Control of the catalytic effect of cetyltrimethylammonium bromide micelles by the addition of background electrolyte and nonionic surfactant

A. B. Mirgorodskaya,[a]* *L. Ya. Zakharova,*[a] *F. G. Valeeva,*[a] *A. V. Zakharov,*[b] *L. Z. Rizvanova,*[a] *L. A. Kudryavtseva,*[a] *H. E. Harlampidi,*[b] *and A. I. Konovalov*[a]

[a]*A. E. Arbuzov Institute of Organic and Physical Chemistry,*
Kazan Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843) 273 2253. E-mail: mirgorod@iopc.knc.ru
[b]*Kazan State Technological University,*
68 ul. K. Marksa, 420015 Kazan, Russian Federation

The variation of the microscopic properties (surface potential, micropolarity, *etc.*) of the interface of cetyltrimethylammonium bromide micelles upon the addition of a background electrolyte or the nonionic surfactant Triton X-100 decreases the rates of ion-molecular reactions, namely, alkaline hydrolysis of carboxylic acid esters and tetracoordinate phosphorus acid esters, and results in the shift of acid-base equilibria.

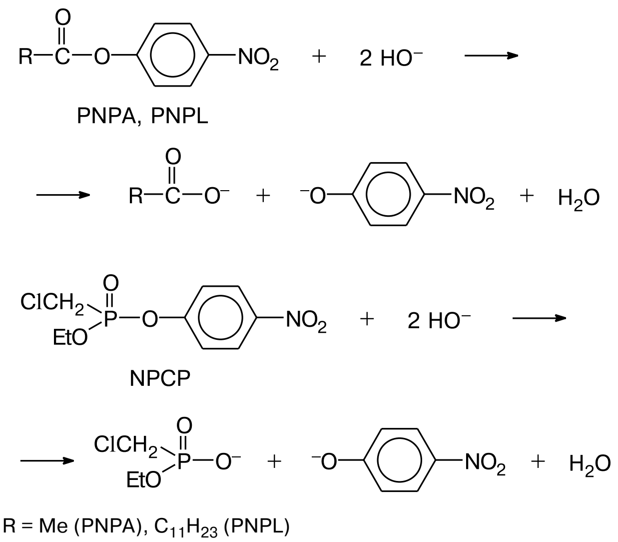
Key words: micelles, cetyltrimethylammonium bromide, background electrolyte, Triton X-100, acid-base properties, surface potential, esters, hydrolysis, kinetics.

Micellar solutions of ionic surfactants provide wide possibilities for controlling the rate of ion-molecular reactions.[1—5] In turn, the reactions themselves, in particular, alkaline hydrolysis of carboxylic acid esters and phosphorus acid esters, are sensitive indicators of the microscopic properties of the medium in the reaction zone. As a rule, similar processes occur in the Stern layer of ionic micelles and depend, to a considerable extent, on the sign of the micellar surface charge. For instance, alkaline hydrolysis of substrates is accelerated in cationic micelles due to the electrostatic attraction of the hydroxyl ions to the micellar surface and is inhibited in anionic micelles because of the electrostatic repulsion of the OH ions from the likely charged surface. Thus, the surface potential plays a key role in similar catalytic systems. The variation of the potential value can be used for the directed control of the rate of ion-molecular reactions in a wide range including the inhibition and catalytic effects.

An increase in the concentration of surfactant counterions achieved by the addition of a background electrolyte neutralized partially the micellar surface charge, which, in turn, decreases the destabilizing repulsion of the likely charged head groups. This results in a drop of the absolute value of the surface potential of the system, a decrease in the critical micelle concentration (CMC), an increase in the aggregation numbers, and a change in the micellar effect on the physicochemical properties and reactivity of solubilized substances.[6—9] Other systems in which the surface potential changes upon the variation of the composition are binary systems containing ionic and nonionic surfactants. The insertion of oxyethylene fragments between the charged ammonium groups decreases the surface charge density, as in the case of the addition of electrolytes.[10,11]

In this work, we studied the catalytic effect of micellar solutions of the cationic surfactant cetyltrimethylammonium bromide (CTAB) on the alkaline hydrolysis of carboxylic acid esters, namely, *p*-nitrophenyl acetate (PNPA), *p*-nitrophenyl laurate (PNPL), and *p*-nitrophenyl *O*-ethylchloromethylphosphonate (NPCP) (Scheme 1).

Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1933—1940, October, 2007.

The objects of the study were CTAB—electrolyte and CTAB—Triton X-100 systems for which the monotonic decrease in the surface potential with an increase in the concentration of electrolytes or nonionic surfactants has been found previously.[7,11] One of indicators of the density of the micellar surface charge is the shift of acid-base equilibria in ionic micelles. Therefore, to test the influence of electrolytes and nonionic surfactants on the surface potential, we studied the change in p*K* of *n*-octylamine in micellar solutions.

Experimental

Commercial preparations of CTAB and Triton X-100 (Sigma) and *n*-octylamine and *p*-nitrophenyl esters of carboxylic acids (Fluka) containing ~99% of the major substance were used. *p*-Nitrophenyl ester of phosphorus acid was synthesized according to an earlier described procedure.[12]

The pK_a values of *n*-octylamine were determined by potentiometric titration with a 0.1 *M* solution of HCl using a pH-340 instrument. The kinetics of the reactions were studied spectrophotometrically on a Specord UV—Vis instrument at 25 °C by monitoring a change in the absorbance of solutions at a wavelength of 400 nm (formation of the *p*-nitrophenoxide anion). The initial concentration of the substrate was $5 \cdot 10^{-5}$ mol L^{-1}, and the conversion was higher than 90%. The apparent rate constants of the pseudo-first order (k_{app}) were determined from the dependence $\log(A_\infty - A_\tau) = -0.434k_{app}\tau$ + const, where A_τ and A_∞ are the absorbances of solutions at the moment τ and after the reaction completion. The k_{app} values were calculated by the least-squares method.

