ANNOTATION OF SCIENTIFIC WORKS,

included in the series "The kinetic theory of micelle formation and relaxation in solutions of non-ionic surfactants" by Corr.-member of RAS, Professor Alexander Kimovich Shchekin, professor, Head of the Statistical Physics Department of SPbU and Professor Loran Tsolakovich Adzhemyan, professor of the Statistical Physics Department of SPbU submitted for the SPbU prize for fundamental achievements in science in 2021

In the first paper of the series (A.K. Shchekin, I.A. Babintsev, L.Ts. Adzhemyan. Full-time kinetics of self-assembly and disassembly in micellar solution via the generalized Smoluchowski equation with fusion and fission of surfactant aggregates. Journal of Chemical Physics, 2016, v. 145, 174105), the kinetics of self-assembly and disassembly of spherical micelles during their fusion and fission in non-ionic micellar solutions was considered in detail for all time scales on the basis of direct numerical solutions of the generalized Smoluchowski equations describing the evolution of time-dependent concentrations of molecular aggregates for each aggregation number. Cases of an instant increase in the monomer concentration or dilution of the surfactant solution below the critical micelle concentration at large initial deviations from the final equilibrium state have been studied. All stages of evolution of micelles have been described and compared with the results of the molecular mechanism with stepwise addition-detachment of a surfactant monomer described by the Becker - Döring kinetic equations.

In the second paper in the series (I.A. Babintsev, L.Ts. Adzhemyan, A.K. Shchekin. Extension of the analytical kinetics of micellar relaxation: improving a relation between the Becker-Döring difference equations and their Fokker-Planck approximation. Physica A: Statistical Mechanics and its Applications, 2017, v. 479, pp. 551–562), the transition from the infinite set of the Becker - Döring difference equations to a single Fokker - Planck type differential equation for the distribution of aggregates over the aggregation numbers has been analyzed in describing the fast relaxation of micellar systems. It is shown within the framework of perturbation theory, that taking into account the corrections to the kinetic equation created by second derivatives in the transition from differences to differentials and by deviations of the aggregation work from the parabolic shape in the vicinity of the minimum work, removes the degeneracy of the eigenvalues and noticeably improves the agreement of the largest time of fast relaxation with the results of the numerical solution of the linearized Becker - Döring difference equations.

In the third paper in the series (L.Ts. Adzhemyan, A.K. Shchekin, and I.A. Babintsev. The “Fine Structure” of the Slow Micellar Relaxation Mode and the Aggregation Rates in the Range between a Potential Hump and Well in the Work of Aggregation. Colloid Journal, 2017, v. 79, No. 3, pp. 295–302), an analytical expression was found for the quasi-stationary size distribution of surfactant aggregates which establishes at the stage of slow relaxation of the micellar system. The obtained expression takes into account the change in the concentration of monomers in the course of slow relaxation and reveals a previously unknown fine structure of the slow relaxation mode, i.e., its dependence on the aggregation numbers in the interval between the maximum and minimum of the aggregation work. In turn, the expression found for the relaxation mode makes it possible to refine a similar “fine structure” of the aggregation rates at different points of the same interval between the maximum and minimum of the aggregation work, where the aggregation rates exhibit non-monotonic behavior. The results are confirmed by the numerical solution of the set of the Becker - Döring difference kinetic equations.

Fourth paper in the series (A.K. Shchekin, L.Ts. Adzhemyan, I. A. Babintsev, and N.A. Volkov. Kinetics of Aggregation and Relaxation in Micellar Surfactant Solutions. Colloid Journal, 2018, v. 80, No. 2, pp. 107–140) presents a review of kinetic theory of aggregation and relaxation in micellar solutions of surfactants since the beginning of the 90s to the present. The results obtained on the basis of the analytical and direct numerical solution of the Becker – Döring kinetic equations and the generalized Smoluchowski equations describing general mechanisms of aggregation and relaxation at all time scales are considered in detail: from ultrafast relaxation when quasi-equilibrium is established in the region of subcritical molecular aggregates to the final stage of slow relaxation micelles to the final aggregative

equilibrium. On the basis of droplet and linear in the number of aggregation models for micelles, the linear and nonlinear in deviations from equilibrium dynamics of rearrangement of micellar systems consisting of only spherical, only cylindrical and coexisting spherical and cylindrical systems is described. A review of the results of molecular modeling of the kinetics of rearrangement of micellar systems after an initial perturbation is given.

In the fifth paper in the series (L.V. Adzhemyan, T.L. Kim, and A.K. Shchekin. The Stage of Ultrafast Relaxation in Micellar Surfactant Solutions. Colloid Journal, 2018, v. 80, No. 3, pp. 243–247), the stage of ultrafast relaxation in micellar solutions of surfactants, which ends with the establishment of a quasi-equilibrium distribution in the premicellar region of aggregate sizes, is considered separately. This is done by analyzing the spectrum of the eigenvalues of the matrix of kinetic coefficients of the set of the linearized Becker – Döring difference equations, which describes the total multistage relaxation in a micellar system. The first of the eigenvalue values ordered in ascending order is equal to zero (infinite relaxation time), which corresponds to the law of conservation of the amount of surfactant. The second value is very small, it differs by several orders of magnitude from subsequent values and determines the reciprocal slow relaxation time. The remaining eigenvalues describe fast relaxation processes and include the contribution of relaxation from both the micellar region of aggregate sizes and the premicellar region. In this part of the spectrum, it is possible to highlight the contribution of ultrafast relaxation processes. This result is confirmed by an analysis of the spectrum of relaxation times of premicellar aggregates only, considered to be a closed system. It is also shown that the spectrum of ultrafast relaxation times is determined mainly by the first diagonal elements of the matrix of linearized Becker – Döring equations and can be described analytically.

