Mixed micellar systems of geminal alkylammonium surfactants and long-chain amines

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Numerical characteristics of the aggregation behavior of geminal alkylammonium surfactants in aqueous solutions (the size of micelles, the packing of surfactant molecules, the surface potential, the extent of counterion binding) were determined. The formation of mixed micelles geminal surfactant/decylamine resulted in substantial decrease in amine pK_a; this is the crucial factor determining the strong catalytic effect of the system in ester bond cleavage processes.

Key words: geminal surfactants, amines, mixed micelles, solubilization, structure, acid-base properties, aminolysis, hydrolysis, kinetics.

The most important feature of aqueous micellar solutions of surfactants is the capability of solubilization of reactive substances possessing different hydrophilic-lipophilic properties; this substantially extends the possibility of their use as reaction media.[1—4] Transfer of the reactants from the bulk of solvent to the micellar pseudophase is accompanied by changes in their microenvironment, which in turn leads to changes in the reactivity, acid-base properties, spectral, and other physicochemical parameters. The most pronounced changes are observed for amphiphilic reagents (long-chain aliphatic amines, alkylphenols),[5—7] which can form mixed micelles with surfactants, containing functional groups sensitive to variation of pH values of the media and the component ratio.

In the last decade, interest in the geminal (dimeric) surfactants and highly organized systems based on them increased sharply. Geminal surfactants contain two hydrophobic radicals and two head (usually, charged) groups linked by spacers with different rigidity. These compounds differ from their amphiphilic analogs containing only one head group and one hydrocarbon chain by lower values of the critical micelle concentration (CMC), high surface activity, and solubilizing action; they are also characterized by unusual morphological behavior.[8—11] A series of papers devoted to the study of the aggregation behaviour and the structural properties of geminal surfactants were published.[12—14] A number of studies[15—18] on the catalytic effect of micellar solutions of these compounds in the nucleophilic substitution reactions were reported.

The present work is dedicated to elucidation of the possibility of using aqueous solutions of geminal cationic surfactants as media for reactions involving hydrophobic alkylamines. Taking *n*-decylamine as an example, data on the solubilizing effect, aggregation properties, and catalytic activity in ester bonds cleavage of two geminal alkylammonium surfactants with different length of hydrophobic fragments six methylene-unit spacers

$[C_{12}H_{25}(CH_3)_2N(CH_2)_6N(CH_3)_2C_{12}H_{25}]^{2+} \cdot 2Br^-$ (Gem-12),
$[C_{16}H_{33}(CH_3)_2N(CH_2)_6N(CH_3)_2C_{16}H_{33}]^{2+} \cdot 2Br^-$ (Gem-16)

were obtained.

A comparative analysis of their properties and those of analogous monomeric cationic surfactants, dodecyltrimethylammonium bromide (DdTAB) and cetyltrimethylammonium bromide (CTAB), was carried out.

Experimental

Commercially available CTAB and DdTAB (Sigma), *n*-decylamine, *n*-octylamine, and also *p*-nitrophenyl acetate (PNPA) (Fluka) with 99% purity were used. The samples of geminal surfactants were synthesized by the reaction of *N*,*N*′-tetrasubstituted hexamethylenediamine with alkyl bromides in acetone followed by double recrystallization from ethanol, by analogy with a known procedure.[18,19]

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ESR spectra were recorded on a RE-1306 spectrometer connected to a personal computer. The spin probe was 5-doxylstearic acid (5-DSA). The amphiphilic properties of its molecules allow them to incorporate into micelles in such a manner that the paramagnetic fragment be situated closer to the micelle surface. The procedure for introducing spin probes into the micellar solutions, the conditions for registration of ESR spectra, and methods of their analysis are described elsewhere.[20,21]

The self-diffusion coefficients of surfactants were measured by ^{1}H NMR spectroscopy with Fourier transform and pulsed magnetic field gradient.[22] A Tesla BS 587 NMR spectrometer equipped with a gradient accessory for production of magnetic field gradients up to 0.5 T m^{-1} was used. The proton resonance frequency was 80 MHz. A Hahn pulse sequence[23] was used for the determination of the self-diffusion coefficients. The measurements were performed at 30 °C in solutions prepared using deuterated water (Aldrich, 99.9%).

