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Influence of the Structure of Cetyltrimethylammonium Bromide Based Microemulsions on Base Hydrolysis of Carboxylic Acid Esters

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Abstract—The structure of water/cetyltrimethylammonium bromide/*n*-butanol/hexane microemulsions was studied by conductometry, viscometry, and Fourier transform ^{1}H NMR spectroscopy with pulse magnetic field gradient. The regions of phase inversion from inverse micelles in hexane through a bicontinual structure to a dispersion of normal micelles in water were determined. The influence of the structure of the microemulsions on the rate of hydrolysis of carboxylic acid *p*-nitrophenyl esters was analyzed. The hydrolysis rate constants considerably increase in going from inverse to normal microemulsions.

A specific feature of microemulsions containing a large amount of cationic surfactants is the possibility of varying the component ratio in the system in a wide range. In so doing, the structure and properties of microemulsions change essentially, and the phase inversion and rearrangement of the interface take place. Transitions are possible from inverse microemulsions (water microdroplets dispersed in nonpolar solvents and stabilized by a layer of surfactants and cosurfactants) to bicontinual systems in which the surfactant molecules form a three-dimensional network and water and oil form two continuous phases and then to normal microemulsions (oil microdroplets in water). In such transitions, the system remains macrohomogeneous and optically transparent; it preserves high solubilizing power toward both polar and nonpolar substances [1–3].

The latte fact is extremely important when a microemulsion is used as a medium for chemical processes, ensuring efficient contact of reactants that differ in the solubility in water and in organic solvents. Localization of the reactants in the system and their microenvironment depend on the type and properties of microemulsions. By varying the ratio of the dispersed phase and dispersion medium, it is possible to vary the site of localization of the reaction event and reaction partners and thus to control the rate and mechanism of chemical processes [4, 5].

To reveal the influence exerted by the structure of the reaction medium on the rate of nucleophilic substitutions, we studied base hydrolysis of carboxylic acid *p*-nitrophenyl esters in water/cetyltrimethylammonium bromide/*n*-butanol/*n*-hexane microemulsions under the conditions of phase transitions initiated by variation of the water : oil ratio. The structure of the microemulsions was studied by a set of physical methods allowing determination of the ranges of phase inversion in the system.

One of the best ways to monitor structural transitions in microemulsions is measuring their electrical conductivity [6–10]. The possible sources of free charges in the aqueous phase are charged head groups of ionic surfactants, their counterions, or ionic additives. The conductivity of the oil phase is lower than that in water by several orders of magnitude. For water/oil microemulsions, the main charge carriers are inverse micelles dispersed in the organic phase. For a number of water/oil microemulsions, small variations of parameters (e.g., variations of component concentrations or temperature) cause a dramatic (by up to 4–5 orders of magnitude) increase in the electrical conductivity (percolation) caused by increased efficiency of intermicellar exchange, primarily with water and dissolved ions, on short agglutination in the course of clusterization [11–13]. Another possible way of realization of percolation transitions is formation of bicontinual structures with long water channels along

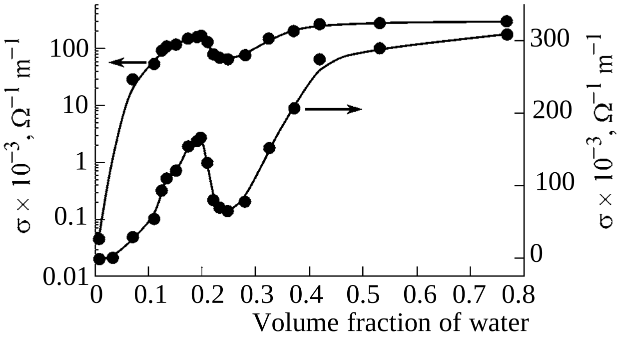

Fig. 1. Electrical conductivity of the microemulsion based on cetyltrimethylammonium bromide as a function of the water content.

which the charge can be transferred [6]. Depending on the microemulsion morphology, both mechanisms of the electrical conductivity may be operative; this is primarily determined by the nature of the surfactant (structure of the polar head group, site of the charge localization, length of the hydrocarbon radical), presence and type of a cosurfactant, temperature, etc. Furthermore, a bicontinual structure can form beyond the range of percolation transition [7].

