ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 2, pp. 163–170. © Pleiades Publishing, Ltd., 2008.
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Role of Surface Potential in the Catalytic Action of Micelles of Cationic Surfactants with a Hydroxyalkyl Fragment in the Head Group

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Received June 17, 2007

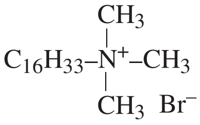
Abstract—The surface potential in aqueous micellar solutions of a series of cetyltrialkylammonium bromides containing a hydroxyalkyl fragment in the head group was determined with a spectral probe (*p*-nitrophenol). It was found that the catalytic effect exerted by these surfactants in solution on the base hydrolysis of carboxylic acid esters is determined by two factors. First, the charged nucleophile is concentrated at the micelle surface. Second, hydrogen bonding of the substrate with the hydroxyalkyl substituents results in its activation.

DOI: 10.1134/S1070363208020023

Cationic surfactants are widely used in the laboratory practice and industry thanks to their capability to solubilize organic compounds in water and to affect the physicochemical properties and reactivity of the solubilized substances [1–4].

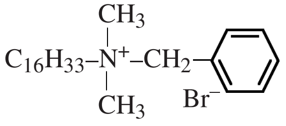
The aggregation behavior of surfactants in solutions is determined by a number of factors: nature of surfactant, structural features of the head group, length and extent of branching of the hydrocarbon radical, salt background, solution acidity, and presence of organic solvents and other organic species. The structure of surfactant ensembles determines such properties of the system as thermodynamic stability, viscoelastic properties, solubilizing capacity for hydrophilic and hydrophobic compounds, and other characteristics [1, 5–8].

This study was aimed to elucidate the effect of the head group of cationic surfactant molecules on their aggregation behavior in aqueous solutions and on their solubilizing properties and catalytic action in hydrolysis of carboxylic acid esters. We examined quaternary ammonium compounds with the same hydrophobic fragment ($C_{16}H_{33}$ radical) and different head groups. We used surfactants containing one or two hydroxyalkyl radicals in the hydrophilic part of the molecule, differing in the distance between the OH group and the cationic center. Hydrophobic, electrostatic, and specific (intermolecular hydrogen bonding) interactions take place in micellar solutions of these surfactants. The properties of hydroxyalkyl surfactants were discussed in comparison with the behavior of related cationic surfactants containing no OH group. The structural formulas of the surfactants examined in this study are given below.

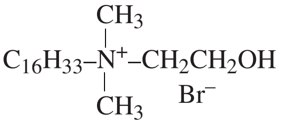


$C_{16}H_{33}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3\ Br^-$

I

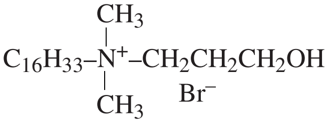


II



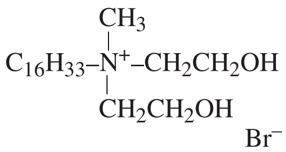
$C_{16}H_{33}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2CH_2OH\ Br^-$

III



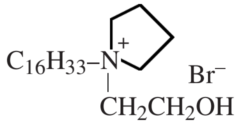
$C_{16}H_{33}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2CH_2CH_2OH\ Br^-$

IV



$C_{16}H_{33}-\overset{CH_3}{\underset{CH_2CH_2OH}{N^+}}-CH_2CH_2OH\ Br^-$

V



VI

The hydrophilic–lipophilic balance and structure of head groups of the surfactants used determine the microscopic properties of the interphase zone, and

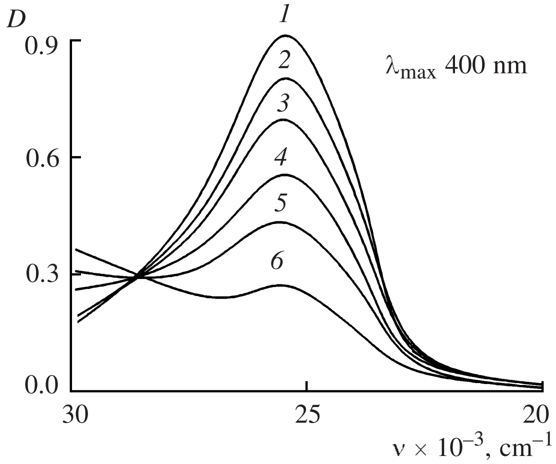


Fig. 1. Spectra of *p*-nitrophenol in an aqueous micellar solution (C_{SA} 0.05 M). pH: (*1*) 10.0, (*2*) 6.6, (*3*) 6.1, (*4*) 5.8, (*5*) 5.6, and (*6*) 5.3.

