tables.

CONTENTS

The first chapter is written as historical and bibliographical review of the theory of micellar solutions. We discuss the main physico-chemical properties of surfactant molecules, give the qualitative picture of micellization, describe the practically important models of spherical micelles, and outline the brief sketch on thermodynamic and kinetic theory of micellization [1-5]. In other words, the first chapter provides a theoretical background which is used the following. Basing on classical nucleation theory, we use the notion of the aggregation work W_n that is the minimal work required to form an aggregate of n surfactant molecules. This work defines the equilibrium distribution of molecular aggregates $c_n^{(eq)}$ by aggregation numbers n :

$$c_n^{(eq)} = c_1^{(eq)} \exp[-W_n] , \quad (1)$$

where W_n is expressed in units of kT (k is the Boltzmann constant, T is the absolute temperature). Also the aggregation work mainly defines the kinetic behavior of the system through the coefficients in Becker-Döring kinetic equations:

$$\frac{\partial c_n}{\partial t} = j_{n-1}^+ [c_{n-1} - c_n e^{W_n - W_{n-1}}] - j_n^+ [c_n - c_{n+1} e^{W_{n+1} - W_n}] \quad (n \geq 2),$$

where j_n^+ is the number of monomers attached to the aggregate of n surfactant molecules by unit time. These coefficients are proportional to the monomer concentration $c_1(t)$:

$$j_n^+ = q_n c_1(t). \quad (2)$$

It allows to rewrite previous equations as:

$$\frac{\partial c_n}{\partial t} = q_{n-1} c_1(t) c_{n-1}(t) + q_n c_{10} c_{n+1}(t) e^{G_{n+1} - G_n} - c_n(t) [q_n c_1(t) + q_{n-1} c_{10} e^{G_n - G_{n-1}}], \quad (3)$$

where c_{10} is such monomer concentration for which the tangent to function W_n at inflection point is horizontal, and the new function G_n does not depend on the monomer concentration:

$$W_n = G_n - (n - 1) \ln \frac{c_1}{c_{10}} . \quad (4)$$

The micelle aggregation number n_s is defined as minimum point of W_n as function of n , i.e., it is the solution of the equation $\partial W_n / \partial n = 0$:

$$\ln \frac{c_1}{c_{10}} = \left(\frac{\partial G_n}{\partial n} \right)_{|n=n_s} \quad (5)$$

The system of molecular aggregates is supposed to be closed: the total concentration c_{tot} of surfactant molecules (in monomers and molecular aggregates) is constant:

$$\frac{\partial c_{tot}}{\partial t} = 0 \quad \text{where} \quad c_{tot} = \sum_{n=1}^{\infty} n c_n(t). \quad (6)$$

This equation taken together with Becker-Döring kinetic equations (3) completely describes the kinetics of the relaxation process in a micellar solution. One sees that the aggregation work turns out to be the most important characteristics for describing the equilibrium and kinetic properties of spherical micelles. The complexity of the internal structure of molecular aggregates and of physico-chemical processes of attachment/detachment of surfactant molecules does not allow to calculate the aggregation work for the whole range of aggregation numbers. Two model expressions of W_n were found:

- in the framework of the *droplet model* [7,9]:

$$W_n = b_1 n^{4/3} - \left(\frac{4}{3} \sqrt{2b_1 b_3} \right) n + b_3 n^{2/3} - (n-1) \ln \frac{c_1}{c_{10}}, \quad (7)$$

where b_1 and b_3 are parameters of the model related with thermodynamic characteristics of the micellar solution (temperature, pressure, etc.);

- in the framework of the *quasi-droplet model* [8,10]

$$W_n = \frac{b}{2} n^2 - \frac{2a}{3} n^{3/2} + \frac{a^2}{4b} n - (n-1) \ln \frac{c_1}{c_{10}}, \quad (8)$$

where a and b are again parameters of the model.

Expression (8) is a particular case of a more general result obtained in [10].