Figure 1 shows the electrical conductivity data for the microemulsions based on cetyltrimethylammonium bromide. The conductivity σ of water/oil microemulsions is determined by the diffusion of microdroplets bearing an noncompensated fluctuation electric charge [8, 9]:

$$\sigma = \frac{\varepsilon_0 \varepsilon k_B T}{2\pi\eta}\frac{\Phi}{r^3}, \tag{1}$$

where ε_0 8.85×10^{-11} F m^{-1} is the dielectric constant; ε, dielectric permittivity of the organic medium; k_B, Boltzmann constant; *T*, absolute temperature; η, viscosity of the organic medium; *r*, hydrodynamic radius of micelles; and Φ, volume fraction of microdroplets in the system.

For the most dilute water/oil microemulsion with the volume fraction of water in the system Φ_w 0.01, using Eq. (1), we estimated the size of microdroplets, which appeared to be 5.3 nm. This is quite reasonable, as the length of the cetyltrimethylammonium bromide molecule is ~2.5 nm [14] and microdroplets also contain water and butanol molecules. In calculations, we assumed that butanol is incorporated in micelles incompletely; as ε and η, we took the corresponding values for hexane.

As the concentration or size of microdroplets increases, their density in the oil medium and the probability of collisions grow. At a definite concentration of the dispersed phase, the microdroplets form a cluster, creating a route for charge transfer between the electrodes; as a result, the electrical conductivity sharply increases [8, 11, 13]. Figure 1 shows that the conductivity of the microemulsion increases by four orders of magnitude in the range of low water concentrations, which is typical of manifestation of percolation in inverse micelle dispersions. As the water concentration is increased further, the electrical conductivity (Fig. 1) shows characteristic features apparently reflecting changes in the microemulsion structure. However, the conductivity data alone do not furnish unambiguous structural information. In this work, to elucidate the structure of the reaction medium, we also used viscometry and Fourier transform ^{1}H NMR spectroscopy with pulse magnetic field gradient. At the same time, the conductometric method is extremely illustrative and allows the more labor-consuming methods to be used more purposefully.

To determine the diffusion coefficients *D* of microemulsion components, we used the strongest signals in the ^{1}H NMR spectra. The diffusion coefficients of water and butanol were determined, respectively, from the signals of water protons (4.80 ppm) and α-CH_2 protons of butanol (3.76 ppm). For cetyltrimethylammonium bromide, we chose the proton signal of its head CH_3 groups, shifted to 3.43 ppm owing to interaction with the positively charged nitrogen atom. The signals of the $(CH_2)_n$ protons of hexane overlap with the related signals of cetyltrimethylammonium bromide and butanol. At a high content of hexane, the diffusion decays of the proton signals of the $(CH_2)_n$ groups of different components (1.47 ppm) are well resolved. At the minimal content of hexane (Φ_w 0.77), the diffusion coefficient of hexane coincides with that of cetyltrimethylammonium bromide (D_{CTAB}). The diffusion coefficients obtained are listed in the table.

Using the modified Stokes–Einstein relationship [Eq. (2)] taking into account direct collisions between microdroplets, we determined from the diffusion coefficients the mean hydrodynamic radii *r* of microdroplets in two microemulsions characterized by Φ_w 0.01 and 0.77.

$$D_{CTAB} = \frac{k_B T}{6\pi\eta r}(1 - 2\Phi). \tag{2}$$

As η we took the viscosity of the pure solvent (water or hexane) forming the dispersion medium in each specific case. We found that, for inverse micelles (Φ_w 0.01), *r* 4.9 nm, which is well consistent with the value obtained conductometrically. The mean hydrodynamic radius of direct micelles (Φ_w 0.77) appeared to be 3.2 nm, which is close to the previously obtained result for the similar microemulsion based on cetylpyridinium bromide [15]. Thus, in the extreme points of the concentration range studied, the microemulsion structure can be described as aqueous and organic microdroplets stabilized by a layer of the surfactant and dispersed in the medium of the opposite polarity.