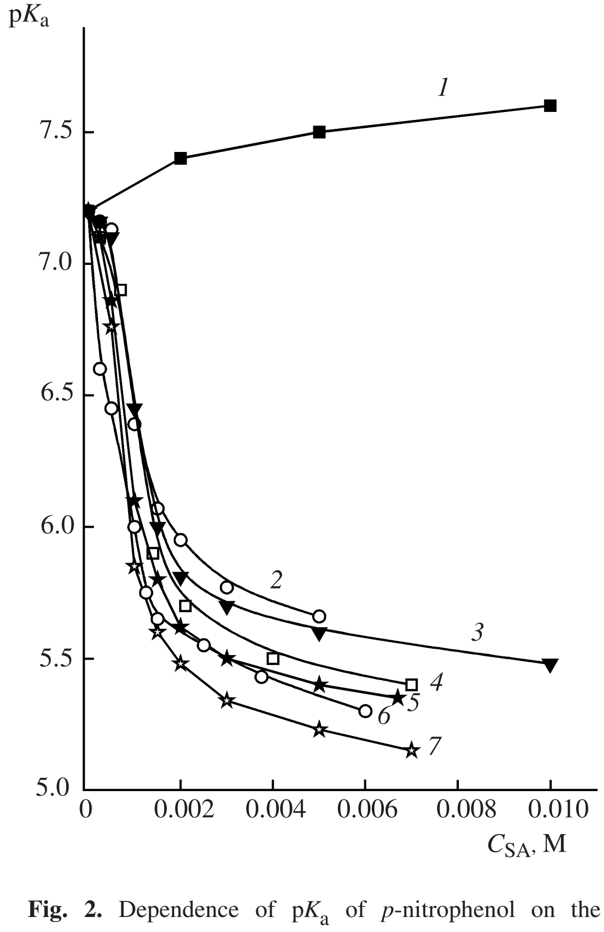


Fig. 2. Dependence of pK_a of *p*-nitrophenol on the surfactant concentration C_{SA} in aqueous solution. Surfactants: (*1*) Triton X-100 (nonionic); (*2*) **I**, (*3*) **III**, (*4*) **IV**, (*5*) **V**, (*6*) **VI**, and (*7*) **II** (all cationic).

primarily the surface potential. The value and sign of the surface potential are important characteristics for ion–molecule reactions in micellar media [5, 9–11]. Cationic surfactants impart the positive charge to the phase boundary. As a result, anions present in the system are concentrated in the Stern layer, and acid properties of compounds are enhanced. The selective solubilizing power of micelles of ionic surfactnats toward acid and base forms of compounds is mainly determined by the surface potential of the micelle (Ψ). Therefore, one of approaches to determination of the surface potential is based on evaluation of the acid–base properties of probe molecules that can be incorporated in the interphase layer and can respond to changes in its structure [9, 10]. In this study, as such a probe we used *p*-nitrophenol whose pK_a values were determined spectrophotometrically. High molar extinction coefficients of this compound allow its use in low concentrations [(2–5) × 10^{-5} M]. At such concentrations, a decrease in the charge density of cationic micelles upon solubilization of negatively charged species is insignificant. Figure 1 shows as example the spectra of *p*-nitrophenol in micellar solutions of surfactant **III**, recorded at various pH values. From the absorption of *p*-nitrophenolate at various pH values, using the Henderson–Hasselbach equation, we calculated the observed pK_a value (p$K_{a,obs}$) [12]:

$$pK_{a,obs} = pH + \log[(phenol)/(phenolate). \qquad (1)$$

The dependences of p$K_{a,obs}$ of *p*-nitrophenol on surfactant concentrations are plotted in Fig. 2.