The kinetic curves obtained were analyzed in the framework of the pseudo-phase approach using the equation[1,2]

$$k_{app} = (k_m K_S C_{Surf} + k_0)/(1 + K_S C_{Surf}), \tag{1}$$

$$k'_{app} = \frac{k_{2,0} + (k_{2,m}/V)K_S K_{OH} C_{Surf}}{(1 + K_S C_{Surf})(1 + K_{OH} C_{Surf})}, \tag{2}$$

where k_0 and k_m (s^{-1}) are the rate constants of the first order in an aqueous medium and in the micellar phase, respectively; k'_{app} (L mol^{-1} s^{-1}) is the second-order rate constant obtained by the division of k_{app} into the total concentration of the hydroxyl ion; $k_{2,0}$ and $k_{2,m}$ (L mol^{-1} s^{-1}) are the second-order rate constants in the aqueous and micellar phases, respectively; K_S and K_{OH} (L mol^{-1}) are the binding constants of the substrate and hydroxyl ions; V (L mol^{-1}) is the molar volume of the surfactant; C (mol L^{-1}) is the total concentration of the surfactant minus CMC.

The surface tension was measured by the De Noüy ring detachment method.

Results and Discussion

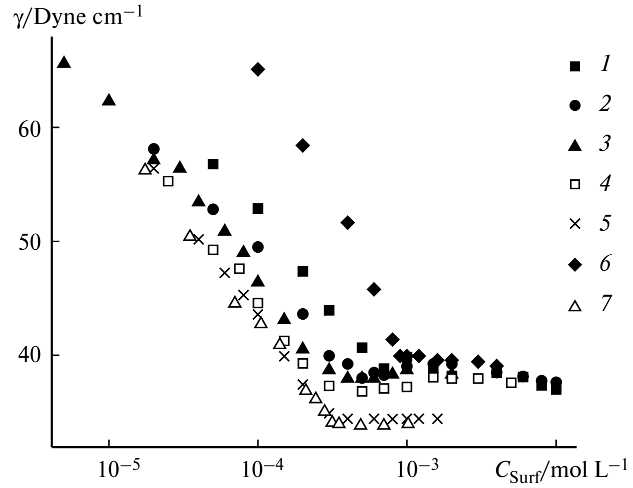


Fig. 1. Isotherms of surface tension (γ) for CTAB—Triton X-100 mixed micellar solutions at the molar ratio of the ionic surfactant α_1 = 0.9 (*1*), 0.7 (*2*), 0.5 (*3*), 0.3 (*4*), 0.1 (*5*), 1.0 (*6*), and 0 (*7*); 25 °C.

Self-organization in a CTAB—Triton X-100 binary system. The formation of mixed micelles in a CTAB—Triton X-100 binary system was confirmed when studying the surface tension of solutions with different fractions of the surfactant (Fig. 1). Micelle formation in a solution of surfactant binary systems is determined to a great extent by their structure: nature of head groups and the length of hydrocarbon radicals. In the case of mixed micelles of ionic and nonionic surfactants, their composition can differ substantially from the composition of the solution. A series of thermodynamic theories and semiempirical models was developed for the quantitative description of the properties of mixed micellar solutions. For non-ideal mixing, some quantitative characteristics of surfactant solutions (CMC, composition of micellar aggregates, concentration of the monomeric form of diphilic molecules) can be predicted in the framework of the semiempirical model based on the regular solution theory[13] in which the activity coefficients of the surfactant (f_1 and f_2)

$$1/C^* = \alpha_1/(f_1C_1) + \alpha_2/(f_2C_2) \tag{3}$$

(α_1 and α_2 are the molar fractions of the ionic and nonionic surfactants in solution, respectively; C^*, C_1, and C_2 are the CMC values for a mixed system, ionic surfactant, and nonionic surfactant, respectively) and the interaction parameter of the surfactant in mixed aggregates (β) were introduced in order to take into account the non-ideal character of the mixture

$$f_1 = \exp[\beta(1 - x_1)^2], \tag{4}$$

$$f_2 = \exp(\beta x_1^2). \tag{5}$$

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

$$\frac{x_1^2 \ln[a_1C^*/(x_1C_1)]}{(1 - x_1)^2 \ln\{[(1 - a_1)C^*]/[(1 - x_1)C_2]\}} = 1 \tag{6}$$

using the iteration procedure.

The mathematical apparatus used in the calculations has been described in detail.[13] The β parameter can be calculated by the equation

$$\beta = \ln[(a_1C^*)/(x_1C_1)]/(1 - x_1)^2. \quad (7)$$

This parameter takes into account the degree of deviation of the system from an ideal mixture and the character of interaction of surfactant monomers in mixed micelles. The negative value of the β parameter assumes that attraction forces between the surfactant molecules predominate, whereas the positive value assumes the predomination of repulsion forces. The increase in the absolute β value indicates the more considerable deviation of the micellar system from an ideal mixture.