The range of transition of the solvents (water or hexane) from the dispersed state to the bulk phase can be clearly traced in Fig. 2. The D/D_0 plots (Fig. 2a), where D_0 is the self-diffusion coefficient of the corresponding pure solvent, reflect the set of factors affecting the diffusion of the solvents. On the one hand, as the micelles grow in size, their diffusion mobility and hence the mobility of the encapsulated solvent should decrease. On the other hand, the probability of exchange between micelles with their contents should simultaneously increase, thus promoting the diffusion of the encapsulated solvent [13]. As the dispersed phase concentratin increases, the hindrance to motion of the dispersion medium grows. At a high concentration of the dispersed phase, when the diffusion mobility of molecules of both solvents could be expected to decrease, formation of a bicontinual structure, relatively open for the diffusion transport of both water and hexane, is probable. Furthermore, the partial mutual solubility of the two liquids (though low) should be taken into account. From the viewpoint of variation of the diffusion coefficients, the critical region is Φ_w ~0.25 for water and Φ_w 0.42–0.5 for hexane.

As compared to diffusion data, changes in the widths of the resonance lines (Fig. 2b) are more pronounced. As the water fraction is increased to Φ_w 0.2–0.25, the size of inverse micelles increases owing to the growth of their aqueous cores, and the water in these cores only slightly differs in the characteristics from the bulk water. At Φ_w 0.2–0.25, water, apparently, gets into the network of narrow channels of the bicontinual structure; the surface of these channels strongly affects averaging of the dipole interaction of water protons, which is manifested in broadening of the line at 4.8 ppm. In the same concentration range, the resonance line of the $(CH_2)_n$ protons broadens jumpwise (Fig. 2b), but the amplitude of this effect is relatively low because of fairly large width of this line even at Φ_w 0.01 (reference value) and redistribution of contributions to this line from cetyltrimethylammonium, hexane, and butanol with changing composition.

In the same concentration range, the microemulsion viscosity dramatically grows (Fig. 2b), which also suggests formation of a bicontinual structure stabilized with cetyltrimethylammonium bromide and butanol throughout the volume of the system. Combined analysis of the plots in Fig. 2 suggests that the microemulsion in the range Φ_w 0.01–0.2 corresponds to dispersion of inverse micelles in hexane; in the range of Φ_w 0.2–0.25, it transforms into a bicontinual structure which is preserved up to Φ_w 0.4–0.5; and at higher water content, a normal microemulsion is formed.

Diffusion coefficients of microemulsion components

Volume fraction of water	$D_{CTAB} \times 10^{10}$, $m^2\ s^{-1}$	$D_{butanol} \times 10^{10}$, $m^2\ s^{-1}$	$D_{water} \times 10^{10}$, $m^2\ s^{-1}$	$D_{hexane} \times 10^{10}$, $m^2\ s^{-1}$
0.035	0.95	10.0	2.4	32.0
0.19	1.08	8.5	6.4	25.0
0.25	–	–	9.4	20.0
0.28	1.48	8.7	10.2	19.0
0.42	1.01	4.6	12.2	10.5
0.53	0.70	6.3	14.4	0.66
0.77	0.31	4.0	14.4	0.41

The microemulsions in hand were studied as a medium for base hydrolysis of carboxylic acid *p*-nitrophenyl esters:

$$RC(O)OC_6H_4NO_2 + 2OH^- \longrightarrow RC(O)O^- + {}^-C_6H_4NO_2,$$
$$R = CH_3,\ C_{11}H_{23}.$$

The observed rate constants of the hydrolysis (k_{obs}) in the microemulsions linearly depend on the concentration of hydroxide ions. Some examples are shown in Fig. 3.