The observed constant of acid–base dissociation (K_{obs}) is related to surfactant concentration as follows [13]:

$$K_{obs} = \frac{1 + K_B(C_{SA} - CMS)}{1 + K_A(C_{SA} - CMC)} K_{a,w}, \qquad (2)$$

where $K_{a,w}$ is the acid–base dissociation constant in water, K_B and K_A are the binding constants of the acid and base forms of a compound, C_{SA} is the surfactant concentration, and CMC is the critical micelle concentration.

Least-squares treatment of the dependence of $(K_{a,w} - K_{obs})/(C_{SA} - CMC)$ on K_{obs} allows determination of the binding constants of both forms of a compound, taking into account that, at $C_{SA} \to \infty$, $K_{obs} = K_{a,w}K_B/K_A = K_{a,m}$, where $K_{a,m}$ is the dissociation constant of a compound in the micellar phase. We determined the CMC values for **I**–**VI** conductometrically as points of intersection of the linear portions in the concentration dependences of the specific electrical conductivity (an example of such dependence is shown in Fig. 3). The CMC values of the micellar solutions of the surfactants under consideration and the binding constants of the charged and neutral forms of *p*-nitrophenol are given in Table 1. The surface potential, in accordance with [9], can be calculated by formula (3):

$$\mathrm{p}K_{\mathrm{a,m}} = \mathrm{p}K_{\mathrm{a,0}} - F\Psi/(2.303RT), \qquad (3)$$

where $\mathrm{p}K_{\mathrm{a,0}}$ is the nonelectrostatic term defined as $\mathrm{p}K_\mathrm{a}$ in micellar solutions based on nonionic surfactants (Triton X-100, $\mathrm{p}K_\mathrm{a}$ of *p*-nitrophenol 7.6) with the same phase volumes as in the systems with cationic surfactants; $F = 96486\ \mathrm{C\ mol^{-1}}$ is the Faraday constant, and $R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$ is the gas constant. The calculation results are given in Table 1.

It can be seen that the binding constant of the anionic form of *p*-nitrophenol is approximately two orders of magnitude higher than that of the neutral form. As a result, $\mathrm{p}K_\mathrm{a}$ of this compound in the micellar phase of the surfactants is lower than that in water by 1.8–2.2 log units. The surfactants containing a hydroxyalkyl fragment bind the phenolate more strongly than does cetyltrimethylammonium bromide, but the surface potentials of these compounds differ insignificantly. It can be expected that the radicals forming the head group can affect the charge density at the quaternary nitrogen atom owing to the inductive effect, which is similar for methyl, 2-hydroxyethyl, and, the more so, 3-hydroxypropyl substituents. Compound **VI** in which the ammonium group is incorporated in a five-membered ring exhibits a higher surface potential.

When surfactant solutions are used as a medium for chemical reactions involving ionic reactants, the surface potential is responsible for their concentrating near the micellar surface. In this study we examined an ion–molecule reaction of base hydrolysis of carboxylic acid esters, *p*-nitrophenyl acetate and *p*-nitrophenyl laurate. The reaction scheme is shown below.

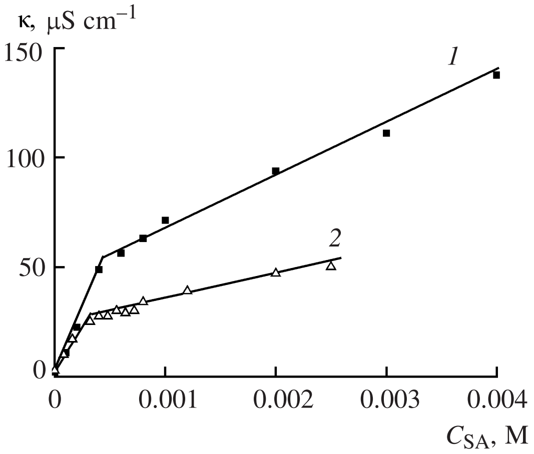
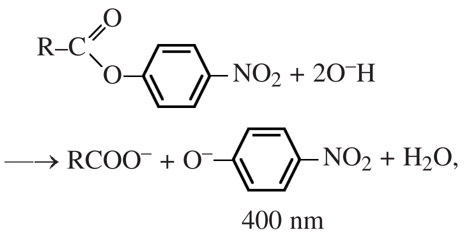


Fig. 3. Concentration dependence of the specific electrical conductivity of aqueous solutions of surfactants (*1*) **VI** and (*2*) **II**.