The common feature of model expressions (7) and (8) is the existence of the maximum W_c of function W_n at point n_c (activation barrier) and the minimum W_s at point n_s (micellar well) under condition $c_1 > c_{10}$. According to usual terminology, all aggregates are divided into subcritical ($n < n_c - \Delta n_c$), critical ($|n - n_c| \leq \Delta n_c$) and supercritical or micellar ($n > n_c + \Delta n_c$), where Δn_c is the half-width of the activation barrier. The micellar well is characterized by its half-width Δn_s . In the framework of the nucleation theory, the process of micelle's formation can be understood as fluctuational overcome of the activation barrier by molecular aggregates and the following accumulation in the micellar well. The decay process is the fluctuational overcome of the activation barrier from the side of the micellar well.

The second chapter begins by deducing the expression for stationary flux $J^{(s)}$ of molecular aggregates (nucleation rate) and its classical approximation $J_a^{(s)}$:

$$J^{(s)} = c_1 \left[\sum_{n=n_c-\Delta n_c}^{n_s-\Delta n_s} \frac{e^{W_n}}{j_n^+} \right]^{-1}, \quad J_a^{(s)} = \frac{c_1 \exp[-W_c]}{\sqrt{\pi} \Delta n_c j_{n_c}^+}. \quad (9)$$

The main attention is paid to the true relative error δ_n of the classical approximation $J_a^{(s)}$ and its analytical estimate δ_a :

$$\delta_n = \frac{|J^{(s)} - J_a^{(s)}|}{J^{(s)}}, \quad \delta_a = \frac{\Delta n_c}{n_c} + \frac{1}{\Delta n_c}. \quad (10)$$

The numerical verification is carried out in the framework of the homogeneous nucleation theory and shows that the true error δ_n is two orders less than its analytical estimate δ_a . This allows to use the classical approximation for stationary flux under weaker assumptions. The application of expression (9) in the micellization theory as a base of the two-flux approximation is discussed.

The third chapter describes an analytical method of parametric equations which allows to determine the dependence of the equilibrium concentrations of molecular aggregates on thermodynamic parameters of a micellar solution. This method is based on the following assumptions:

- general model representation of the aggregation work G_n (i.e. W_n):

$$G_n = \sum_{m=0}^M g_m(a_1, \dots, a_K) n^{m\rho}, \quad (11)$$

where a_1, \dots, a_K are the thermodynamic parameters, g_m are coefficients of this decomposition (dependent on parameters), $\rho > 0$ is the characteristic exponent of the model (for example, one has $\rho = 1/3$ for the droplet model and $\rho = 1/2$ for the quasi-droplet model);

- the aggregation work possesses an essential minimum corresponding to spherical micelles (in particular, the concentration of surfactant molecules in micelles comparable to or greater than the monomer concentration);
- the closure of the system.

The representation of the mass conservation law (6) as an integral of motion in phase space of thermodynamic parameters a_1, \dots, a_K and the use of relation (5) allow to obtain *parametric equations* for the micelle aggregation number n_s as function of thermodynamic parameters a_1, \dots, a_K :

$$\frac{\partial n_s}{\partial a_k} = - \frac{\sum_m g_{m,k}(\rho m - 1) n_s^{\rho m}}{\sum_m g_m \rho m (\rho m - 1) n_s^{\rho m - 1}}, \quad g_{m,k} = \frac{\partial g_m}{\partial a_k} \quad (k = 1 \dots K). \quad (12)$$

Once solving the system of parametric equations for the micelle aggregation number n_s , one finds the dependence of the equilibrium monomer concentration $c_1^{(eq)}$ on thermodynamic parameters of a micellar solution through relation (5). At the same time, one determines the equilibrium concentrations $c_n^{(eq)}$ of molecular aggregates (as function of a_1, \dots, a_K) using (1).

The method of parametric equations has been applied to find the equilibrium monomer concentration in the framework of droplet and quasi-droplet models. In the first case, the parametric equations have been solved exactly, whereas for the second case the accurate approximation was found. Note that the parametric equations themselves have been deduced with the help of certain approximations. As a consequence, these equations and their solutions are approximate ones. The comparison of these approximate but analytical solutions with numerical solutions of equation (6) with respect to $c_1^{(eq)}$ shows that the method of parametric equations provides the highly accurate results.