The plot of k_{obs} of hydrolysis vs. volume fraction of water at 0.01 M alkali content in the microemulsion (Fig. 4) consists of three pronounced regions whose boundaries are close to the points of transition from inverse microemulsions to bicontinual structures (Φ_w 0.25) and then to normal microemulsions. Variation of k_{obs} caused by structural rearrangements is a resultant of several oppositely acting effects. On the one hand, the alkali concentration in the aqueous phase changes: in going from the microemulsion with Φ_w 0.75 to that with Φ_w 0.14, the content of hydroxide ion increases by a factor of ~5. This makes an appreciable positive contribution to the hydrolysis rate constant in the case of microemulsions with a low water content. On the other hand, in normal microemulsions the transfer of the substrate encapsulated in oil microdroplets of radius 3.2 nm to the interface on which the reaction with OH^- takes place occurs more readily than in the systems where oil forms a bulk phase. Also, with an increase in the water content in the system, the polarity of the medium in the site of the reaction event can increase, which is a favorable factor for S_N2 reactions such as the base hydrolysis studied in this work.

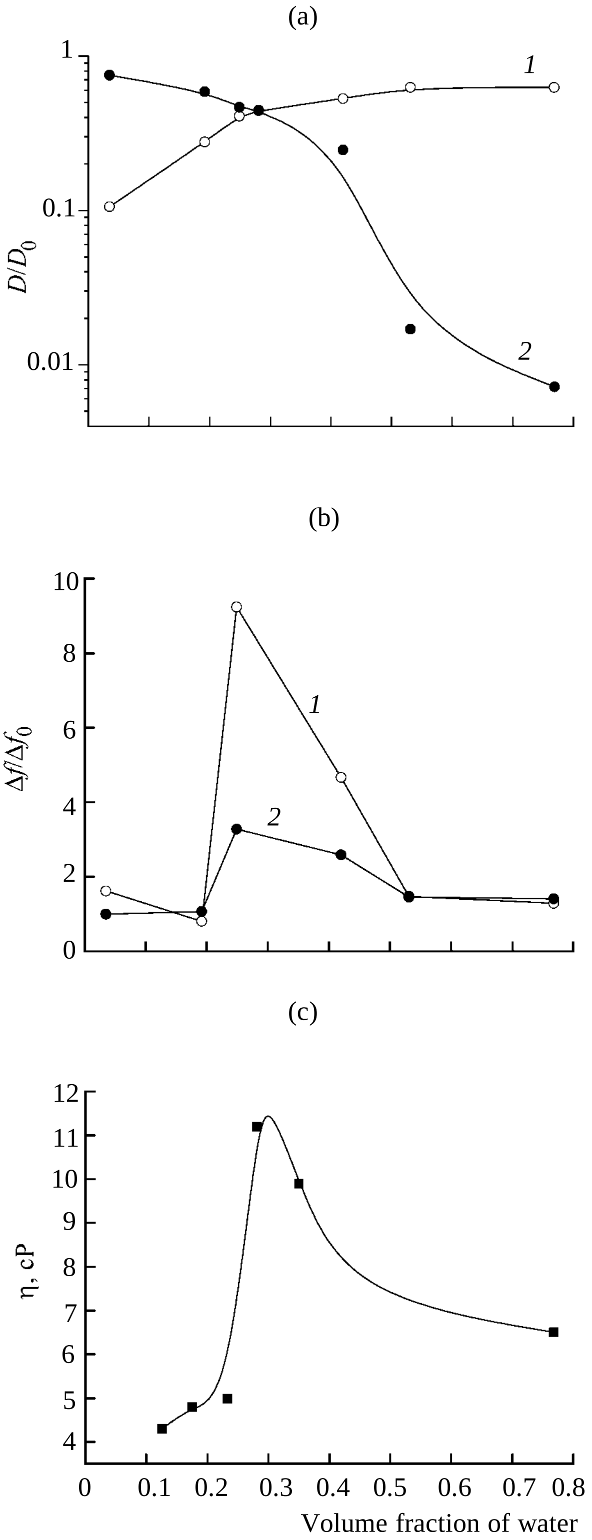

Fig. 2. (a) Diffusion coefficients of (*1*) water and (*2*) hexane (relative to those in the respective pure solvents), (b) width of the resonance lines of (*1*) water protons and (*2*) $(CH_2)_n$ protons (total of signals of hexane, cetyltrimethylammonium bromide, and butanol) relative to the width at Φ_w 0.01, and (c) microemulsion viscosity, as functions of the volume fraction of water.