The esters differ in their hydrophobic properties. The distribution constant between oil and water is 10.8 for *p*-nitrophenyl acetate and 205.4 for *p*-nitrophenyl laurate [15]. It can be expected that the laurate is localized in the oil core of the micelle, whereas the acetate is localized closer to the surface layer, which (along with the hydrophilic–lipophilic properties of the nucleophile) should result in different effect of surfactants on the rate of reactions involving these esters. The presence of a hydroxy group in surfactant molecules may lead to specific binding in the system via hydrogen bonds, which should affect the rate of base hydrolysis.



Note that surfactants containing a hydroxyalkyl substituent in the head group exhibit acid properties ($\mathrm{p}K_\mathrm{a}$ 12.4–12.6) and in strongly alkaline solutions can act as zwitterionic compounds [16, 17]. However, under our experimental conditions (pH 10.0, buffer based on sodium tetraborate and sodium hydroxide), the compounds are typical cationic surfactants. Kinetic studies showed that, for both substrates, the shape of the dependence of the observed rate constant (k_obs)

Table 1. Values of CMC, surface potential, binding constants, and $\mathrm{p}K_{\mathrm{a,m}}$[a] of *p*-nitrophenol in micelles based on cationic surfactants **I**–**VI** (20°C)

Comp. no.	CCM, M	K_HA, M	K_A, M	$\mathrm{p}K_{\mathrm{a,m}}$	Ψ, mV
I	0.0008	230	17300	5.32	133
II	0.00045	590	51030	5.26	136
III	0.00075[b]	465	35290	5.41	127
IV	0.0008	540	51960	5.31	133
V	0.00065[b]	305	37400	5.10	145
VI	0.0005	280	49290	4.97	151

[a] $\mathrm{p}K_\mathrm{a}$ of *p*-nitrophenol in water, as we determined spectrophotometrically, is 7.2. [b] According to [27], CMC (M) of **III** is 0.0072 (fluorimetry), 0.0078 (conductometry), or 0.0083 (microcalorimetry), and that of **V** is 0.0072 (fluorimetry), 0.0070 (conductometry), or 0.0077 (microcalorimetry).

