# Micelle-forming, liquid-crystalline properties, and catalytic effect of the mixed cetyltrimethylammonium bromide—polyethylene glycol(~9) monoalkanoate(~14)—water micellar system

L. Ya. Zakharova,<sup>a</sup>\* F. G. Valeeva,<sup>a</sup> A. R. Ibragimova,<sup>a</sup> L. A. Kudryavtseva,<sup>a</sup> N. N. Valeev,<sup>b</sup> T. L. Didenko,<sup>b</sup> V. I. Kovalenko,<sup>a,b</sup> and A. I. Konovalov<sup>a</sup>

 <sup>a</sup>A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation. Fax: +7 (843 2) 75 2253. E-mail: lucia@iopc.knc.ru
 <sup>b</sup>Kazan State Technological University, 68 ul. K. Marksa, 420015 Kazan, Russian Federation

> The formation of mixed micelles in the surfactant cetyltrimethylammonium bromide—polyethylene glycol(~9) monoalkanoate(~14) binary system was shown. The stable lyomesophase involving monomers of both surfactants forms in the region of high surfactant concentrations in the temperature interval from 25 to 96 °C. In the binary micellar system, the alkaline hydrolysis of *O*-ethyl-*O*-*p*-nitrophenyl chloromethyl phosphonate is accelerated up to 30-fold compared with the reaction in water in the absence of a surfactant. The efficiency of catalysis depends on the molar ratio between both surfactants. The sign of the catalytic effect changes at high surfactant concentrations.

> Key words: mixed micelles, lyomesophase, micellar catalysis, kinetics, hydrolysis, phosphonates.

Surfactants widely used in industry are, as a rule, mixtures of different detergents. Mixed micellar systems are of interest from the viewpoint of the theory of solutions and practical use.<sup>1,2</sup> The properties of mixed solutions (critical micelle formation concentration (CMC), aggregation number, solubilizing ability) differ from those for solutions of individual surfactants.<sup>3–5</sup> This difference allows the required parameters to be obtained by the variation in the composition of the micellar system. In most cases, mixed systems are better than pure compounds because the composition of the mixture can be optimized for each particular case.

2176

This work is devoted to the study of the properties of the mixed cetyltrimethylammonium bromide (CTAB)—polyethylene glycol(~9) monoalkanoate (~14) ( $C_{14}E_9$ )—water system. With this purpose, we studied the aggregating ability of the system in a wide interval of concentrations. In the region of low surfactant concentrations (formation of direct micelles), it was necessary to reveal whether the surfactants associate in combination (synergistic behavior) or separate micellization occurs and individual surfactants produce two types of aggregates (antagonistic behavior). The region of high surfactant concentrations, in which liquid-crystalline structures and their precursors (long cylindrical micelles) form, is of special interest from the practical point of view. In this region, the viscosity of solutions increases, which stimulates their use as thickeners in the production of varnishes, paints, shampoos, *etc*. The data obtained in this part of the work were used for the interpretation of the kinetic experiment. However, they are also important for the elucidation of the nature of mixed surfactant solutions.<sup>3–7</sup>

In this work, we studied the catalytic effect of mixed  $CTAB-C_{14}E_9$  micelles in the alkaline hydrolysis of *O*-ethyl-*O*-*p*-nitrophenyl chloromethylphosphonate (1) (Scheme 1).

#### Scheme 1



Studies in the field of kinetics and catalysis in mixed micellar systems are few to date.<sup>8-12</sup>

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 12, pp. 2019-2025, December, 2002.

1066-5285/02/5112-2176 \$27.00 © 2002 Plenum Publishing Corporation

#### **Experimental**

*O*-Ethyl-*O*-*p*-nitrophenyl chloromethylphosphonate (1) was synthesized using a previously published procedure.<sup>13</sup> Cetyltrimethylammonium bromide (Sigma) and an industrial sample of  $C_{14}E_9$  were used. The kinetics of hydrolysis was studied spectrophotometrically on a Specord M-400 instrument under the pseudo-first order conditions by a change in the absorption of the *p*-nitrophenoxide anion at 400 nm. The apparent rate constants ( $k_{app}$ ) were calculated using the weighted least-squares method. The temperature observations of the lyotropic mesophase were carried out using a MIN-8 polarization microscope equipped with a Boetius heating stage. The accuracy of temperature measurements was  $\pm 0.2$  °C. Electroconductivity was measured on a CDM-2-d conductometer (Denmark). The surface tension was determined by the ring detachment method using a Du Noüyl<sup>14</sup> tensometer at 35 °C.