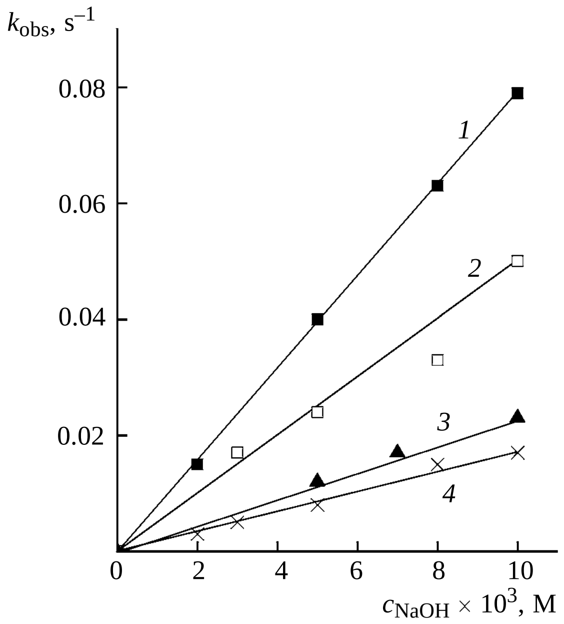

Fig. 3. Observed rate constant of hydrolysis of carboxylic acid esters in various microemulsions as a function of alkali concentration: (*1*) *p*-nitrophenyl acetate, Φ_w 0.74; (*2*) *p*-nitrophenyl acetate, Φ_w 0.35; (*3*) *p*-nitrophenyl acetate, Φ_w 0.14; and (*4*) *p*-nitrophenyl laurate, Φ_w 0.74.

When the alkali concentration in the aqueous phase is made constant, it becomes possible to reveal the effect of the microenvironment of the reactants on k_{obs} (Fig. 4). The laurate appears to be more sensitive to structural rearrangements as compared to its short-chain homolog: In going from a microemulsion with the lowest water content to that with the highest water content, the hydrolysis rate constant increases by ~1 order of magnitude in the case of *p*-nitrophenyl acetate and by ~2 orders of magnitude in the case of *p*-nitrophenyl laurate. The chosen esters differ in their hydrophobicity: The distribution constant between oil and water is 10.8 for the acetate and 205.4 for the larate [4]. Presumably, the laurate is localized in the oil phase, and the acetate, closer to the surface layer. The microenvironment of the acetate changes less strongly, compared to the laurate, with structural transformations of the microemulsions, which is reflected in the hydrolysis rate constants. Also, it should be taken into account that significant changes in the viscosity, accompanying the structural transformations, can also contribute to the hydrolysis rate in the form of the diffusion constituent; its role is especially significant in bicontinual microemulsions [1].