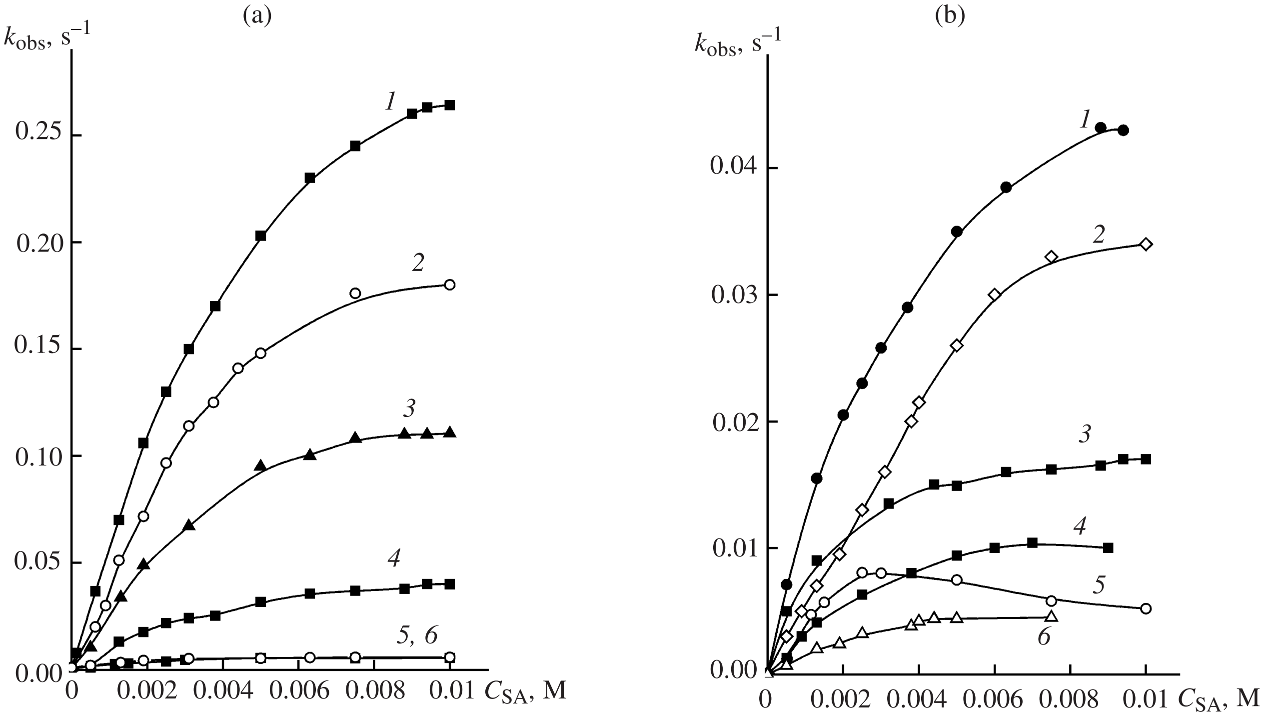


Fig. 4. Observed rate constant of the base hydrolysis (pH 10.0, 25°C) of (a) *p*-nitrophenyl acetate and (b) *p*-nitrophenyl laurate as a function of surfactant concentration: (*1*) **VI**, (*2*) **V**, (*3*) **III**, (*4*) **IV**, (*5*) **I**, and (*6*) **II**.

of hydrolysis on the surfactant concentration has a shape typical of micelle-catalyzed processes with relatively steep ascent followed by flattening out, but for the laurate the range of the rate variation is considerably wider. It is known that the rate constants of base hydrolysis without surfactants for *p*-nitrophenyl acetate are 20 times higher than for *p*-nitrophenyl laurate owing to self-association of the latter and shielding of the carbon atom subject to nucleophilic attack [18]. In micellar solutions, the structures of these associates change, and differences in the reactivity of the two esters are leveled off (Figs. 4a, 4b).

Table 2. Parameters of micelle-catalyzed base hydrolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl laurate (PNPL) in aqueous solutions of various surfactants (pH 10.0, 25°C)

Comp. no.	Substrate	k_m, s^{-1}	K_s, M^{-1}	CMC, M	k_m/k_0 [a]
I	PNPA	0.0073	450	0.0004	7
	PNPL	0.011	1100	0.00044	275
II	PNPA	0.0065	980	0.00024	6.5
	PNPL	0.0063	460	0.00027	158
III	PNPA	0.14	380	0.00034	140
	PNPL	0.019	750	0.000028	475
IV	PNPA	0.053	300	0.00017	53
	PNPL	0.014	420	0.00026	350
V	PNPA	0.28	230	0.00034	280
	PNPL	0.069	120	0.00022	1725
VI	PNPA	0.38	230	0.000077	380
	PNPL	0.063	250	0.000027	1575

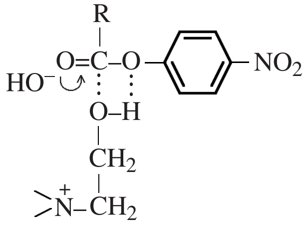
[a] The k_m/k_0 ratio characterizes the micellar-catalytic effect (for the hydrolysis without surfactant at pH 10.0, k_0 = 0.001 s^{-1} for PNPA and 0.00004 s^{-1} for PNPL).

Quantitative characteristics reflecting the substrate–micelle interaction can be derived from the experimental kinetic data using the pseudo-phase model of micellar catalysis [19]:

$$k_{obs} = \frac{k_m K_s(C_{SA} - \mathrm{CMC}) + k_0}{1 + K_s(C_{SA} - \mathrm{CMC})}, \qquad (4)$$

where k_0 and k_m are the rate constants in the aqueous medium and in the micellar phase, respectively, and K_s is the substrate binding constant.