### **Results and Discussion**

Micellization of nonionic surfactants is characterized by CMC values lower than those of ionic detergents because the latter make the unfavorable contribution to the free energy of micellization due to the electrostatic repulsion of the head groups.<sup>15</sup> The CMC value for CTAB is 0.85 mmol  $L^{-1}$ , and that for  $C_{14}E_9$  is 0.052 mmol  $L^{-1}$ (Fig. 1).

We performed the conductometric and tensometric studies of aggregation in the mixed CTAB- $C_{14}E_9$  systems. The CMC values were determined by the tensometric method from the inflection point in the plots of the surface tension *vs.* overall surfactant concentration at different molar fractions of the ionic ( $\alpha_1$ ) and nonionic ( $\alpha_2$ ) surfactants for several micellar compositions (see Fig. 1). The studied concentration interval contains only one inflection corresponding to the formation of mixed



**Fig. 1.** Plots of the surface tension ( $\gamma$ ) of mixed CTAB- $C_{14}E_9$  micellar solutions at 25 °C and different molar ratios *vs.* overall concentration of the surfactant ( $C_{surf}$ ):  $\alpha_1 = 0$  (*I*), 0.17 (*2*), 0.33 (*3*), 0.50 (*4*), 0.67 (*5*), and 0.91 (*6*).



**Fig. 2.** Plots of the electroconductivity (*k*) of mixed CTAB $-C_{14}E_9$  micellar solutions at 35 °C and different molar ratios *vs.* overall concentration of the surfactant ( $C_{surf}$ ):  $\alpha_1 = 1$  (*I*), 0.83 (*2*), 0.50 (*3*), and 0.17 (*4*).

aggregates (CMC-1, see Fig. 1), although the tensometric study<sup>5</sup> of micellization found the second inflection corresponding to CMC-2 in addition to CMC-1.

The conductometric study of mixed solutions in a wide interval of surfactant concentrations showed the inflection in the plots of specific electroconductivity *vs.* overall surfactant concentration (Fig. 2). As established previously,<sup>16</sup> the CMC values determined conductometrically and tensometrically can somewhat differ. However, the surfactant concentrations corresponding to the inflections in Fig. 2 are higher by an order of magnitude and more than the CMC-1 values determined tensometrically (Table 1). Probably, these critical concentrations (see Fig. 2) should be treated as CMC-2 values. In the systems with  $\alpha_1 \ge 0.5$ , the CMC-2 value is close to 0.001 mol L<sup>-1</sup> and decreases to 0.4–0.5 mmol L<sup>-1</sup> only with the further

**Table 1.** The CMC-1 and CMC-2 values of the mixed CTAB- $C_{14}E_9$  micellar system determined by measurements of the surface tension and electroconductivity at different molar fractions of the surfactant ( $\alpha_1$ )

α <sub>1</sub>	CMC-1	CMC-2
	1	nol L <sup>-1</sup>
0	0.052	_
0.17	0.055	0.4
0.33	0.061	0.47
0.50	0.073	0.98
0.60	_	0.90
0.67	0.109	_
0.83	_	1.07
0.91	0.25	_
1	0.85	_



**Fig. 3.** Plots of the CMC of mixed CTAB— $C_{14}E_9$  micellar systems (experimental (1) and calculated values at  $\beta = -2.5$  (2) and -2.6 (3), for ideal mixing (4)) vs. molar fraction of CTAB ( $\alpha_1$ ) and the ratio between the molar fraction of CTAB in a solution  $\alpha_1$ ) and in micelles ( $x_1$ ) (5).

increase in the fraction of the nonionic surfactant (see Table 1).

Figure 3 presents the dependence of the experimental CMC values for the mixed  $CTAB-C_{14}E_9$  system on the molar fraction of the ionic surfactant (CTAB) and the CMC values calculated for the case of ideal mixing<sup>3</sup> using the equation

$$1/C^* = \alpha_1/C_1 + \alpha_2/C_2,$$
 (1)

where  $\alpha_1$  and  $\alpha_2$  are the molar fractions of the ionic and nonionic surfactants, respectively, in a solution;  $C^*$ ,  $C_1$ , and  $C_2$  are the CMC values for the mixed system, ionic surfactant, and nonionic surfactant, respectively.