The fourth chapter is devoted to the study of relaxation processes in a micellar solution perturbed from its equilibrium state by instantaneous change of thermodynamic parameters (e.g., temperature). According to the theoretical predictions [1-5], the transition to a new equilibrium state takes several stages. On the first stage, the distribution of small aggregates in subcritical domain (dimers, trimers, etc.) reaches a quasi-equilibrium state. At the end of this stage, concentrations of small aggregates follow the equilibrium law (1) with current monomer concentration $c_1(t)$:

$$c_n^{(q)}(t) = \exp[-G_n + nc_1(t)] \quad (n \leq n_c - \Delta n_c). \quad (13)$$

On the second stage (“fast” relaxation), the distribution of micellar aggregates is modified in order to follow the shift of the micellar well. This stage is completed by the establishment of a quasi-equilibrium state in the micellar domain. The main parameter that characterizes the second stage is the total number of surfactant molecules in micellar domain:

$$C_M(t) = \sum_{n=n_s-2\Delta n_s}^{n_s+2\Delta n_s} nc_n(t). \quad (14)$$

The most prolonged is the third stage (“slow” relaxation) when the matter is redistributed through the activation barrier. The third stage is completed by the establishment of the final equilibrium state in a micellar solution.

Thermodynamic and kinetic theory of micellization [1-5] provides theoretical formulae for characteristic times: lower and upper estimates for the time of the establishment of a quasi-equilibrium state in domain with aggregation numbers less than n :

$$t_{min}^{(1)}(n) = \frac{e^{W_{n-1}-W_n}}{j_{n-1}^+}, \quad t_{max}^{(1)}(n) = \frac{n e^{W_{n-1}-W_n}}{j_{n-1}^+}; \quad (15)$$

relaxation times for second and third stages:

$$t_{th}^{(2)} = \frac{1}{j_{n_s}^+} \left(\frac{2}{(\Delta n_s)^2} + \frac{c_M}{c_1} \right)^{-1}, \quad t_{th}^{(3)} = \frac{\sqrt{\pi} c_M \Delta n_c \exp[W_c]}{c_1 j_{n_c}^+ (1 + n_s^2 c_M / c_1)} \quad (16)$$

(here c_M is the micelle concentration). One of the main goals of the thesis is the study of this complex many-stage relaxation process using the droplet and quasi-droplet models of spherical micelles. For these purposes, one fixes the values of model parameters (b_1, b_3 for droplet model and a, b for quasi-droplet model) in model expressions (7) and (8). Since physico-chemical processes of attachment-detachment of monomers by molecular aggregate are extremely complex, the dependence of j_n^+ on aggregation number remains unknown. For the numerical experiment the coefficient q_n in relation (2) is supposed to be constant: $q_n \simeq q$. This assumption seems to be quite reasonable for our purposes since a probable dependence of q_n on n oughts to be smooth in comparison with the dependence on n of exponential factors $e^{G_n - G_{n-1}}$ present in Becker-Döring kinetic equations (3). Using dimensionless time $\tau = tqc_{10}$ and measuring all concentrations in units¹ c_{10} , one eliminates coefficients q and c_{10} from kinetic equations (3):

$$\frac{\partial c_n}{\partial \tau} = c_1(\tau)c_{n-1}(\tau) + c_{n+1}(\tau)e^{G_{n+1}-G_n} - c_n(\tau)[c_1(\tau) + e^{G_n-G_{n-1}}]. \quad (17)$$

These equations with the mass conservation law (6) completely describe the kinetics of the relaxation process in a micellar solution. The initial state of the system is taken to be an equilibrium one. An instantaneous change of thermodynamic parameters disturbs the micellar solution that initiates the relaxation process to a new equilibrium state.

Two first stages of the relaxation process are studied with the help of a finite difference scheme. For its practical realization one introduces the supplementary boundary condition $c_{n_{max}}(\tau) = 0$ for sufficiently large n_{max} . As an example of relaxation process, one considers the instantaneous change of parameter a (quasi-droplet model). The following table shows the values of main characteristics of the micellar solution for initial ($a = 1.35$) and final ($a = 1.30$) equilibrium states. The values of parameter b and total surfactant molecules concentration c_{tot} remain constant: $b = 0.1, c_{tot} = 2.1 \cdot 10^{-2}$.