The size of micellar aggregates Gem-16 as also determined by dynamic light scattering on a Photocor Complex spectrometer (He—Ne-laser, 633 nm). Prior to measuring, the solutions studied were filtered on Milipor filters (pore diameter 0.4 μm). The autocorrelation functions were analyzed using the Cumulant and Dynals software supplied with the spectrometer. The hydrodynamic radius was determined at least 3 times for each sample. The measurement error did not exceed 4%.

The bromine ions concentration in the surfactant solutions studied was determined by bromine-selective electrode on an I-160MI ion-meter. The fraction of unbound counterions (β) was calculated as $\beta = C_{Br^-}/C_{surf}$.

The amine pK_a values were determined by potentiometric titration of their solutions with 0.1 *M* hydrochloric acid. The surfactant concentrations were varied from 0 to 0.02 mol L^{-1}. The fraction of the neutral form (α) was calculated using the amine pK_a values and the pH value of the medium according to equation $\alpha = K_a/(K_a + [H^+])$.

In order to study the solubilizing effect of micellar solutions of surfactants, amine was added in small portions (on vigorous stirring and at constant temperature for 5 h), until violation of homogeneity was observed visually. Then the aliquot was collected; the concentration of amine in the solution was determined by titration with hydrochloric acid.

The acid-base properties of *p*-nitrophenol were studied by measuring the optical absorbance of its ionized form at different pH values. The spectra were recorded on a Specord UV—Vis spectrophotometer in quartz cells (absorbing layer thickness (*L*) 1 cm) in the wavelength region 250—700 nm. The extinction coefficient (ε) of the phenolate form was determined taking into account optical density (*A*) measured at the wavelength of absorbance maximum. The concentration of *p*-nitrophenolate (C_{PhO^-}) at a given pH was determined from the expression $C_{PhO^-} = \varepsilon DL$. The average results of 3—5 measurements at different pH values were used.

The kinetics of PNPA cleavage was studied in freshly prepared micellar solutions by spectrophotometry on a Specord UV—Vis instrument at 25 °C under pseudofirst-order conditions. The pH value was maintained constant with the use of a buffer solution based on sodium tetraborate (pH 9.2). The course of the process was monitored from the changes in the density at 400 nm (formation of *p*-nitrophenolate-anion). The initial concentration of the substrate was $5 \cdot 10^{-5}$ mol L^{-1}, the conversion was >90%. The observed pseudofirst-order constants (k_{app}) were determined using the dependence $\log(A_\infty - A_t) = -0.434k_{app}t + \text{const}$, where A_t and A_∞ are the optical densities of the solutions at the instant *t* and after completion of the reaction. The k_{app} values were calculated using the least squares method. The kinetic data were analyzed in the pseudophase model of micellar catalysis using the equation relating k_{app} to the parameters of the process in the micellar phase:[2]

$$k_{app} = \frac{k_m K_{bond} (C_{surf} - CMC) + k_0}{1 + K_{bond} (C_{surf} - CMC)}, \quad (1)$$

where k_0 and k_m are the rate constants in the aqueous solution and in the micellar phase, respectively, and K_{bond} is the bonding constant of the substrate.

Results and Discussion

The use of water as a reaction medium for processes involving long-chain aliphatic amines is complicated by limited solubility of the amines. The use of cationic surfactants partially solves this problem. The solubility of decylamine in water and in aqueous solutions of Gem-12, Gem-16, DdTAB, and CTAB was determined by potentiometric titration. From the data listed in Table 1 one can see that all surfactants studied increase the solubility of decylamine, the solutions of Gem-16 having the highest solubilizing effect. In particular, the maximum content of decylamine in these solutions is 25 times higher than in water and almost one order of magnitude higher than in the solutions of analogous monomeric surfactant, CTAB.

Previously,[5,24,25] we have shown that solubilization of amphiphilic amine by micelles of monomeric surfactants is accompanied by formation of mixed aggregates. The formation of such aggregates in the case of geminal surfactants and decylamine in the present work is confirmed by independent physical methods, such as spin-probe ESR spectroscopy, ^{1}H NMR spectroscopy, and dynamic light scattering.