Different thermodynamic<sup>17–19</sup> and model<sup>3,4</sup> approaches are known for the description of micellization in mixed systems. The pseudo-phase separation model,<sup>4</sup> which has been checked for many experimental data,<sup>5–7,20</sup> is most widely and successfully used in the present time. In the framework of this approach, to take into account non-ideality of the mixture, the activity coefficients of surfactants  $f_1$ ,  $f_2$  and the parameter of surfactant interaction in mixed aggregates  $\beta$  are introduced into Eq. (1)

$$1/C^* = \alpha_1/(f_1C_1) + \alpha_2/(f_2C_2), \tag{2}$$

$$f_1 = \exp[\beta(1 - x_1)^2],$$
 (3)

$$f_2 = \exp(\beta x_1^2). \tag{4}$$

Here  $x_1$  is the molar fraction of the ionic surfactant in mixed micelles, which can be calculated using the solution of the equation

$$\frac{x_1^2 \ln[\alpha_1 C^* / (x_1 C_1)]}{(1 - x_1) \ln\{(1 - \alpha_1) C^* / [(1 - x_1) C_2]\}} = 1$$
(5)

by the iteration method.

The mathematical apparatus used in the calculations has been described in detail.<sup>4</sup> The  $\beta$  parameter can be calculated from the equation

$$\beta = \frac{\ln[\alpha_1 C^* / (x_1 C_1)]}{(1 - x_1)^2}.$$
(6)

The empirical parameter  $\beta$  takes into account the degree of deviation of the system from the ideal mixture and the character of interaction of the surfactant monomers in mixed solutions. The negative value of the  $\beta$  parameter assumes attraction forces and indicates the synergistic effect related to the involvement of both surfactants in micellization. The positive values of the  $\beta$  parameter mean the predomination of repulsion forces between the surfactant molecules characterizing the antagonistic effect. Due to this effect, aggregates based on individual surfactants can form in the system. An increase in the absolute  $\beta$  value indicates a greater deviation of the micellar system from the behavior of ideal mixing.

Analysis of the data presented in Fig. 1 using Eqs. (1)–(6) allowed the  $x_1, x_2$ , and  $\beta$  values to be calculated. As can be seen in Fig. 3, the molar fraction of CTAB in mixed aggregates  $(x_1)$  is decreased compared to its fraction in a solution  $(\alpha_1)$ . This is probably caused by the more efficient micelle-forming properties of the nonionic surfactant because unfavorable electrostatic interactions are absent. It is also seen that the experimental CMC values do not match the curve corresponding to the ideal mixing. The  $\beta$  parameters calculated from Eqs. (1)—(5) are approximately -2.5. The exception is the micelle composition corresponding to the high CTAB content ( $\alpha_1 = 0.91$ ), for which  $\beta = -2.0$  was obtained. The  $\beta$  values point out to the predomination attraction forces in mixed aggregates, and the lower  $\beta$  modulus at  $\alpha_1 = 0.91$  can likely be explained by an increase in the contribution of the Coulomb repulsion of the likely charged head groups of CTAB with an increase in the fraction of the latter in micelles. The  $C^*$  values calculated in the framework of the theory of regular solutions using the calculated values of the micelle composition for  $\beta = -2.5$  and -2.6 are presented in Fig. 3. The calculated  $C^*$  values agree well with the experimental values in a wide interval of surfactant molar ratios.

The ability of surfactants to form lyomesophases in the region of high concentrations is an interesting and important feature of their behavior in solutions. According to published data,<sup>21</sup> the hexagonal ( $H_{\alpha}$ ), cubic ( $Q_{\alpha}$ ), and lamellar ( $L_{\alpha}$ ) mesophases form in the CTAB-water system. The region of the stable state of the hexagonal phase lies<sup>21</sup> in the concentration interval from 40 to 60 wt.% and in the temperature interval from 30 to 200 °C. The regions of optical anisotropy have also been found for aqueous solutions of nonionic surfactants.<sup>22,23</sup> We have previously<sup>24</sup> shown the formation of the lamellar  $L_{\beta}$  phase (gel phase) with the melting point ~60 °C (m.p. of the surfactant itself is ~28 °C) in the  $C_{14}E_9$ -water system in the concentration interval from 45 to 65 wt.%. In this work, the aqueous  $C_{14}E_9$ —CTAB system ( $\alpha_1 = 0.60$ ) was studied at different temperatures by polarization microscopy. The texture of the studied sample in the temperature interval from 25 to 96 °C is shown in Fig. 4. The formation of the stable mesophase in this system is probably associated with the involvement of the surfactants of both types, because the temperature and concentration intervals of lyomesophase formation differ from those for individual solutions.<sup>21,24</sup> The observation of the sample using a polarization microscope revealed reproducible changes in the texture at the temperature close to 60 °C. This can be attributed to the coexistence at temperatures below 60 °C of a mixed lyomesophase enriched in individual CTAB molecules and a gel phase formed by the  $C_{14}E_9$  molecules.