In the sixth paper in the series (I.A. Babintsev, A.K. Shchekin, L.Ts. Adzhemyan. Numerical Solution of Smoluchowski Generalized Equations for Cylindrical Micelles. Colloid Journal, 2018, v. 80, No. 5, pp. 459–466), a numerical study of the relaxation kinetics of polydisperse cylindrical micelles with different initial conditions corresponding to rapid concentrating and dilution of the surfactant solution has been carried out. The kinetic description was based on the system of generalized difference equations of Smoluchowski, which takes into account both the capture and emission of surfactant monomers by micelles and the fusion and fission of micelles. The dependences of the fusion coefficients for cylindrical aggregates on the aggregation numbers were constructed on the basis of the Burgers – Oseen formulas for the translational motion of spherocylindrical particles in a viscous fluid. The obtained solution of the set generalized Smoluchowski kinetic equations in the form of the nonequilibrium distribution over the aggregation numbers of cylindrical micelles was compared with the numerical solution of the Becker – Döring kinetic equations for cylindrical micelles with the same initial conditions at the molecular mechanism of aggregation through the capture and emission of surfactant monomers.

In the seventh paper in the series (L.Ts. Adzhemyan, Yu.A. Eroshkin, A.K. Shchekin, I.A. Babintsev. Improved kinetic description of fast relaxation of cylindrical micelles. Physica A: Statistical Mechanics and its Applications, 2019, v. 518, n. 15, pp. 299-311), based on the linearized analytical and numerical kinetic description of the molecular mechanism of aggregation, hierarchical relaxation times were found for a polydisperse micellar system. The description was based on the Becker – Döring difference and differential kinetic equations with using a fitted boundary condition and improved models for the rate of addition of surfactant monomers to cylindrical aggregates. Two such models were considered: a linear model for the rate of attachment to cylindrical aggregates and a model for the rate of attachment to elongated spheroidal aggregates. The rate of attachment of monomers to an elongated spheroidal aggregate was found explicitly as a function of the aggregation number. An analytical solution of the differential kinetic equations for the fast relaxation of polydisperse micellar systems was obtained for a linear model of the aggregation rate. In the case of the rate of attachment to an elongated spheroidal aggregate, a new semi-analytical solution was found.

Eighth work in the series (L.T. Adzhemyan, Y.A. Eroshkin, I.A. Babintsev, A.K. Shchekin. Analytical description of the molecular mechanism of fast relaxation of spherical micelles with the extended Becker – Döring differential equation. Journal of Molecular Liquids, 2019, v. 284, pp 725-734)

improves and expands the kinetic analysis of fast relaxation in an ensemble of spherical micelles in surfactant solutions with a general scheme for reducing the set of linearized Becker - Dering difference equations to a single differential equation of arbitrary order in terms of the aggregation number. The perturbation theory was formulated for any model of spherical micelles, where the main approximation corresponds to the Aniansson kinetic equation for the case of a symmetric potential well of the aggregation work, and the perturbation operator is written in the Hermitian form. The latter allows one to use standard perturbation methods to find fast relaxation times with the help of the extended differential kinetic equation. The calculations were performed in the second order of perturbation theory, and the longest fast relaxation times were found in their dependence on the surfactant concentration for the droplet and quasi-droplet models of direct spherical micelles and the star model of diblock-polymer spherical micelles. In the case of the droplet model, the corrections give the concentration dependence of the longest fast relaxation time, which practically coincides with the results of the numerical solution of the system of linearized Becker - Dering difference equations. For the quasi-droplet model, the fast relaxation times found in the main approximation deviate significantly from the numerical result (up to 50%). Adding corrections allows one to reduce these deviations to a much smaller value (up to 10%). Good agreement between the analytical and numerical solutions was obtained for the star micelle model.

In the ninth paper in the series (L.V. Adzhemyan, Yu.A. Eroshkin, T.L. Kim, and A.K. Shchekin. A Numerical Description of Fast Relaxation in Micellar Solutions on the Basis of the Spherocylinder Model. Colloid Journal, 2019, Vol. 81, No. 3, pp. 205–210), based on the results obtained in the seventh work from the series, a semi-analytical method for calculating the fast relaxation time in solutions with cylindrical micelles was developed, which allows significantly reducing the calculation procedure without loss of accuracy. For the kinetic coefficients of the addition of monomers to the aggregate, a micelle model in the form of an elongated ellipsoid has been used, for which the problem of finding the diffusion flux of monomers per micelle has an analytical solution. Also numerical calculations of the diffusion flux and fast relaxation time for a more realistic model of a micelle in the form of a spherocylinder have been performed.

It was shown in the last paper in the series (Yu. A. Eroshkin, L. Ts. Adzhemyan, A. K. Shchekin. General approach to the description of fast relaxation taking into account the specifics of micellar models. Colloid Journal, 2020, Volume 82, No. 5, p. 560 –568), that when passing from the finite-difference Becker – Döring equations to a single differential kinetic equation for the aggregation distribution function of aggregates, the magnitude of errors in calculating the fast relaxation times of a micellar solution is associated with the use of an approximation for the behavior of the aggregation work in the vicinity of its minimum. The approach developed in this paper (based on perturbation theory) allows one to take into account, in the main order, the possible significant asymmetry of the aggregation work in the vicinity of its minimum. The obtained values of a number of characteristic fast relaxation times show a noticeable improvement in accuracy. The advantages of this approach are its ease of use and versatility, the possibility of applying both to spherical direct and reverse micelles, and to cylindrical micelles. In this case, the complexity of the method does not depend on the explicit specification of the used aggregation work and the attachment coefficients as functions of the aggregation number.