State	a	n_c	n_s	W_c	W_s	c_1	$c_M, \times 10^{-5}$
Initial	1.35	23.7	74.5	20.50	8.54	0.0149527	5.00
Final	1.30	26.0	62.4	20.43	15.66	0.0178011	0.005

The numerical experiment provides the dependence of different concentrations $c_n(\tau)$ on time τ that allows to study the kinetics of the relaxation process and to compute characteristic times for two first stages. Basing on such data, one can proceed the comparative analysis of theoretical predictions obtained in [1-5]. In particular, we confirmed the establishment of a quasi-equilibrium state into

¹Strictly speaking, one needs to use slightly different units c_0 related with c_{10} by simple expression.

subcritical domain at the end of the first stage. Fig.1 shows the dependence of the dimer concentration $c_2(\tau)$ on time τ during the first stage. The solid line represents the computed behavior of this concentration, whereas the dashed line corresponds to the quasi-equilibrium distribution given by (13) with current monomer concentration $c_1(\tau)$.

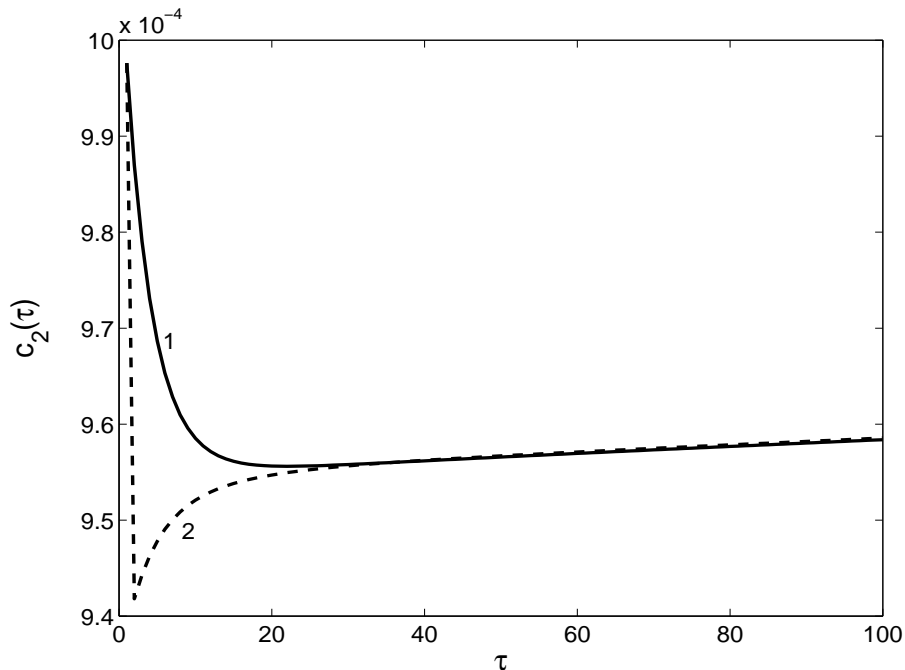


Figure 1. *Dependence of dimer concentration on time during the first stage of the relaxation process.*

The following table contains the values of characteristic times $\tau^{(1)}(n)$ required to reach a quasi-equilibrium state in domain with aggregate numbers less than n , and its analytical lower and upper estimates $\tau_{min}^{(1)}(n)$ and $\tau_{max}^{(1)}(n)$.

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

The characteristic time of the first stage can be then estimated as: $\tau^{(1)} \sim 10^2$.

During the second stage of the relaxation process the quasi-equilibrium state is establishing in the micellar domain, see Fig.2. Enumerated curves represent profiles of molecular aggregate concentrations (dependencies of $c_n(\tau)$ on n) normalized by corresponding quasi-equilibrium concentrations $c_n^{(q)}(\tau)$ for different time moments $\tau_k = 10^k$ with $k = 1, \dots, 7$. Beginning with $k = 4$, the concentration profiles in the micellar domain do not depend on n . That corresponds to the quasi-equilibrium state of micellar aggregates.