Thus, combined use of conductometry, viscometry, and NMR spectroscopy allowed evaluation of a num-

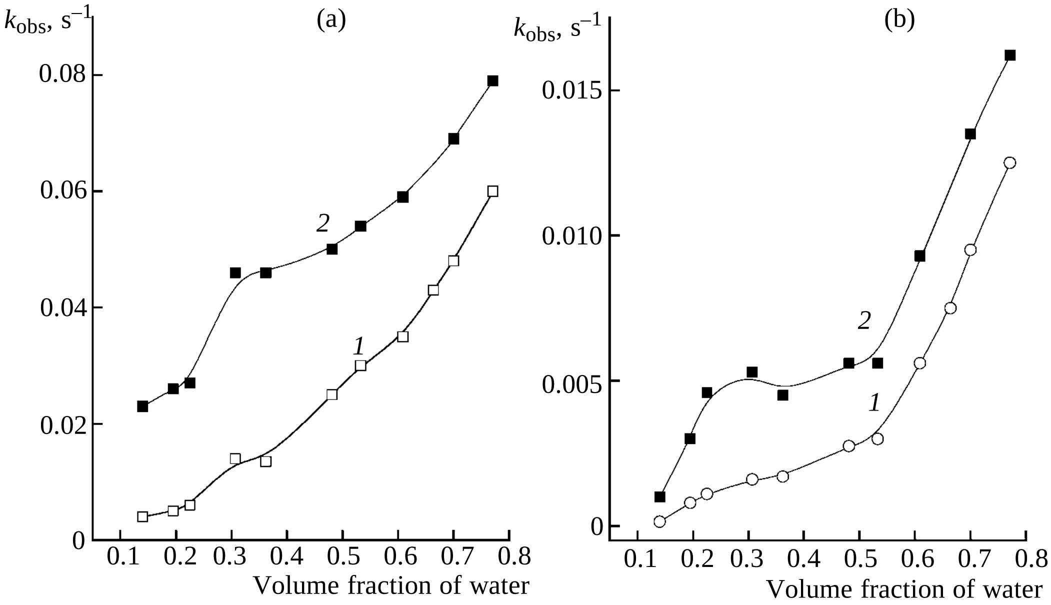

Fig. 4. Observed rate constant of hydrolysis of (a) *p*-nitrophenyl acetate and (b) *p*-nitrophenyl laurate as a function of the volume fraction of water in microemulsions at constant concentration of alkali (0.01 M) in the (*1*) microemulsion and (*2*) aqueous phase.

ber of characteristic parameters of microemulsions based on cetyltrimethylammonium bromide at widely varied hexane/water ratio and determination of the range of transition from inverse microemulsions to bicontinual systems and then to normal microemulsions. Variation of the rate of the base hydrolysis of carboxylic acid *p*-nitrophenyl esters is associated with structural rearrangements of the microemulsions: The reaction rate considerably increases in going from inverse to normal microemulsions, which is determined by the site of reactant localization in the system.

EXPERIMENTAL

Phase inversion in microemulsions based on cetyltrimethylammonium bromide (Merck) was studied at 20°C. As the medium we chose a system containing 0.942 g of cetyltrimethylammonium bromide and 0.942 g of butanol (molar ratio of surfactant to cosurfactant 1 : 5), with which the phase separation on successive variation of the water : hexane ratio within wide limits could be avoided. In NMR experiments, we used D_2O (Aldrich) instead of double-distilled water.

The electrical conductivity was measured with a Radelkis OK-102/1 conductometer (Hungary) at frequencies of 80 Hz and 3 kHz in a temperature-controlled plane-parallel cell. The viscosity was measured with a capillary Ostwald viscometer.

The molecular structure of microemulsions was studied by Fourier transform ^{1}H NMR spectroscopy with pulse magnetic field gradient [16, 17]. Diffusion measurements were performed with a modified Tesla BS-587A NMR specrometer at a proton resonance frequency of 80 MHz. The spectrometer was equipped with a unit generating a pulse magnetic field gradient of up to 50 G cm^{-1}.