The use of high-resolution, pulsed field gradient ^{1}H NMR spectroscopy to study the structure of surfactant solutions both in the presence and in the absence of decylamine allowed us to obtain the diffusion decays of reso-

Table 1. The solubility and pK_a values of decylamine in water and in aqueous micellar solutions of cationic surfactants (C_{surf} = 0.01 mol L^{-1}, 25 °C)

Surfactant	C_{max}*/mol L^{-1}	pK_a
— (water)	0.004	10.1
DdPB	0.008	9.8
CTAB	0.014	9.4
Gem-12	0.012	9.3
Gem-16	0.10	9.1

* The maximum concentration of decylamine in solution.

nance signals and to determine the self-diffusion coefficients of (D_i) of the components of the system. The micelle self-diffusion coefficients (at $C_{surf} >> CMC$, $D_{mic} \approx D_{surf}$) were measured using the signal of the head Me-group protons of the surfactants studied, which is shifted to the region δ 3.23—3.28 because of the interaction with the positively charged nitrogen atom. Using the data obtained and the Stokes—Einstein equation $D = kT/(6\pi\eta R)$ (k is the Boltzmann constant, T is the temperature, η is the viscosity), the average hydrodynamic radius of micelles (R) was estimated in the presence and in the absence of decylamine.

The expedience of the use of ESR spectroscopy for the study of mixed micellar solutions is due to the fact that amphiphilic spin probes are introduced into the surface layer of microaggregates and the signal of paramagnetic fragment characterizes the changes in the environment of the N—O group, which appear during solubilization of amine with surfactant micelles.[20] On the basis of ESR spectra, one can judge not only about the mobility of spine-labelled fragment of the probe and the polarity of its microenvironment, but also about the packing density of surfactant molecules inside the micelle. The quantity sensible to the changes in this parameter is the isotropic hyperfine splitting constant (a_N) characterizing the interaction of the spin of the unpaired electron of the probe with the nuclear magnetic moment of the nitrogen atom.

According to NMR and ESR spectroscopy data (see Table 2), the initial micelles of the surfactants studied differ in size and in the extent of packing of hydrocarbon radicals. The obtained values of the hydrodynamic radius of the CTAB and Gem-12 micelles are in good agreement with the spherical shape with completely elongated conformation of hydrocarbon radicals in the surfactants. Despite the equal length of the hydrocarbon radicals in CTAB and in its dimeric analog Gem-16, the average hydrodynamic radius of Gem-16 micelles is much larger than that of the CTAB micelles, which can be a result of non-spherical shape of the Gem-16 aggregates. The Gem-16 micelles are characterized by more dense packing compared to CTAB, as follows from the increase in the $2A_{max}$ value (see Table 2). However, the mobility of radicals in the CTAB and Gem-16 micelles is much lower than in the Gem-12 micelles whose triplet ESR spectra are characteristic of rapid rotation of the paramagnetic fragment of the probe.

The formation of mixed micellar aggregates surfactant/decylamine is clearly followed from the increase in the size of micellar aggregates and from the decrease in the mobility of hydrocarbon fragments of the surfactants (see Table 2). In the presence of decylamine, the effective micelle radius increases from ~10% for Gem-12 to ~25% for Gem-16 possessing the highest solubilization capacity toward decylamine. The results obtained by NMR spectroscopy are in agreement with the dynamic light scattering data (see Table 2).

It should be noted that Gem-16 micelles are characterized by a higher a_N value than the CTAB micelles; this suggests a higher polarity in the region of location of the nitroxyl fragment of the probe. The introduction of decylamine into the system is accompanied by the increase in a_N values of both monomeric and dimeric surfactants, which also suggests the incorporation of the amine into the surfactant micelles. Decylamine can form hydrogen bonds with the water molecules and thus increase the amount of bound water in the surface layer of the micelle, which affects the polarity of the microenvironment of the spin fragment of the probe. In addition, the incorporation of neutral decylamine molecules into cationic surfactant micelles decreases the density of the positive charge on the

Table 2. Micelle characteristics obtained by different physicochemical methods

Surfactant[a]	Decylamine concentration /mol L^{-1}	NMR		ESR			β (bromine-selective electrode)
		$D \cdot 10^{10}$ /m^2 s^{-1}	R^b /nm	$2A_{max}$ /G	τ /ns	a_N /G	
CTAB	0	0.94	2.4	38.87	—	14.0	0.21
	0.005	0.78	2.9	40.73	—	14.3	0.28
	0.01	0.79	2.9	41.23	—	14.4	0.29
Gem-12	0	1.09	2.0	—	1.80	14.2	—
	0.005	1.03	2.1	—	1.88	14.2	—
	0.01	0.95	2.3	—	2.27	14.4	—
Gem-16[c]	0	0.66	3.4	41.80	—	14.4	0.37
	0.005	0.68	—	43.80	—	14.6	0.43
	0.01	0.54	4.2	44.65	—	14.7	0.46