An analysis of the tensiometric data using Eqs (3)—(7) showed the negative deviation of the system from an ideal mixture, the interaction parameter being $\beta = -1.05$. The value obtained indicates the synergetic behavior of a CTAB—Triton X-100 system, *i.e.*, formation of aggregates of the mixed type. We have earlier[14,15] found a similar effect for binary solutions of CTAB with the nonionic surfactants Brij-97 and $C_{14}EO_9$. The CMC values determined experimentally and calculated by Eq. (3) are given in Fig. 2. The good agreement confirms that the model and conclusions about mixed micelle formation are adequate. The calculated molar fractions of CTAB in mixed aggregates (x_1) are lower than the stoichiometric fraction of CTAB in the solution α_1, *i.e.*, mixed micelles are enriched in the nonionic surfactant (see Fig. 2).

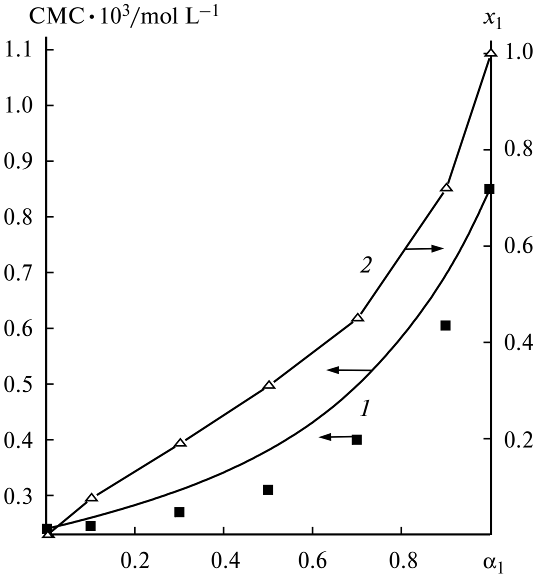


Fig. 2. Plots of the CMC of a CTAB—Triton X-100 mixed micellar system (*1*) (points are experimental data, and line is the calculation by Eq. (3)) and the molar fraction of CTAB in mixed aggregates (x_1) (*2*) *vs* surfactant fraction in the solution (α_1).

Shift of pK_a of aliphatic amines. It is known that the shift of acid-base equilibria occurs in aqueous micellar solutions of surfactants. The cationic surfactants exhibit the enhancement and the anionic surfactants show the weakening of the acidic properties of the compounds. This is due to the selective solubilizing effect of micelles with respect to the acidic and basic forms of the compounds. For ionic surfactant, this is mainly determined by the surface potential of a micelle.[16—18] Additives of a background electrolyte decrease the surface potential, thus affecting the value of the pK_a shift.

The plots of pK_a of *n*-octylamine solubilized by CTAB micelles *vs* surfactant and potassium bromide contents are shown in Fig. 3. In the absence of electrolytes, the surface potential of CTAB is 130—140 mV.[7,19] Due to the electrostatic repulsion, the protonated form of *n*-octylamine is bound by CTAB micelles less efficiently than the neutral form. Therefore, an increase in the surfactant concentration decreases the pK_a value of amine (see Fig. 3, curve *1*). The addition of potassium bromide decreases

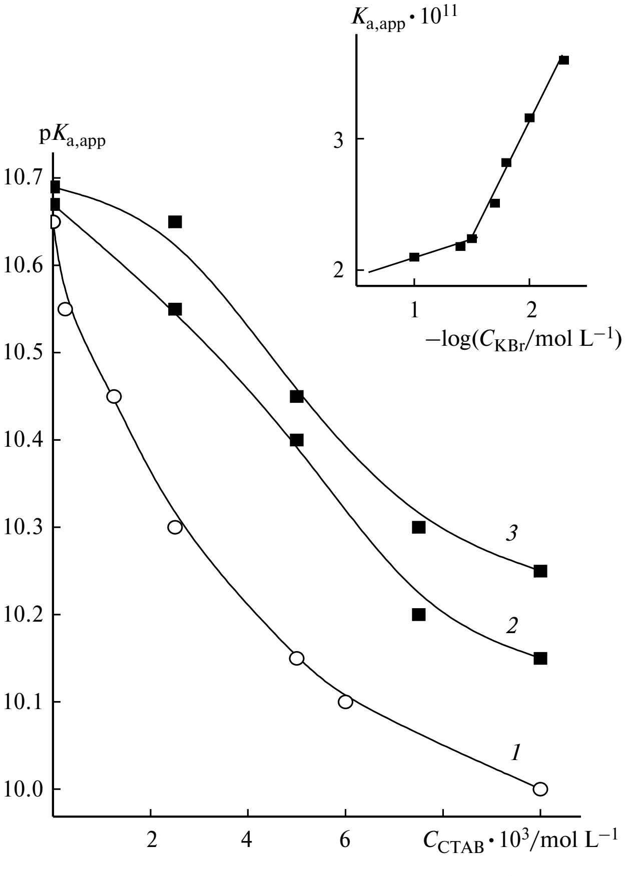


Fig. 3. Plots of pK_a of *n*-octylamine (0.005 mol L^{-1}) *vs* CTAB concentration at a KBr content of 0 (*1*), 0.01 (*2*), and 0.02 mol L^{-1} (*3*). The dependence of the apparent rate of the acid-base equilibrium of *n*-octylamine in a micellar solution of CTAB (0.0025 mol L^{-1}) on the logarithm of the potassium bromide concentration is shown in inset; 25 °C (C_{cr} = 0.028 mol L^{-1}).

the surface potential of CTAB due to an additional binding of the counterions with the head groups. For instance, when the KBr concentration increases in solution to 0.02 mol L^{-1}, the surface potential decreases[7] to 118 mV. When the micellar charge is compensated by the counterions, the influence of CTAB on pK_a of *n*-octylamine decreases (see Fig. 3, curves *2* and *3*).