The results of calculations from the data plotted in Figs. 4a and 4b are given in Table 2. The CMC values found from the kinetic data are somewhat lower than those determined conductometrically. This phenomenon is observed frequently and can be accounted for by the fact that a substrate is bound by surfactant molecules before the micellization is complete, and in these premicellar associates the hydrolysis occurs faster than in molecular solutions. The binding constants of the esters under consideration are not very high, and in most cases a more hydrophobic substrate, *p*-nitrophenyl laurate, is bound by the micelle somewhat better than *p*-nitrophenyl acetate. From the rate constants of hydrolysis in the micellar phase, we can evaluate the micellar-catalytic effect characterized by the ratio k_m/k_0, which is higher for laurate than for acetate (Table 2). The highest rate constants are observed with the systems based on surfactants **V** and **VI**, which are characterized by the highest positive surface potential and hence by the most pronounced concentration of the nucleophile at the surface of the micelle in which the substrate is solubiitzed. This fact, however, does not account for the stronger accelerating effect exerted on the hydrolysis of both substrates by the surfactants containing a hydroxyalkyl fragment, compared to celyltrimethylammonium bromide **I**. For *p*-nitrophenyl laurate, the rate constants of the hydrolysis in solutions of **III**–**VI** exceed those obtained with **I** by a factor of 1.5–6, and for *p*-nitrophenyl acetate the difference is still larger, by a factor of 7.5–55. Apparently, the less hydrophobic substrate is localized near the head groups of the surfactants. with the formation of a hydrogen-bonded complex in which the carbonyl center acquires an additional positive charge facilitating an attack by hydroxide ion:



Such a type of substrate activation, leading to acceleration of the base hydrolysis of phosphorus acid esters by more than two orders of magnitude, was observed with betaine forms of hydroxyethyl surfactants [16]. *p*-Nitrophenyl laurate, tending to localize in the micelle core, is disconnected from the hydroxy group of the head fragment, which prevents hydrogen bonding and activation of the carbonyl center. With this substrate, the observed catalytic effect is mainly due to the fact that the anionic nucleophile is concentrated at the positively charged micelle surface, i.e., the effect is governed by Ψ.

It is known [9, 20–22] that the surface potential in micellar solutions of ionic surfactants can be controlled by supporting electrolyte additions. This is due to the fact that an increase in the concentration of surfactant counterions with addition of an electrolyte leads to partial neutralization of the surface charge of the micelles, which, in turn, decreases the destabilizing repulsion of similarly charged head groups. In the process, the surface potential of the system decreases in the absolute value, CMC decreases, the aggregation numbers increase, and the micellar effect on physicochemical properties and reactivity of solubilized substances changes [23–25]. In this study, we added a supporting electrolyte (KBr) to micellar solutions of cetyltrimethylammonium bromide **I** and cetyldimethyl(2-hydroxyethyl)ammonium bromide **III**, to decrease the surface potential. In these systems, we studied the kinetics of hydrolysis of *p*-nitrophenyl acetate. The results are shown in Figs. 5 and 6. The potentials that we determined spectrophotometrically were 120 mV for **I** and 112 mV for **III** with 0.01 M KBr, and 107 and 102 mV, respectively, with 0.02 M KBr. The dependence of the observed rate constant of hydrolysis of *p*-nitrophenyl acetate on the surfactant concentration (Fig. 5) shows that the catalytic effect caused by concentrating of hydroxide ion at the positively charged interphase surface decreases, and its value with cetyltrimethylammonium bromide does not exceed 2. However, for **III** the catalytic effect is also due