For kinetic studies, we used carboxylic acid *p*-nitrophenyl esters purified by common procedures. The reaction kinetics was studied spectrophotometrically in freshly prepared microemulsions in temperature-controlled cells of a Specord UV-Vis device. The reaction progress was monitored by variation of the optical density of the solutions at 400 nm (formation of *p*-nitrophenolate anion). The initial concentration of the substrate was 5×10^{-5} M; the reaction was performed to >90% conversion.

The observed pseudo-first-order rate constants (k_{obs}) were determined by least-squares treatment of the dependence $\log(D_\infty - D_\tau) = -0.434k_{obs}\tau + \text{const}$, where D_τ and D_∞ are the solution optical densities at moment τ and after reaction completion, respectively.

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REFERENCES

1. *Microemulsions: Structure and Dynamics*, Friberg, S.E. and Bothorel, P., Eds., Boca Raton: CRC, 1987.
2. *Micellization, Solubilization, and Microemulsions: Proc. Symp. on Micellizaiton, Solubilization, and Microemulsions* (Albany, 1976), Mittal, K.L., Ed., New York: Plenum, 1977.
3. Matveenko, V.N., Svitova, T.F., and Volchkova, I.L., *Vestn. Mosk. Gos. Univ.*, 1996, vol. 37, no. 2, p. 99.
4. Bhattacharya, S. and Senhalatha, K., *J. Chem. Soc., Perkin Trans. 2,* 1996, no. 9, p. 2021.
5. Mirgorodskaya, A.B., Kudryavtseva, L.A., Zuev, Yu.F., Idiyatullin, B.Z., and Fedotov, V.D., *Mendeleev Commun.*, 2000, no. 5, p. 205.
6. Borcovec, M., Eicke, H.-F., Hammerich, H., and Das Gupta, B., *J. Phys. Chem.*, 1988, vol. 92, no. 1, p. 206.
7. Maitra, A., Mathew, C., and Varshnew, M., *J. Phys. Chem.*, 1990, vol. 94, no. 13, p. 5290.
8. Cametti, C., Codastefano, P., Tartaglia, P., Rouch, J., and Chen, S.H., *Phys. Rev. Lett.*, 1990, vol. 64, no. 12, p. 1461.
9. Eicke, H.-F., Borcovec, M., and Das Gupta, B., *J. Phys. Chem.*, 1989, vol. 93, no. 1, p. 314.
10. Kamenka, N., Burgand, I., Zana, R., and Lindman, B., *J. Phys. Chem.*, 1994, vol. 98, no. 27, p. 6785.
11. Feldman, Yu., Nir, I., Garti, N., Archipov, V., Idiatullin, Z., Zuev, Yu., and Fedotov, V., *J. Phys. Chem.*, 1996, vol. 100, no. 9, p. 3745.
12. Arkhipov, V.P., Idiyatullin, Z.Sh., Arkhipov, R.V., Zakharchenko, N.L., Zuev, Yu.F., and Fedotov, V.D., *Kolloidn. Zh.*, 2000, vol. 62, no. 4, p. 456.
13. Hait, S.K., Moulik, S.P., Rodgers, M.P., Burke, S.E., and Palepu, R., *J. Phys. Chem. (B)*, 2001, vol. 105, no. 30, p. 7145.
14. Rusanov, A.I., *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellization in Surfactant Solutions), St. Petersburg: Khimiya, 1992.
15. Mirgorodskaya, A.B., Kudryavtseva, L.A., Zuev, Yu.F., Idiyatullin, B.Z., and Fedotov, V.D., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, no. 2, p. 238.
16. Lindman, B., Stilbs, P., and Moseley, M.E., *J. Colloid Interface Sci.*, 1981, vol. 83, no. 2, p. 569.
17. Fedotov, V.D., Zuev, Yu.F., Archipov, V.P., Idiyatullin, Z.Sh., and Garti, N., *Colloids Surf. (A)*, 1997, vol. 128, nos. 1–3, p. 39.