In some cases, the introduction of an electrolyte into surfactant solutions results in structural rearrangements in the system, in particular, induces sphere—cylinder micellar transitions.[19—22] The violation in stationarity of the ion-exchange processes that occur in the systems can reflect the character of dependences of the apparent acid-base equilibrium constants on the logarithm of the salt concentration (see Fig. 3, inset), which gain the shape of broken straight lines with breaks in the points related to qualitative changes in the state of micelles (critical points, C_{cr}). The C_{cr} values obtained when studying the effect of potassium bromide on pK_a of *n*-octylamine (C_{cr} = 0.028 mol L^{-1} at C_{CTAB} = 0.0025 mol L^{-1}) are close to those obtained earlier.[19]

Another way to exert influence upon the surface potential of a micelle is the addition of a nonionic detergent to a solution of a cationic surfactant. In mixed compositions, the surface potential depends on the molar fraction of each component of the mixture. The decrease in the potential observed[11] upon the addition of Triton X-100 to a solution of CTAB reflects on the pK_a values of *n*-octylamine (Fig. 4). The shift of pK_a related to a change in the basicity of *n*-octylamine on going from an aqueous medium to the micellar phase (ΔpK) decreases with an increase in the fraction of Triton X-100 (α_2) in a CTAB—Triton X-100 system (see Fig. 4, inset). In the case when the contents of the surfactant and *n*-octylamine in the solution are comparable, the neutral form of the latter can also play the role of a nonionic amphiphile, which can be incorporated into the interfacial layer and induce a decrease in the charge density in the layer.

Catalytic effect of CTAB—electolyte systems. Micellar solutions of CTAB containing KBr were used as reaction media for the alkaline hydrolysis of carboxylic acid esters, *viz.*, PNPA and PNPL.

The application of a cationic surfactant provides a positive charge on the micellar surface and induces the concentrating of hydroxyl ions in the Stern layer. In this case, the ester solubilized by the micelle is brought together with the highly hydrophilic nucleophile, providing hydrolysis acceleration. The introduction of a background electrolyte into a CTAB solution decreases the surface potential of the system, decreases the attraction of the hydroxyl ion to the interface, and should decrease the micellar catalytic effect. The plots of the apparent rate constant of alkaline hydrolysis for two esters differed in hydrophilic—lipophilic balance *vs* cationic surfactant concentration (in the absence of the background electrolyte and in the presence of 0.01 *M* KBr) are presented in Fig. 5. The experimental kinetic data were analyzed in the framework of the pseudo-phase model of micellar catalysis according to Eq. (1). The results are given in Table 1. They show (see Fig. 5 and Table 1) that the micellar catalytic effect for the esters under study differs substantially. In the systems containing no potassium bromide, the maximum k_m/k_0 ratio for PNPA is about four, whereas for PNPL it is by two orders of magnitude higher. It is known that the laurate self-associates in aqueous solutions, resulting in the shielding of the reaction center and an anomalously low rate of alkaline hydrolysis compared to the acetate (the second-order rate constant is 8.4 and 0.024 L mol^{-1} s^{-1} for PNPA and PNPL, respectively). In micellar solutions of cationic surfactants, molecules become separated and globular associates of hydrophobic PNPL are untwisted when the PNPL is incorporated into the CTAB-based micelle. This makes the substrate accessible for the attack by the nucleophile and accelerates considerably the process. The presence of the electrolyte

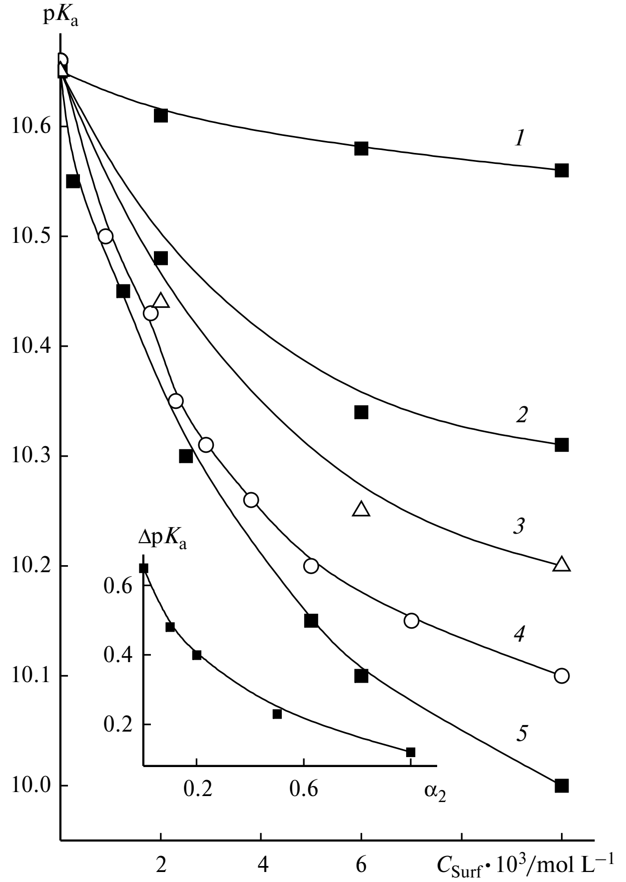


Fig. 4. Plots of pK_a of *n*-octylamine *vs* total surfactant concentration in a CTAB—Triton X-100 mixed micellar solution at the molar fraction of Triton X-100 α_2 = 1.0 (*1*), 0.5 (*2*), 0.2 (*3*), 0.1 (*4*), and 0 (*5*). The dependence of the shift of pK_a of *n*-octylamine on the molar fraction of Triton X-100 in the mixed composition is shown in inset.