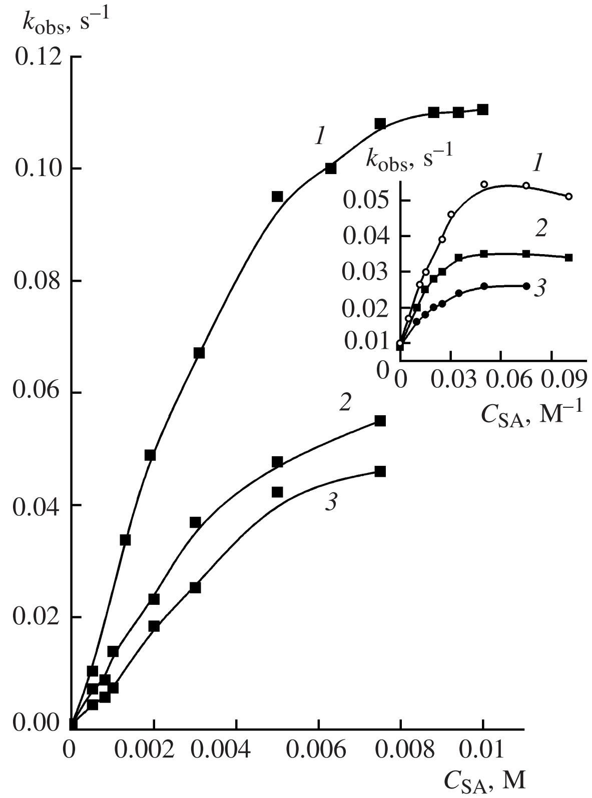


Fig. 5. Observed rate constant of base hydrolysis (pH 10.0, 25°C) of *p*-nitrophenyl acetate as a function of the concentration of surfactant **III** at KBr concentrations of (*1*) 0, (*2*) 0.01, and (*3*) 0.02 M. The insert shows the corresponding plots for cetyltrimethylammonium bromide.

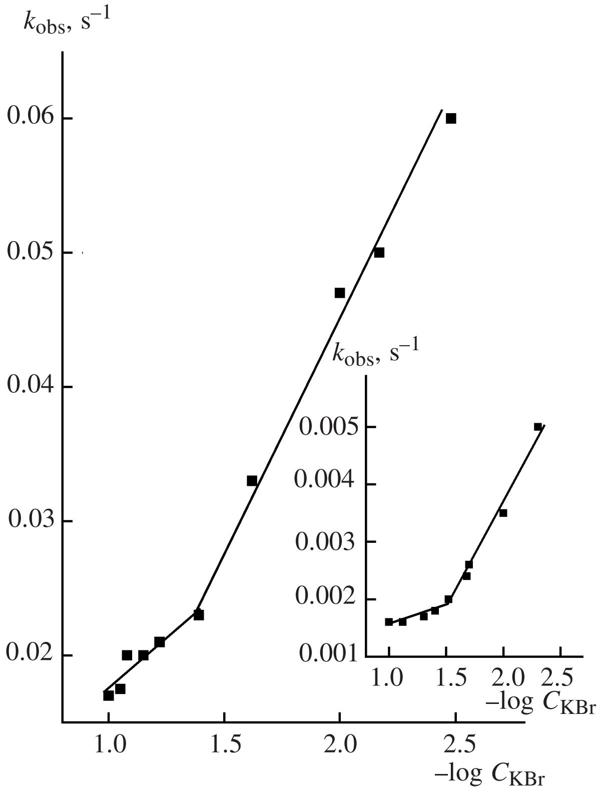


Fig. 6. Observed rate constant of base hydrolysis of *p*-nitrophenyl acetate in micellar solutions of surfactant **III** as a function of logarithm of KBr concentration (C_{SA} = 0.005 M, pH 10.0, 25°C). The insert shows the corresponding plots for cetyltrimethylammonium bromide.

to substrate activation by hydrogen bonding with the head group of the surfactant, and therefore the response of this system to supporting electrolyte addition is weaker, and the value of the catalytic effect reaches almost two orders of magnitude.

Addition of an electrolyte to surfactant solutions in some cases induces structural rearrangements in the system, in particular, sphere–cylinder micellar transitions [8, 20, 22, 26]. Disturbance of the steady state of ion-exchange processes occurring in these systems can be reflected in the character of concentration dependences of kinetic characteristics. Critical points (C_{cr}) associated with qualitative changes in the micelle state can apear in these dependences. A study of the kinetics of base hydrolysis of *p*-nitrophenyl acetate in relation to the KBr concentration at a constant concentration of hydroxyalkyl surfactant **III** in solution (0.005 M) shows that, with increasing KBr concentration, the observed rate constant decreases nonuniformly. The dependences k_{obs}–$\log C_{KBr}$ (Fig. 6) acquire a characteristic shape with a break at C_{KBr} = 0.04 M. Similar dependences are obtained in micellar solutions of cetyltrimethylammonium bromide as a reaction medium for the hydrolysis of *p*-nitrophenyl acetate (Fig. 5, insert). The value of C_{cr} = 0.03 M, determined for this surfactant, is consistent with the values given in [20, 26]. Presumably, in solutions of the surfactants under consideration, addition of an electrolyte causes a sphere–cylinder micelle transition. This is accompanied by an increase in the packing density of surfactant molecules in the aggregate, enhancement of hydrophobic interactions, changes in the degree of hydration, decrease in the degree of ionization of the head groups, and weakening of the micellar catalytic effect [8]. Note that initiation of this transition in the case of hydroxyalkyl surfactant **III** requires adition of a somewhat larger amount of the electrolyte than in the case of cetyltrimethylammonium bromide. Furthermore, the possibility of the substrate activation by intermolecular hydrogen bonding leads to the high catalytic effect with both spherical and cylindrical aggregates of surfactant **III**.