The dependence of the apparent rate constant for alkaline hydrolysis of **1** on the surfactant concentration was studied in kinetic experiments. In a micellar solution of CTAB, the reaction is accelerated 20-fold (compared to



**Fig. 4.** Texture of a liquid-crystalline mixed  $C_{14}E_9$ —CTAB (1 : 1, mol/mol) solution at 25 (*a*), 50 (*b*), 70 (*c*), and 96 °C (*d*).

the reaction in water in the absence of a surfactant) due to the solubilization of the substrate in the micellar pseudophase and simultaneous concentrating of the hydroxide ions on the positively charged micellar surface. In a micellar solution of the nonionic surfactant  $C_{14}E_9$ , the reaction rate remains unchanged. The kinetic data for the hydrolysis of 1 in mixed  $CTAB-C_{14}E_9$  micellar systems are presented in Fig. 5 as a dependence of  $k_{app}$  on the surfactant concentration in the micelles  $(C_{surf})$  at the unchanged CTAB :  $C_{14}E_9$  molar ratio. With an increase in the content of the nonionic surfactant to  $\alpha_2 = 0.4$ , the  $k_{\rm app}$  value somewhat increases, and the further increase in  $\alpha_2$  results in a smooth decrease in  $k_{app}$ . The quantitative analysis of the kinetic data was performed using the pseudo-phase model.<sup>25</sup> According to the latter, the dependence of the apparent second order rate constant  $k'_{app}$ 



Fig. 5. Plots of the apparent rate constant for alkaline hydrolysis of 1 ( $k_{app}$ ) in mixed CTAB—C<sub>14</sub>E<sub>9</sub> micellar systems vs. overall surfactant concentration at different molar ratios:  $\alpha_1 = 1.0$  (*I*), 0.83 (*2*), 0.67 (*3*), 0.60 (*4*), 0.50 (*5*), and 0.33 (*6*); insert, simulation of the apparent rate constant for alkaline hydrolysis of 1 ( $k_{app}$ ) in a mixed CTAB—C<sub>14</sub>E<sub>9</sub> micellar system ( $\alpha_1 = 0.5$ ) using Eq. (7) at  $C_{surf}$  equal to the overall surfactant concentration (*I*) and at the CTAB concentration corresponding to the molar fractions  $\alpha_1$  (*2*) and  $x_1$  (*3*). Points are experiment, and lines are calculation.

(the first order rate constant divided into the nucleophile concentration) on  $C_{\text{surf}}$  has the following form:

$$k'_{app} = \frac{k_{2,w} + k_{2,m} K_S K_{OH} C_{surf} / V}{(1 + K_S C_{surf})(1 + K_{OH} C_{surf})}.$$
(7)

The calculated second order rate constants in aqueous and micellar phases,  $k_{2,w}$  and  $k_{2,m}$ , and binding constants of the substrate and nucleophile,  $K_S$  and  $K_{OH}$ , are presented in Table 2. Individual micellar solutions of nonionic surfactants have no effect on the reaction kinetics (see above), and the mixed systems demonstrate a considerable decrease in the catalytic effect with an decrease in the molar fraction of CTAB. Therefore, different  $C_{\text{surf}}$ values were used for the simulation of the composition of micellar aggregates: the overall surfactant concentration, the stoichiometric concentration of CTAB in a solution calculated from the  $\alpha_1$  value, and the CTAB concentration in the micellar pseudo-phase calculated using the  $x_1$ value. As can be seen from such a simulation for one surfactant composition with  $\alpha_1 = 0.5$  (see Fig. 5, insert), the maximum divergence between the experiment and calculation is observed when formal CTAB concentrations are used (initial concentrations of the surfactant in a solution, unlike to the true concentrations in the aggregate composition). The best convergence of the calculation and experiment was obtained when the  $C_{\text{surf}}$  values equal to the CTAB concentration in the composition of mixed micelles or the overall concentration of the surfactant were substituted into Eq. (7), although the coincidence of the results is better in the latter case. Perhaps, this confirms that mixed associates formed by the molecules of both surfactants rather than only by cationic detergents participate in the hydrolysis catalysis.