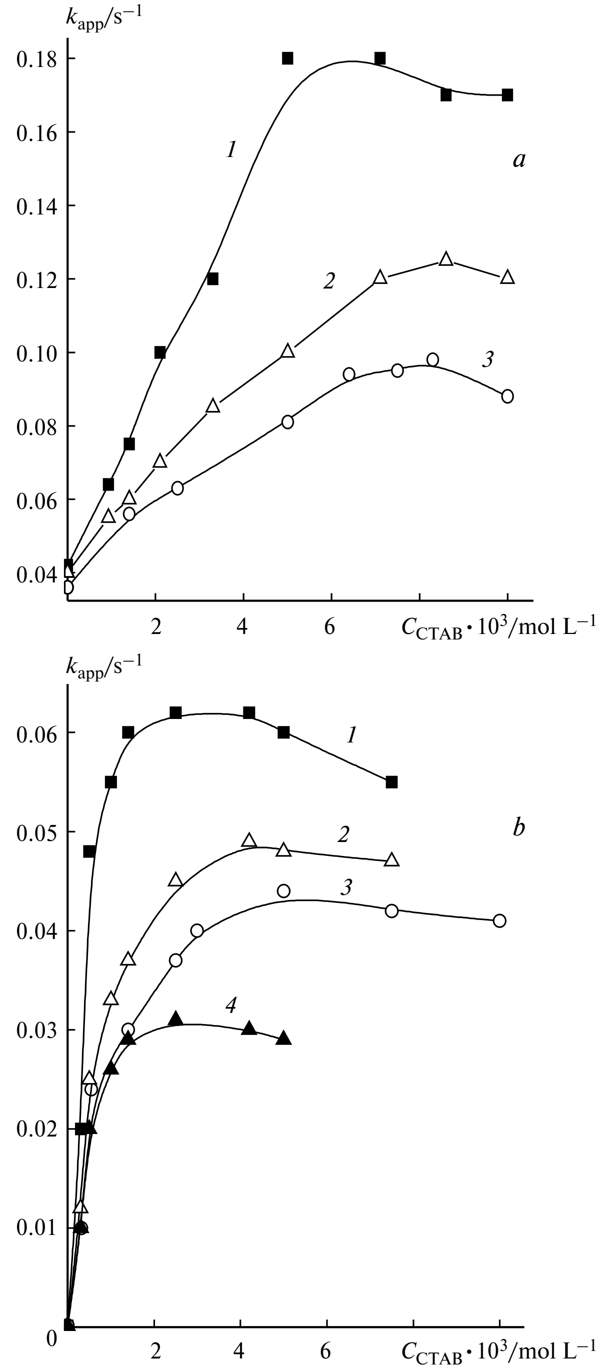


Fig. 5. Plots of the apparent rate constant of alkaline hydrolysis of PNPA (*a*) and PNPL (*b*) *vs* CTAB concentration (0.005 *M* NaOH, 25 °C) in the absence of an electrolyte (*1*) and in the presence of KBr in a concentration of 0.005 (*2*), 0.01 (*3*), and 0.015 mol L^{-1} (*4*).

does not basically change the situation; however, the catalytic effect value is somewhat lower in this case (see Fig. 5, Table 1).

Table 1. Quantitative analysis according to Eq. (1) of the kinetic data for the alkaline hydrolysis of carboxylic acid esters in a CTAB micellar solution in the absence of a background electrolyte in the presence of potassium bromide (see Fig. 5)

Sub-strate	C_{KBr} /mol L^{-1}	k_0	k_m	K_s*	CMC /mol L^{-1}	k_m /k_0**
		s^{-1}				
PNPA	0	0.042	0.18	420	0.0005	4.3
	0.005	0.036	0.08	280	0.0003	2.2
	0.010	0.032	0.06	230	0.0002	1.9
PNPL	0	0.00012	0.063	7000	0.0003	525
	0.005	0.00017	0.053	2100	0.00017	317
	0.010	0.00019	0.047	2200	0.00015	247
	0.015	0.00017	0.031	2000	0.00025	163

* In L mol^{-1}.

** The k_m/k_0 ratio is a measure of the catalytic effect.

The results in Table 1 show that PNPL is much strongly bound by a micelle than PNPA and the addition of potassium bromide decreases the binding constant of the both substrates. In micellar solutions of CTAB, differences in the reaction behavior of the substrates under study are aligned and their k_m values become close, whereas the micellar effect for PNPL is substantially higher (acceleration by more than 500 times). As already assumed, the decrease in the surface potential due to the addition of potassium bromide weakens the attraction of the hydroxyl ion to the micellar surface and thus decreases the catalytic effect of the system.

The apparent rate constant decreases nonmonotonically with a decrease in the potassium bromide content, and the plot of k_{app} *vs* logC_{KBr} (Fig. 6), as for the acid-base equilibrium constants, has a critical point caused by structural rearrangements in the system. Since the C_{cr} value characterizes the properties of the micellar system itself, its value is virtually independent of the type of the process and equals the total concentration all bromide ions that are present in the solution (~0.03 mol L^{-1}), which virtually coincides with the value obtained by the shift of pK_a of *n*-octylamine (0.028 mol L^{-1}).