Thus, the effect of the head group of the surfactant on the catalytic properties of the system in ion–molecule processes, on the one hand, consists in changes in the electron density at the quaternary nitrogen atom and hence in the surface potential, which leads to changes in the concentration gradient of an ionic reagent in the micellar system. On the other hand, the substrate can specifically interact (hydrogen bonding) with the hydroxyalkyl substituent, which enhances the reactivity. Addition of a supporting electrolyte is an additional tool to control the catalytic effect of the system by affecting the surface potential and structure of micelles.

EXPERIMENTAL

Commercial cetyltrimethylammonium bromide and Triton X-100 (Sigma) used in this study contained about 99% main substance. Cationic surfactants with a hydroxyalkyl substituent were prepared by quaternization of the corresponding amino alcohols with cetyl bromide by the procedure given in [14, 27]. The structure of the compounds was proved by elemental analysis (Table 3) and ^{1}H NMR spectroscopy. *p*-Nitrophenol and its carboxylic acid esters (Fluka) were purified by standard procedures. Solutions were prepared in double-distilled water.

The specific electrical conductivities of surfactant solutions prepared in double-distilled water with the conductivity no greater than 1.8 μS cm^{-1} were measured with a CDM-2d device (Denmark).

Table 3. Characteristics of the synthesized samples of cationic surfactants

Surfactant	T_m, °C	C, %		H, %		N, %		Br, %	
		found	calculated	found	calculated	found	calculated	found	calculated
II	68–69	68.09	68.16	10.58	10.52	3.21	3.18	18.09	18.04
III	203–205	60.84	60.89	11.32	11.24	3.52	3.52	20.17	20.25
IV	89–90	61.72	61.74	11.40	11.35	3.46	3.43	19.55	19.56
V	116–118	59.39	59.42	10.94	10.92	3.38	3.30	18.80	18.82
VI	212–214	62.75	62.84	11.05	11.03	3.40	3.33	19.23	19.00

Acid–base properties of *p*-nitrophenol were studied by measuring the absorption of the ionized form at various pH values. The spectra were recorded with a Specord UV0VIS spectrophotometer in quartz cells with the absorbing layer thickness $L = 1$ cm in the range from 250 to 400 nm. The extinction coefficient ε of the phenolate form was determined from the optical density D in the absorption maximum. The concentration of *p*-nitrophenol C_{PhO^-} at a given pH was determined from the relationship $C_{\mathrm{PhO}^-} = D/(\varepsilon L)$. Three to five replicate measurements at each pH value were made, and their results were averaged. Their reproducibility was within ±0.05.

The reaction kinetics were studied spectrophotometrically on a Specord UV-VIS device in temperature-controlled cells. The reaction progress was monitored by variation of the optical density of the solutions at a wavelength of 400 nm (formation of *p*-nitrophenolate anion). The initial concentration of the substrate was $(2–8) \times 10^{-5}$ M, and the degree of conversion was more than 90%. The observed pseudo-first-order rate constants k_{obs} were determined from the relationship $\log(D_\infty - D_\tau) = -0.434k_{\mathrm{obs}}\tau + \mathrm{const}$ (D_τ and D_∞ are the optical densities of the solutions at time τ and after the reaction completion, respectively). The quantities k_{obs} were calculated by the least-squares method. The experimental data were described by a first-order equation with the correlation coefficient higher than 0.99. The values of k_{obs} obtained from two replicate experiments were averaged, and the differences between them did not exceed 4%.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 05-03-33110).

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