For analysis of the kinetic data, the surface potential  $(\Psi)$  of mixed micelles was calculated using the Nernst correlation<sup>26</sup> between the surface potential and CMC of the surfactant. As shown previously,<sup>27</sup> a similar relation holds for the mixed systems containing the ionic and nonionic surfactants

$$d|\Psi|/d(\log a_1) = 59.16 \text{ mV},$$
(8)

where  $a_1$  is the activity of free monomers of the ionic surfactant in a mixed micellar solution calculated in the framework of the theory of regular solutions.<sup>4</sup> Figure 6 presents a plot of the surface potential vs. activity of the potential-determining CTAB ion and its molar fraction in a mixed solution calculated using Eq. (8).

Analysis of the main factors responsible for a change in the rate in micelles, *viz.*, the factor of concentrating  $(F_c)$  and the factor of micellar microenvironment  $(F_m)$ (see Note to Table 2), allows some conclusions about a change in the rate under conditions of mixed micellization to be drawn. At a low content of the nonionic surfactant,



**Fig. 6.** Plots of the surface potential ( $\Psi$ ) of mixed CTAB-C<sub>14</sub>E<sub>9</sub> micelles *vs.* logarithm of the activity of the CTAB monomer in the micellar pseudo-phase (log*a*<sub>1</sub>) (*1*) and *vs.* molar fraction of CTAB in micelles ( $\alpha_1$ ) (*2*).

the rate constant in the micellar pseudo-phase  $k_{2,m}$  increases and the binding constant of both reactants decreases. A decrease in the concentrating factor in this concentration region is mainly caused by a decrease in the binding constant of the hydroxide ions. As can be seen in Fig. 6, this is precisely the interval of the  $\alpha_1$  values where the surface potential of micelles decreases substantially in the regions of concentrations higher than CMC, and further (at  $\alpha_1 = 0.2 - 0.6$ ) it changes more smoothly. Despite the compensation character of changing the  $F_{\rm c}$ and  $F_{\rm m}$  factors, the resulting catalytic effect increases. The further increase in the fraction of the nonionic surfactant results in a sharp increase in the efficiency of binding for both reactants accompanied, however, by a considerable decrease in  $k_{2,m}$  on going from the aqueous to micellar phase. Superposition of these effects decreases the efficiency of catalysis with an increase in the  $C_{14}E_9$ content.

The increase in  $k_{app}$  with an insignificant decrease in the molar fraction of CTAB in a solution to  $\alpha_1 = 0.67$ additionally confirms that the total decrease in the efficiency of catalysis in the mixed micelles is not a result of a decrease in the fraction of the CTAB micelles. Taking into account the data in Table 2, the initial increase in the rate with a decrease in the molar fraction of the ionic surfactant is related to the favorable influence of the micellar microenvironment on the transition state of the reaction. As can be seen in Fig. 3, the composition of micellar aggregates changes drastically with a decrease in

$\overline{\alpha_1}$	$k_{2,m}^{a}$	$(k_{\rm app}/k_{\rm w})_{\rm max}$	K <sub>S</sub>	K <sub>OH</sub>	F <sub>c</sub> <sup>b</sup>	$F_{\rm m}^{\ b}$	$F_{\rm c}F_{\rm m}$			
$L \text{ mol}^{-1}$										
1	0.62	20.3	593	69	127.5	0.16	20.1			
0.83	2.9	32.4	398	15.8	36.7	0.76	28.1			
0.67	2.1	30	494	21.9	49.8	0.54	27.2			
0.60	0.75	19	600	50	100	0.19	19.0			
0.50	0.20	14.4	1282	149	276	0.052	14.2			
0.33	0.07	8.2	1839	265	464	0.018	8.4			