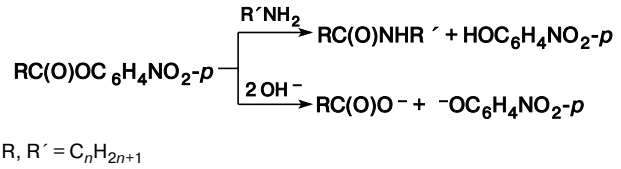
[a] $C = 0.01$ mol L^{-1}.
[b] Radius of micelle.
[c] According to the light scattering data the radius of micelles for Gem-16 is 3.2, 4.2, and 5.1 nm at decylamine concentrations 0, 0.005, and 0.01 mol L^{-1}, respectively.

surface of micelles, which is accompanied by changes in the degree of ionization; we revealed the increase in the fraction of free counterions using the bromine-selective electrode (see Table 2).

During solubilization of decylamine by surfactant micelles, not only the structural properties of the system, but also the physicochemical properties of the amine itself are changed considerably. In particular, dissolution of decylamine in the micelles of the cationic surfactants studied is accompanied by a considerable decrease in pK_a compared to the pK_a values in water (see Table 1). The main reason for this influence is the preferential solubilization of the neural form of amines by micelles with the positively charged surface. It should be noted that it is the nonprotonated form of amines that exhibits the nucleophilic properties often used in chemical processes. Thus, the use of cationic surfactants (first of all, Gem-16) extends the possibilities of the amine application in the chemical synthesis; it allows one to carry out reactions in aqueous solutions and under mild conditions (in weakly basic media). This can be illustrated by the reaction of nucleophilic substitution in esters (*e.g., p*-nitrophenylacetate) in the presence of amines.

In molecular aqueous solutions, cleavage of carboxylic acid esters mainly follows two channels, *vis.*, aminolysis (the main reaction) and basic hydrolysis (the side reaction) (Scheme 1)[24,26].

Scheme 1



R, R´ = C_nH_{2n+1}

In the micellar solutions of cationic surfactants both these processes can accelerate. The study of the kinetics of the cleavage of esters in the presence and in the absence of amine at the same value of pH allows separation of the contributions of aminolysis and hydrolysis to the total rate of the process. The dependences of the observed rate constant (k_{app}) of *p*-nitrophenyl acetate cleavage on the surfactant concentration at pH 9.2 in the absence of amines and at a dodecylamine concentration of 0.0025 mol L^{-1} are demonstrated in Fig. 1. From the data obtained it is seen that under the experimental conditions the contribution of basic hydrolysis to the total rate of the process is negligible (see Fig. 1, curve *7*). However, one should remember that this contribution can increase as the basicity of the solution increases, while the amine content decreases in the system. In the reaction of PNPA with decylamine, Gem-16 exhibits the stronger catalytic effect, while the influence of CTAB and Gem-12 is comparable. At a high CMC for DdTAB (0.015 mol L^{-1}), a weak catalytic effect is observed, which manifests itself only at rather high surfactant concentrations (see Fig. 1, curve *5*).

In the decylamine—Gem-16 system in the whole interval of studied surfactant concentrations, acceleration of the PNPA cleavage is 2—3 times higher than in the decylamine—CTAB system (see Fig. 1). It is known that the most important reason for acceleration of chemical reactions in surfactant solutions is the accumulation of the reagents in the micelle, which increases the possibility of their reaction contact (cage effect).[1,4] The main driving forces of the accumulation are hydrophobic electrostatic interactions in the system. The distribution of reactants between the bulk phase and the micelle depends on their own properties and on the micelle size, the charge density on its surface, and on the mobility of hydrocarbon chains. Under conditions of kinetic experiment at concentrations <0.01 mol L^{-1}, the surfactants studied form spheroidal aggregates with close sizes (see Table 2). Probably, the