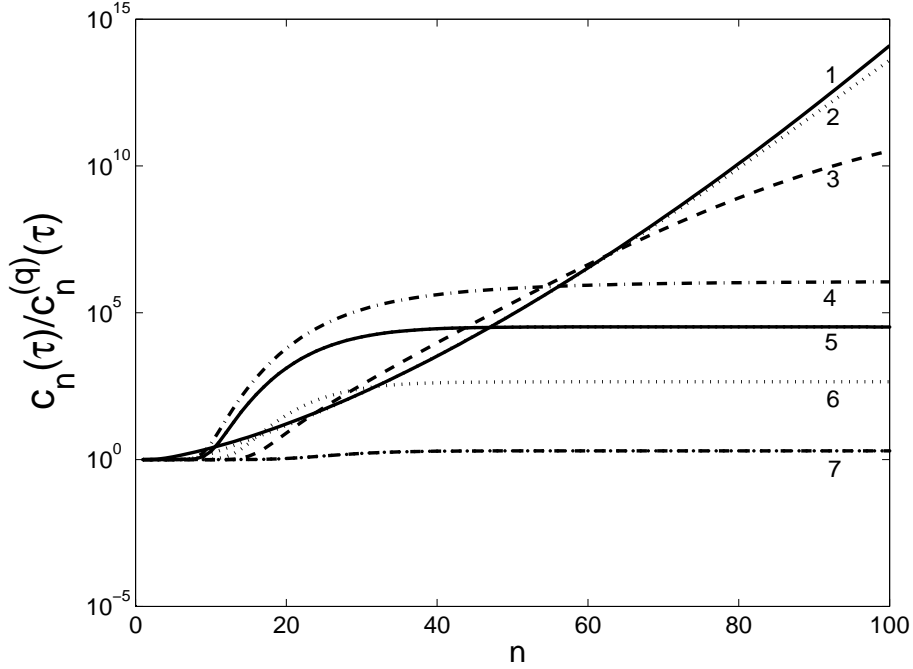


Figure 2. *Molecular aggregate concentrations normalized by corresponding quasi-equilibrium concentrations for different time moments.*

The theoretical expression (16) for the relaxation time of the second stage gives $\tau_{th}^{(2)} \simeq 3200$. The numerical values of this time are calculated under assumption that the total concentration $C_M(\tau)$ of surfactant molecules in micelles tends to its quasi-equilibrium value *exponentially*. It allows to compute $\tau^{(2)}$ knowing $\dot{C}_M(\tau)$ at two different points τ_1 and τ_2 :

$$\tau^{(2)} = \frac{\tau_2 - \tau_1}{\ln[\dot{C}_M(\tau_1)/\dot{C}_M(\tau_2)]},$$

where dot denotes time derivative. The following table shows the numerical values of $\tau^{(2)}$ calculated for several τ_1 and $\tau_2 = \tau_1 + 1000$. If the exponential relaxation completely held, these values would not depend on τ_1 and τ_2 . Note that the numerical values are sufficiently close to the theoretical prediction $\tau_{th}^{(2)}$.

τ_1	1000	2000	3000	4000
$\tau^{(2)}$	2400	2900	3400	3900

The study of the third stage of the relaxation process is complicated by the fact that the characteristic time of this *slow relaxation* is considerably longer than other relaxation times. As a consequence, one cannot apply directly the finite difference scheme since it would lead to extremely long calculations. Therefore we developed the numerical algorithm consisting of several steps:

1. Finite difference scheme is applied to proceed two first stages which finish by quasi-equilibrium state; variations of all concentrations with time become small.

2. Concentration rates are calculated and used for the *linear extrapolation* of concentrations $c_n(\tau)$ for long time periods; in other words, one performs a “time jump”.
3. Finite difference scheme is used again in order to provide a new quasi-equilibrium state of molecular aggregates.
4. Steps 2-3 are repeated several times to reach a required proximity to the final equilibrium state.

“Calming” of the system after the “time jump” is required since the linear extrapolation breaks the quasi-equilibrium state. Indeed, such extrapolation simulates the exchange of surfactant molecules between subcritical and micellar domains (long time process). However, it does not take into account fast relaxation processes responsible for the redistribution of surfactant molecules inside subcritical domain (like first stage) and micellar domain (like second stage). Applying again the finite difference scheme (step 3), one introduces the possibility to realize these fast processes and, consequently, to reach a new quasi-equilibrium state. The efficiency of such “calming” step is based on the hierarchy of time scales established by thermodynamic and kinetic theory of micellization [1-5] and checked by the present numerical experiment.