We have earlier studied the salt effect in the alkaline hydrolysis of phosphorus acid esters in micellar solutions of cationic surfactants with the pyridinium head group[8] and found a sharp change in the reactivity of the phosphonates in the region of sphere—rod micellar transitions. Continuing these studies, we measured the kinetics of alkaline hydrolysis of phosphonate **1** in micellar solutions of CTAB (0.001 mol L^{-1}) in the presence of several sodium salts (Fig. 7). When choosing counterions, their hydrophilicity was taken into account. In addition to inorganic salts, we studied sodium salicylate (NaSal), which is characterized[23] by high affinity to micelles of cationic surfactants. As in the case of hydrolysis of carboxylic acid esters, the apparent rate constant decreases considerably. The inhibiting salt effect increases in the order $Cl^- < Br^- < Sal^-$. It is seen that for the organic salicylate

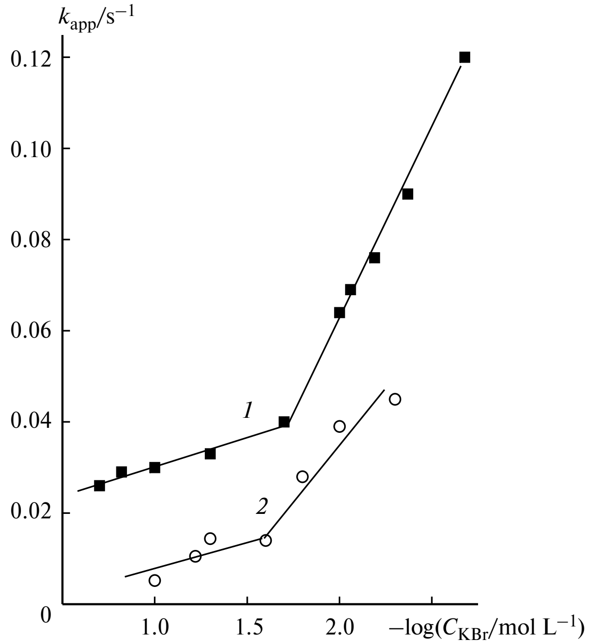


Fig. 6. Plots of the apparent rate constant of alkaline hydrolysis of carboxylic acid esters in micellar solutions of CTAB *vs* logarithm of the potassium bromide concentration (0.005 *M* NaOH, C_{CTAB} = 0.0025 mol L^{-1}, 25 °C): *1*, PNPA (C_{cr} = 0.022 mol L^{-1}); *2*, PNPL (C_{cr} = 0.027 mol L^{-1}).

ion the reaction is significantly retarded (by more than an order of magnitude) at much smaller salt concentrations. It can be assumed that the surface charge of the micelles is efficiently compensated and also the substrate is displaced from the reaction zone (Stern layer) by the hydrophobic salicylate ions.

We analyzed the kinetic data for the hydrolysis of NPCP in the presence of NaBr in the logarithmic coordinates (see Fig. 7, inset). The presence of the break in the line in the k_{app}—logC_{NaBr} coordinates indicates a sharp change in the reactivity of the phosphonate. The value C_{cr} = 0.028 mol L^{-1} coincides with analogous values in Figs 3 and 6 and with the data obtained earlier.[21] Thus, the C_{cr} value is independent of the type of the process under study, *i.e.*, C_{cr} is an indicator of the critical state of micellar aggregates, particularly, of the rearrangement of spherical micelles into cylindrical ones.[19] These results confirm the conclusions about the role of the structural factor in micellar catalysis.[7,8,19,21]

Thus, the addition of a background electrolyte, on the one hand, decreases the surface potential of the micellar system and, on the other hand, favors structural rearrangements in the system, which reflects the reactivity of the substances solubilized by micelles.

Catalytic effect of a CTAB—Triton X-100 system. The results of studying the kinetics of alkaline hydrolysis of the phosphonate in a CTAB—Triton X-100 mixed micellar system with the variation of the ionic/nonionic surfactant ratio are presented in Fig. 8. It turned out that the catalytic effect of this system differs significantly from those of the earlier[14,15] studied CTAB—Brij-97 and CTAB—$C_{14}EO_9$ binary solutions for which the nonmonotonic change in the rate constant was observed at small molar fractions of the nonionic surfactant. In particular, at α_1 = 0.6—0.9 the reaction rate constant increases with an increase in the content of the nonionic surfactant, *i.e.*, with a decrease in the surface potential. In the system under study (see Fig. 8), even a minor additive of the nonionic surfactant (α_1 = 0.9) decreases considerably the apparent rate constant, which continues to decrease smoothly with an increase in the molar fraction of Triton X-100. At α_1 = 0.1 the sign of the catalytic effect changes, *i.e.*, transition from the acceleration of the hydrolysis to its inhibition occurs.