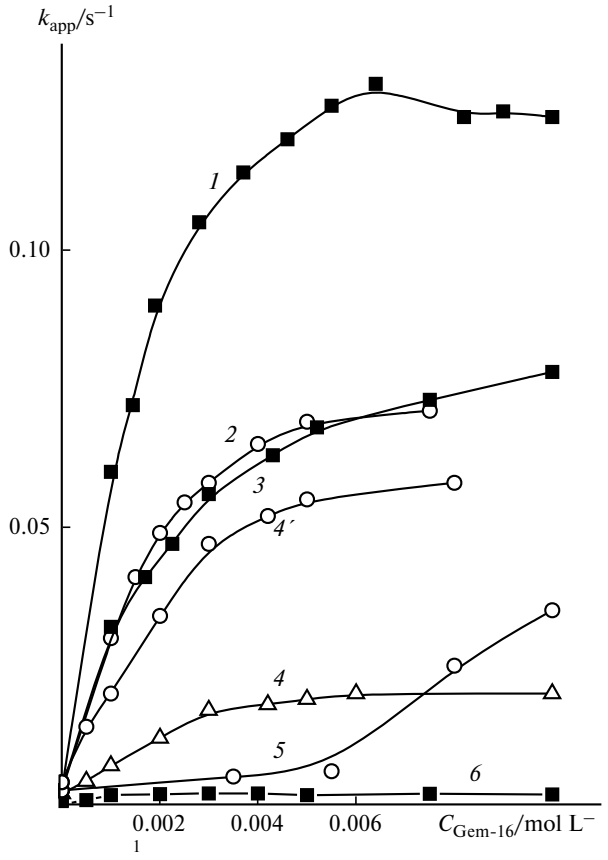


Fig. 1. Dependence of the observed rate constant for *p*-nitrophenolat cleavage on the surfactant concentration in the presence (*1*—*5*) and in the absence (*6*) of amines (25 °C, pH 9.2) at C_{am} = 0.0025 mol L^{-1}: *1* — Gem-16, decylamine, *2* — Gem-12, decylamine, *3* — CTAB, decylamine, *4* — Gem-16, octylamine, *5* — DdTAB, decylamine; at C_{am} = 0.0074 mol L^{-1}: *4´* — Gem-16, octylamine.

action of geminal surfactants is to a greater extent due to peculiarities of the micelle structure and their surface potential (Ψ), which affect the processes involving charged particles and changes the properties of reactants participating in acid-base equilibria.

To estimate the surface potential we used an approach which supposes investigation of the spectral properties of the probe molecules which can corporate into the interphase layer and responce to the changes in its structure.[27] In the present work, the surface potential of the surfactants studied was estimated using *p*-nitrophenol as a probe. The pK_a values of this compound were determined by spectrophotometry using the absorption band of its anionic form in the region 400 nm (ε ~18000). The high values of the molecular extinction coefficient allow the use of *p*-nitrophenol in low concentrations ($(2—5)\cdot10^{-5}$ mol L^{-1}). This makes possible to avoid the substantial decrease in the charge density of cationic micelles during solubilization of *p*-nitrophenolate. As an example, the spectra of *p*-nitrophenol in the solutions of Gem-16 recorded at different pH values are shown in Fig. 2. The observed value of pK_a ($pK_{a,app}$)[28] was calculated based on the determination of *p*-nitrophenolate absorption at varied pH according to the Henderson—Hasselbach equation

$$pK_{a,app} = pH + \log[\text{phenol}]/[\text{phenolate}]. \quad (2)$$

The dependences of the $pK_{a,app}$ values of *p*-nitrophenol on the concentrations of the surfactants studied are demonstrated in Fig. 3.

The observed constant of acid-base dissociation (K_{app}) is related to the surfactant concentration:[27,29]

$$K_{app} = \frac{1 + K_B(C_{surf} - CMC)K_{a,w}}{1 + K_A(C_{surf} - CMC)}, \quad (3)$$

where $K_{a,w}$ is the constant of the acid-base dissociation in water, and K_B and K_A are the binding constants of the base and acid forms, respectively.

Analyzing the dependence $(K_{a,w} - K_{app})/(C_{surf} - CMC)$ on K_{app} with the use of the least squares method, one can determine the binding constants of both forms of the compound. Since $C_{surf} \to \infty$, then $K_{app} = K_{a,w}K_B/K_A = K_{a,m}$ ($K_{a,m}$ is the dissociation constant in the micellar phase). The CMC values of the studied surfactants used for the calculations according Eq. (3), as well as the values of the binding constants of the charged and the neutral forms of *p*-nitrophenol are listed in Table 3. Note that for Gem-16 the binding constant of both forms of the spectral probe are an order of magnitude higher than the corresponding values obtained in the CTAB and Gem-12 solutions. This characterizes the higher solubilization capacity of Gem-16 toward *p*-nitrophenol compared with other surfactants. A similar situation was also observed in the case of decylamine.