**Table 2.** Results of the quantitative analysis of the kinetic data using Eq. (7) for the CTAB $-C_{14}E_{9}$  system

<sup>*a*</sup>  $k_{2,w} = 4.0 \text{ L mol}^{-1} \text{ s}^{-1}$ . <sup>*b*</sup> Calculated using the equation

$$(k_{\rm app}/k_{\rm w})_{\rm max} = \frac{k_{2,\rm m}}{k_{2,\rm w}} \frac{K_{\rm S}K_{\rm OH}}{V(\sqrt{K_{\rm S}} + \sqrt{K_{\rm OH}})^2}.$$

The right part represents the maximum acceleration of the reaction equal to the ratio of the apparent rate constant  $(k_{app})$  to the pseudo-first order rate constant in water  $(k_w)$ . The first factor in the right part expresses the influence of the micellar microenvironment on the reactivity  $(F_m)$ , and the second factor reflects the effect of concentrating of the reactants in micelles  $(F_c)$ .

the molar fraction of CTAB in a solution to 0.67 The subsequent sharp decrease in  $k_{2,m}$  (see Table 2) at low  $\alpha_1$  values (during this, the composition of micelles changes slightly, see Fig. 3) is not likely related to a change in the micropolarity. We can assume that the entropy factor is a reason for a decrease in the reactivity at low  $\alpha_1$  (similarly to that observed previously<sup>28</sup>).

The influence of the nature of nanoparticles formed in a mixed micellar system is poorly studied. In this work, the kinetics of alkaline hydrolysis of 1 was studied at high surfactant concentrations (the region of formation of lyomesophases or preceding nanostructures) at an unchanged content of one of the detergents. In the studied region of surfactant concentrations, anisotropy was not observed by polarization microscopy. However, it is known<sup>15,29</sup> that at high concentrations of ionic and nonionic surfactants the sphere-cylinder micellar transition occurs to form long worm-like micelles, whose interaction produces a three-dimensional spatial network.

The plots of  $k_{app}$  vs. concentrations of the nonionic surfactant and CTAB are presented in Fig. 7. At a constant CTAB concentration, the apparent rate constant and catalytic effect decrease smoothly to transform into the inhibition of the process at  $[C_{14}E_9] = 0.2 \text{ mol } L^{-1}$ . The  $k_{\rm app}-C_{\rm surf}$  kinetic plot at an unchanged content of the nonionic surfactant shows that at the  $C_{14}E_9$  concentration equal to 0.15 mol  $L^{-1}$  the hydrolysis of 1 is catalyzed only, whereas at the constant concentration of  $C_{14}E_9$  $(0.3 \text{ mol } L^{-1})$  inhibition is replaced by catalysis with an increase in the CTAB concentration. These data agree with the earlier  $^{30,31}$  conclusions about the influence of the properties of organized solutions on their catalytic effect. The micellar system under study shows up to



Fig. 7. Apparent rate constant for alkaline hydrolysis of 1  $(k_{app})$ in mixed CTAB- $C_{14}E_9$  micellar systems as a function of the concentration of the nonionic surfactant at the unchanged CTAB concentration equal to 0.003 mol  $L^{-1}$  (1) and of the CTAB concentration at the unchanged  $C_{14}E_9$  concentration equal to 0.15 (2) and 0.3 mol L<sup>-1</sup> (3); 25 °C, 0.1 mol L<sup>-1</sup> NaOH.

30-fold accelation of alkaline hydrolysis of O-ethyl-O*p*-nitrophenyl chloromethyl phosphonate.

Thus, the study of the micelle-forming properties of the mixed cetyltrimethylammonium bromide-polyethylene glycol(~9) monoalkanoate (~14) micellar system by measurements of the surface tension and electroconductivity followed by analysis of the data in the framework of the pseudo-phase separation theory revealed the synergistic effect.