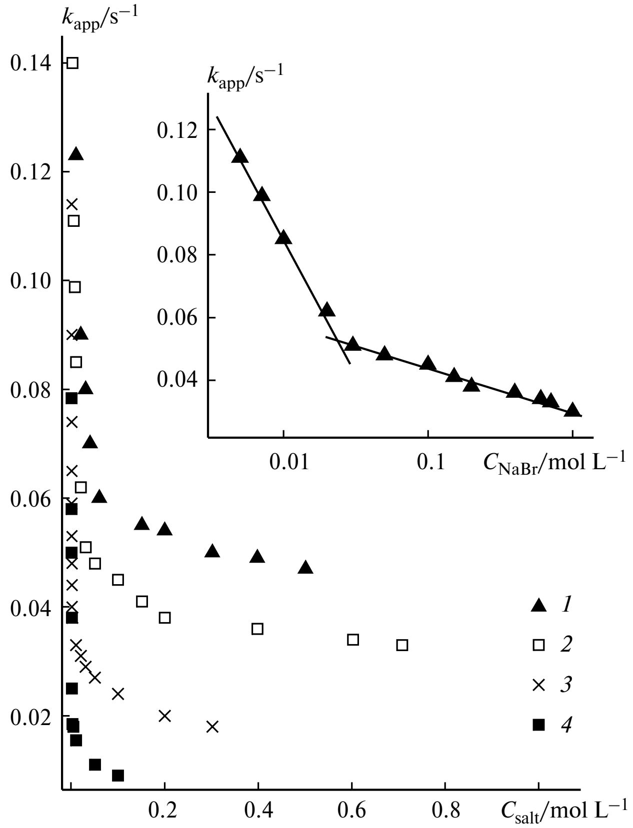


Fig. 7. Plots of the apparent rate constant of alkaline hydrolysis of NPCP *vs* electrolyte concentration: *1*, NaCl; *2*, NaBr; *3*, *4*, NaSal; 0.005 *(1—3)* and 0.01 *M* NaOH (*4*); 0.001 *M* CTAB, 25 °C. In inset the dependence of k_{app} for alkaline hydrolysis of NPCP on the NaBr concentration (logarithmic scale) under the same conditions.

The data obtained were analyzed in the framework of the pseudo-phase approach using Eq. (2). A possibility of using this equation for mixed systems was shown,[14,15] and examples for the calculation of the binding constants and molar volume of the surfactant at different ratios were

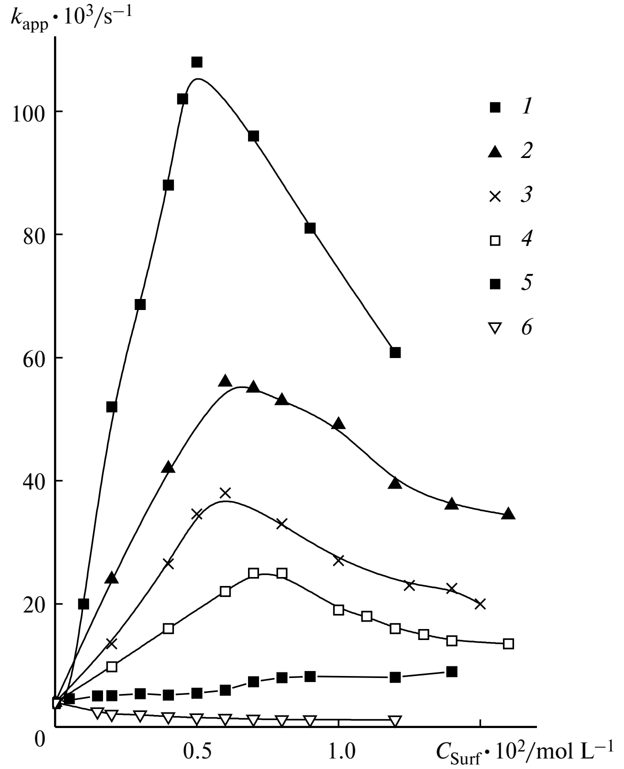


Fig. 8. Plots of the apparent rate constant of alkaline hydrolysis of NPCP *vs* total surfactant concentration at the CTAB molar fraction α_1 = 1.0 (*1*), 0.9 (*2*), 0.7 (*3*), 0.5 (*4*), 0.3 (*5*), and 0.1 (*6*); 0.001 *M* NaOH, 25 °C.

presented. As can be seen from the data in Table 2, the main contribution to the catalytic effect is made by the factor of reactant concentrating and the micellar microenvironment exerts a negative effect on the reactivity of the substrate. A decrease in the molar fraction of CTAB in the system results in the further decrease in the F_m factor, which causes the resulting diminishing of the catalytic effect. Probably, the change in the microscopic properties of the interface and, first of all, of the micropolarity upon the insertion of the oxyethylene fragments between the cationic head groups destabilizes the transition state of the reaction. Despite the decrease in the surface potential of the mixed micelles from 130 to 70 mV in the α_1 interval from 1.0 to 0.3,[11] the K_{OH} binding constants change insignificantly and the concentrating factor somewhat increases. The same regularity has been found earlier[14,15] for other binary systems based on CTAB. Probably, in ionic—nonionic surfactant binary systems the surface potential plays the secondary role in controlling the reactivity of compounds, and the major effect is made by the change in the microscopic properties of the interface with the variation of the surfactant ratio.

It can be noted in conclusion that the modification of micellar solutions of ionic surfactants by additives of a background electrolyte or a nonionic surfactant can serve as a tool of directed control of the rate of ion-molecular reactions in micellar solutions of ionic surfactants due to a change in the microscopic properties of the interface, such as surface potential, micropolarity, *etc*. This makes it possible to consider surfactant—electrolyte micellar systems as efficient catalytic systems with a wide range of action, including inhibition and catalysis, for the hydrolytic cleavage of ester bonds.

Table 2. Quantitative analysis according to Eq. (2) of the kinetic data for the alkaline hydrolysis of NPCP in a CTAB—Triton X-100 mixed micellar system (see Fig. 8)[a]

α_1	$(k_{app}/k_0)_{max}$	K_S	K_{OH}	$k_{2,m}$[b]	F_c[c]	F_m[c]	F_cF_m
		L mol^{-1}					
1.0	20.3	593	69	0.62	127.5	0.16	20.1
0.9	14.0	2828	51	0.40	132	0.10	13.8
0.7	9.5	1600	90	0.19	200	0.05	9.7
0.5	6.2	1300	85	0.15	180	0.04	7.0

[a] $k_{2,0}$ = 4.0 L mol^{-1} s^{-1}.