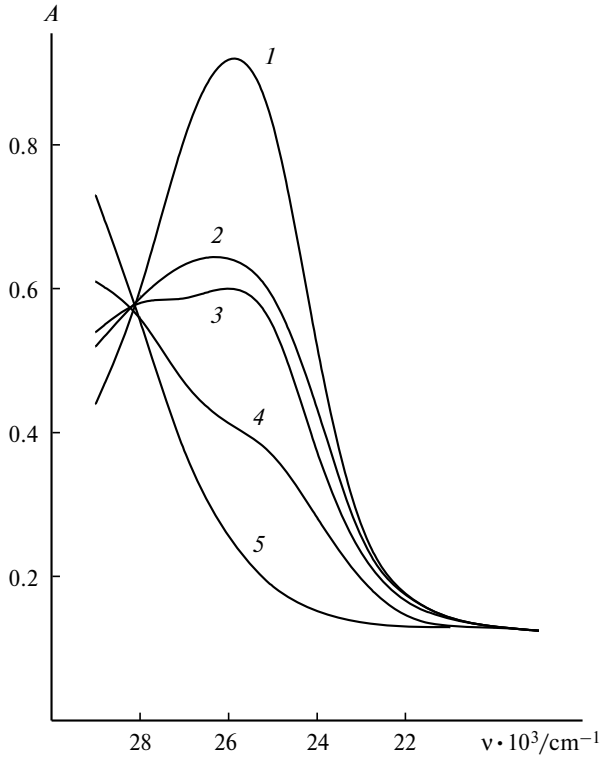


Fig. 2. Absorption spectra of *p*-nitrophenol ($4.5\cdot10^{-5}$ mol L^{-1}) in the Gem-16 micellar solution (0.05 mol L^{-1}) at different pH values: 10.0 (*1*), 5.3 (*2*), 5.1 (*3*), 4.8 (*4*), and 4.2 (*5*); $\lambda_{max} = 400$ nm.

The surface potential can estimated using the formula[27,29]

$$pK_{a,m} = pK_{a,0} - F\Psi/(2.303RT), \quad (4)$$

where $pK_{a,0}$ is the non-electrostatic component defined as pK_a in micellar solutions based on nonionic surfactants (Triton-X-100, pK_a *p*-nitrophenol is 7.6); $F = 96486$ C mol^{-1} is the Faraday´s constant, and $R = 8.314$ J K^{-1} mol^{-1} is the gas constant.

As follows from the data obtained using the spectral probe (see Table 3), Gem-16 is characterized by the maximal value of Ψ; and for this compound the greatest de-

Table 3. The values of CMC, surface potential (Ψ), binding constants (K_{bond}), and $pK_{a,m}$ of *p*-nitrophenol in the micelles of cationic surfactants* (20 °C)

Sufractant	CMC /mol L^{-1}	K_{bond}		$pK_{a,m}$	Ψ/mV
		Neutral	Anion		
CTAB	0.0008	319	20920	5.38	129
Gem-12	0.00125	620	48254	5.31	134
Gem-16	0.00004	2657	449841	4.97	153

* The high value of CMC of DdTAB complicates the determination of $pK_{a,m}$ and, consequently, Ψ.