The described numerical algorithm allows to study in details the third stage of the relaxation process and to compute corresponding relaxation time. As for the two first stages the theoretical prediction of the third relaxation time $\tau^{(3)}$ is found to be sufficiently close to its numerical value. For a chosen numerical experiment, formula (16) gives $\tau_{th}^{(3)} = 1.9 \cdot 10^6$, whereas numerical data are shown in the following table. Since all concentrations tend to their equilibrium values, the numerical values shown in the table do not vary considerably.

$\tau_1, \times 10^6$	2	3	4	5	6
$\tau^{(3)}, \times 10^6$	1.64	1.80	1.89	1.94	1.97

This calculation has been made under assumption that the monomer concentration tends to its equilibrium value exponentially. The relaxation time has been computed with two different points τ_1 and $\tau_2 = \tau_1 + 10^6$ according to

$$\tau^{(3)} = \frac{\tau_2 - \tau_1}{\ln[(c_1(\tau_1) - c_1^{(eq)})/(c_1(\tau_2) - c_1^{(eq)})]} .$$

In the fourth chapter we discuss also the role of preliminary stage of micelle formation which becomes important under certain conditions [4].

The numerical experiment can be realized for different model micellar solutions. All of them are characterized by dependence of the aggregation work W_n and

coefficient q_n on the aggregation number n . For example, the relaxation processes have been studied not only within the quasi-droplet model, but also in the framework of the droplet model. In the last case the model expression (7) has been used instead of (8).

The important advantage of the numerical simulation is the possibility to describe the kinetics of a micellar solution even in the case when the thermodynamic and kinetic theory of micellization [1-5] cannot be applied. In particular, it allows to study the range of applicability of the theory and to understand which conditions and limitations are really essential. For example, the numerical simulation shows that the theory still works for relative height of activation barrier $\Delta W = W_c - W_s$ even of the order of 1, whereas the formal condition requires $\Delta W \gg 1$. This provides an extension of the range of applicability of the theory [1-5].

In **Conclusion** we evaluate the obtained results and discuss the possible perspectives of further development in this field. **Appendix** describes the kinetic approach developed by Aniansson and Wall [11] which was used as a base for the successive theories of relaxation of micellar solutions.

Author's publications on the subject of the PhD thesis:

1. D.S. Grebenkov, A.P. Grinin, F.M. Kuni *Numerical verification of the accuracy of some analytical results in the nucleation theory*, Vestnik Sankt-Peterburgskogo Universiteta, Series 4, **2** (11), 3-10 (1999).
2. I.S. Siparov, D.S. Grebenkov *Numerical simulation of the relaxation process of micellar solution*, Proceedings of the student conference, Saint Petersburg, 18-20 october (2000).
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4. D.S. Grebenkov *Parametric Equations of the Theory of Formation of Spherical Micelles*, J.Coll.Int.Sci. **249**, 162-171 (2002).
5. A.P. Grinin, D.S. Grebenkov *Study of Relaxation in Micellar Solution by the Numerical Experiment*, Colloid Journal **65** (5), 552-561 (2003) (pages 603-613 in russian version).

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8. A.P. Grinin *Model of Accounting of Hydrophobic and Hydrophilic Effects in Thermodynamics of Spherical Micelles with Moderate Aggregation Numbers*, Vestnik Sankt-Peterburgskogo Universiteta, Series 4, **1** (4), 3-9 (1996).
9. A.I. Rusanov, A.P. Grinin, F.M. Kuni, A.K. Shchekin *Nano-Structural Models of Micelles and Pre-Micellar Aggregates*, Zhurnal Obshey Khimii **72** (4), 651-666 (2002).
10. A.P. Grinin, A.I. Rusanov, F.M. Kuni, A.K. Shchekin *Thermodynamic Characteristics of Spherical Molecular Aggregates at Quasi-Droplet Model*, Colloid Journal **65** (2), 168-177 (2003).
11. E.A.G. Aniansson, S.N. Wall *On the Kinetics of Step-Wise Micelle Association*, J.Phys.Chem. **78** (10), 1024 (1974).