[b] In L mol^{-1} s^{-1}.

[c] Calculated using the equation $(k_{app}/k_0)_{max} = \frac{k_{2,m}}{k_{2,0}} \cdot \frac{K_S K_{OH}}{V\left(\sqrt{K_S} + \sqrt{K_{OH}}\right)^2}$. The maximum acceleration of the reaction equal to the ratio of the apparent rate constant (k_{app}) to the rate constant of the pseudo-first order in water (k_0) is given in the right part. The first cofactor in the right part takes into account the influence of the micellar microenvironment on the reactivity (F_m), and the second cofactor takes into account the effect of reactant concentrating in micelles (F_c).

References

1. I. V. Berezin, K. Martinek, and A. K. Yatsimirskii, *Usp. Khim.*, 1973, **42**, 1729 [*Russ. Chem. Rev.*, 1973, **42**, 1343 (Engl. Transl.)].
2. C. A. Bunton and G. Savelli, *Adv. Phys. Chem.*, 1986, **22**, 213.
3. L. S. Romsted, *Surfactants in Solution*, Ed. K. L. Mittal, Plenum Press, New York—London, 1984, **4**, 1015.
4. E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, 1970, **8**, 271.
5. K. Holmberg, *Current Opinion in Colloid Interface Sci.*, 2003, **8**, 187.
6. K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, *Colloid Surfactants. Some Physicochemical Properties*, Academic Press, New York—London, 1963.
7. D. B. Kudryavtsev, L. Ya. Zakharova, and L. A. Kudryavtseva, *Zh. Fiz. Khim.*, 2003, **77**, 443 [*Russ. J. Phys. Chem.*, 2003, **77** (Engl. Transl.)].
8. L. Ya. Zakharova, D. B. Kudryavtsev, F. G. Valeeva, and L. A. Kudryavtseva, *Zh. Obshch. Khim.*, 2002, **72**, 1296 [*Russ. J. Gen. Chem.*, 2002, **72** (Engl. Transl.)].
9. R. A. Hobson, F. Grieser, and T. W. Healy, *J. Phys. Chem.*, 1994, **98**, 274.

10. N. A. Smirnova, *Usp. Khim.*, 2005, **74**, 138 [*Russ. Chem. Rev.*, 2005, **74** (Engl. Transl.)].
11. L. Ya. Zakharova, F. G. Valeeva, A. V. Zakharov, A. B. Mirgorodskaya, L. A. Kudryavtseva, and A. I. Konovalov, *Kinet. Katal.*, 2007, **48**, 221 [*Kinet. Catal.*, 2007, **48** (Engl. Transl.)].
12. US Pat. N 2922810 (1960); *Chem. Abstrs*, 1960, **54**, 9848.
13. D. N. Rubingh, *Solution Chemistry of Surfactants*, Ed. K. L. Mittal, Plenum Press, New York, 1979, Vol. **1**, p. 337.
14. L. Ya. Zakharova, F. G. Valeeva, A. R. Ibragimova, L. A. Kudryavtseva, N. N. Valeev, T. L. Didenko, V. I. Kovalenko, and A. I. Konovalov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 2019 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 2176].
15. L. Zakharova, F. Valeeva, A. Zakharov, A. Ibragimova, L. Kudryavtseva, and H. Harlampidi, *J. Colloid Interface Sci.*, 2003, **263**, 597.
16. N. O. Mchedlov-Petrosyan, *Differentsirovanie sily organicheskikh kislot v istinnykh i organizovannykh rastvorakh* [*Differentiation of the Strength of Organic Acids in True and Organized Solutions*], Izd-vo Khar´kov Nats. Univ., Kharkov, 2004, 326 (in Russian).
17. A. B. Mirgorodskaya, L. A. Kudryavtseva, L. Ya. Zakharova, and V. E. Bel´skii, *Izv. Akad. Nauk*, *Ser. Khim.*, 1998, 1333 [*Russ. Chem. Bull.*, 1998, **47**, 1296 (Engl. Transl.)].
18. K. M. Solntsev, S. A. Al-Ainain, Y. V. Il´ichev, and M. G. Kuzmin, *J. Phys. Chem., A*, 2004, **108**, 8212.
19. L. Ya. Zakharova, S. B. Fedorov, L. A. Kudryavtseva, V. E. Bel´skii, and B. E. Ivanov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1993, 1396 [*Russ. Chem. Bull.*, 1993, **42**, 1329 (Engl. Transl.)].
20. L. Ya. Zakharova, D. B. Kudryavtsev, L. A. Kudryavtseva, A. I. Konovalov, Y. F. Zuev, N. N. Vylegzhanina, N. L. Zakhartchenko, and Z. Sh. Idiyatullin, *Mendeleev Commun.*, 1999, 245.
21. A. I. Serdyuk and R. V. Kucher, *Mitsellyarnye perekhody v rastvorakh poverkhnostno-aktivnykh veshchestv* [*Micellar Transitions in Surfactant Solutions*], Naukova Dumka, Kiev, 1987, 208 (in Russian).
22. V. R. Aswal and P. S. Goyal, *Phys. Rev. E*, 2000, **61**, 2947.
23. L. J. Magid, Z. Han, G. G. Warr, M. A. Kassidi, P. B. Bulter, and W. A. Hamilton, *J. Phys. Chem. B*, 1997, **101**, 7919.

Received June 25, 2007