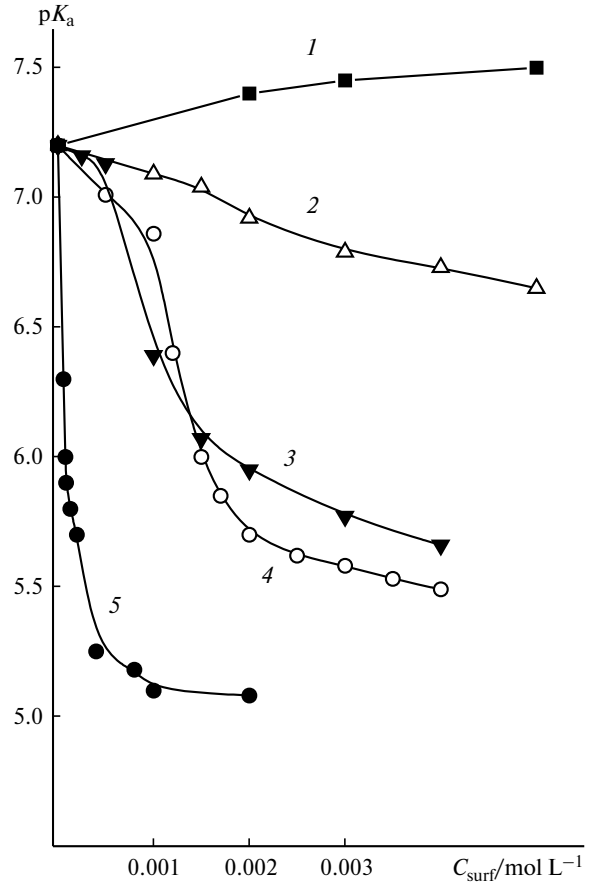


Fig. 3. Dependence of the *p*-nitrophenol pK_a on the surfactant concentration: nonionic surfactant is Triton-X-100 (*1*); cationic surfactants are DdTAB (*2*), CTAB (*3*), Gem-12 (*4*), and Gem-16 (*5*).

crease in pK_a is observed. A possible reason for acceleration of the reaction is the decrease in the amine pK_a resulting in an increase in the proportion of the neutral form. The observed catalytic action (maximum for Gem-16) agrees with the influence of surfactants on the decylamine pK_a (see Table 1). We compared the rates of PNPA cleavage in the Gem-16 solutions in the presence of decylamine and octylamine. At a concentration of 0.0025 mol L^{-1}, octylamine is much less active (see Fig. 1, curve *5*). In spite of a great decrease in pK_a of octylamine in the micellar solution (from 10.6 in water to 9.9 in 0.01 *M* solution of Gem-16), the fraction of its neutral form (α) at pH 9.2 is ~0.17, whereas for decylamine under the same conditions one has α is ~0.5. To compare the reactivities of the compounds studied, the concentrations of their neutral form should be equal. This is achieved, for example, at the concentrations of decylamine 2.5 mmol L^{-1} and octylamine 7.4 mmol L^{-1}; the concentration of the non-protonated forms of these compounds in the Gem-16 solution at pH 9.2 will be the same and equals 1.25 mmol L^{-1}. However, in this case decylamine also exhibits the higher activity in the reaction with *p*-nitrophenyl acetate (see Fig. 1, curves *1* and *4*). Previously,[5,24] we have shown that the formation of mixed aggregates of long-chain amines with the monomeric cationic surfactants is the main reason for the high nucleophility of the amine. Probably, the formation of mixed micelles decylamine/geminal surfactant is the crucial factor of the increase in the rate of PNPA aminolysis.

The data demonstrated in Fig. 1 were analyzed in the framework of pseudophase model of micellar catalysis using Eq. (1). From the results obtained it follows that the addition of a long-chain amine to cationic surfactants deteriorates the substrate binding by the micelle. In the absence of amine, the K_{bond} values of PNPA are equal to 450, 820, and 2000 L mol^{-1} in the presence of CTAB, Gem-12, and Gem-16, respectively,[18] whereas in the presence of decylamine this value is nearly halved (Table 4). However, the accumulation of the neutral amine form in the micelle leads to acceleration of the process by an order of magnitude or higher. It should be remembered that the rate of the process is also influenced by the polarity of the interphase layer, which is the reaction zone. The higher polarity of the near-surface zone of Gem-16 micelles as compared to CTAB, which was detected by ESR spectroscopy (see Table 2) provides an additional contribution to the catalytic effect.

Summing up, the strong catalytic effect in ester bonds cleavage observed in the Gem-16 and decylamine micellar solutions is due to the formation of functionalized mixed micellar aggregates, what causes a substantial decrease in the amine pK_a and an increase in the micropolarity in the reaction zone.

Table 4. Parameters of micelle-catalyzed reaction of *p*-nitrophenyl acetate cleavage in micellar solutions in the presence of decylamine and octylamine*

Surfactant	Amine	k_0	k_m	K_s /L mol^{-1}	CMC /mol L^{-1}	$k_{app}(max)/k_0$
		s^{-1}				
CTAB	Decylamine	0.0025	0.097	440	0.00016	39
Gem-12	Decylamine	0.0025	0.092	610	0.00025	37
Gem-16	Decylamine	0.0025	0.16	700	0.0002	64
	Octylamine	0.002	0.028	430	0.0003	14

* pH = 9.2, C_{am} = 2.5 mmol L^{-1}, 25 °C.

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