## References

- P. M. Holland and D. N. Rubingh, in *Mixed Surfactant Systems*, Eds. P. M. Holland and D. N. Rubingh, ACS Symposium Series 501, American Chemical Society, Washington, DC, 1992, 1.
- M. J. Rosen, in *Phenomena in Mixed Surfactant Systems*, Ed. J. F. Scamehorn, ACS Symposium Series 311, American Chemical Society, Washington, DC, 1986, 144.
- 3. J. Clint, J. Chem. Soc., Faraday Trans. 1, 1975, 71, 1327.
- D. N. Rubingh, Solution Chemistry of Surfactants, Ed. K. L. Mittal, Plenum Press, New York, 1979, 1, 337.
- 5. M. S. Bakshi, J. Inclusion Phenomena, 2000, 36, 39.
- 6. C. C. Ruiz and J. Aguiar, Langmuir, 2000, 16, 7946.
- 7. H. Maeda, J. Colloid. Interface Sci., 1995, 172, 98.
- 8. C. A. Bunton, S. Wright, P. M. Holland, and F. Nome, *Langmuir*, 1993, **9**, 117.
- 9. C. R. A. Bertoncini, M. F. S. Neves, F. Nome, and C. A. Bunton, *Langmuir*, 1993, **9**, 1274.
- V. L. A. Frescura, D. M. O. Marconi, D. Zanette, F. Nome, A. Blasko, and C. A. Bunton, *J. Phys. Chem.*, 1995, **99**, 11494.
- 11. D. M. Davies and S. J. Foggo, J. Chem. Soc., Perkin Trans. 2, 1998, 247.
- 12. E. Iglesias and L. Montenegro, *Phys. Chem., Chem. Phys.*, 1999, **1**, 4865.
- 13. US Pat. N 2922810, 1960; Chem. Abstrs., 1960, 54, 9848.
- 14. V. I. Baranova, E. E. Bibik, N. M. Kozhevnikov, I. S. Lavrov, and V. A. Malov, *Praktikum po kolloidnoi khimii [Practical Works on Colloidal Chemistry*], Vysshaya Shkola, Moscow, 1983, 215 pp. (in Russian).
- K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, *Colloidal Surfactants*, Academic Press, New York–London, 1963.
- S.-Y. Lin, Y.-Y. Lin, E.-M. Chen, C.-T. Hsu, and C.-C. Kwan, *Langmuir*, 1999, 15, 4370.
- 17. R. Nagarajan and E. Ruckenstein, Langmuir, 1991, 7, 2934.

- S. Puvvada and D. Blankschtein, J. Phys. Chem., 1992, 96, 5567.
- 19. D. Blankschtein, Langmuir, 1998, 14, 7166.
- 20. Z.-G. Cui and J. P. Canselier, *Colloid Polym. Sci.*, 2001, 279, 259.
- X. Auvray, C. Petipas, R. Anthore, I. Rico, and A. Lattes, J. Phys. Chem., 1989, 93, 7458.
- 22. S. S. Funari and G. Rapp, J. Phys. Chem., B, 1997, 101, 732.
- 23. B. Hakansson, P. Hansson, O. Regev, and O. Soderman, *Langmuir*, 1998, **14**, 5730.
- 24. V. I. Kovalenko, T. L. Didenko, L. A. Kudryavtseva, and L. Ya. Zakharova, Sb. statei VIII Vseross. konf. "Struktura i dinamika molekulyarnykh sistem, Yal'chik, 2001" [Abstracts of VIII All-Russian Conf. "Structure and Dynamics of Molecular Systems, Yal'chik, 2001"], Yal'chik, 2001, Part 2, 215 (in Russian).
- K. Martinek, A. K. Yatsimirsky, A. V. Levashov, and I. V. Beresin, *Micellization, Solubilization, and Microemulsions*, Ed. K. L. Mittal, Plenum Press, New York–London, 1977, 489.
- 26. R. A. Hobson, F. Grieser, and T. W. Healy, J. Phys. Chem., 1994, 98, 274.
- 27. T. W. Healy, C. J. Drummond, F. Grieser, and B. S. Murray, *Langmuir*, 1990, **6**, 506.
- 28. R. A. Shagidullina, L. Ya. Zakharova, F. G. Valeeva, and L. A. Kudryavtseva, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1125 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1181].
- 29. S. May and A. Ben-Shaul, J. Phys. Chem., B, 2001, 105, 630.
- L. Y. Zakharova, D. B. Kudryavtsev, L. A. Kudryavtseva, A. I. Konovalov, Y. F. Zuev, N. N. Vylegzhanina, N. L. Zakhartchenko, and Z. S. Idiatullin, *Mendeleev Commun.*, 1999, 9, 245.
- L. Ya. Zakharova, L. A. Kudryavtseva, and A. I. Konovalov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1922 [*Russ. Chem. Bull.*, 1998, 47, 1868 (Engl. Transl.)].

Received December 29, 2001; in revised form July 23, 2002