Interaction between primary aliphatic amines and carboxylic acid esters in aqueous micellar solutions of cationic surfactants

A. B. Mirgorodskaya, L. A. Kudryavtseva, L. Ya. Zakharova, and V. E. Bel'skii*

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan' Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: +7 (843 2) 75 2253

The effects of cetylpyridinium bromide (CPB) on the acid-base equilibria of primary aliphatic amines and on the kinetics of reactions of the amines with *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl caprylate (PNPC) were studied by potentiometric titration and UV spectroscopy. The values of apparent pK_a of the amines in the micellar phase, binding constants of their neutral forms, and the surface potentials of micelles were determined. Cetylpyridinium bromide accelerates the aminolysis of PNPA by factors of 3 to 8 by forming mixed micellar aggregates with the amines. The shift of pK_a values of the amines in micellar solutions is not the only factor that enhances their reactivity. The substrate specificity was found: in contrast to the reaction with PNPA, CPB accelerates (by factors of 15 to 65) or retards (by factors of 4 to 6) the aminolysis of PNPA depending on the hydrophobicity of the nucleophilic reagent. The binding constants of substrates, the rate constants in the micellar phase, and the critical concentrations of micellization were determined from the data obtained.

Key words: amines, basicity, kinetics, aminolysis, esters of carboxylic acids, micelles, cetylpyridinium bromide, surface potential.

One way of controlling the reactivity of organic compounds is based on micellar catalysis. The micellar effect observed in aqueous solutions of surfactants (Surf) is due to the concentration of reagents in the micellar pseudophase, which in turn is accompanied by changes in the microenvironment, solvation, and orientation of reacting species.[1–3] The substances that can participate in the acid-base equilibria, for instance, amines, are of particular interest in studies of micellar catalysis. Their reactivities change due to pK shift caused by different solubilization of neutral and ionized forms with micellar aggregates.[4,5] The distribution of reactants between a solvent and micelles is governed by their polarity and hydrophobicity.

In this work, the reactions between *p*-nitrophenyl esters of carboxylic acids and primary amines in micellar solutions of cationic surfactant, cetylpyridinium bromide (CPB), were studied. *p*-Nitrophenyl acetate (PNPA) and *p*-nitrophenyl caprylate (PNPC) were used as substrates. Normal *n*-alkylamines differing in the length of the hydrocarbon radical were chosen as nucleophiles.

Experimental

The amines and *p*-nitrophenyl carboxylates used were purified by conventional techniques. Specimens of CPB were precipitated twice with ether from ethanol solution.

The pK_a values of the amines were determined by potentiometric titration with 0.1 or 0.2 *N* solution of HCl. The CPB concentration was varied from 0 to 0.02 mol L^{-1}.

The kinetics of reactions were studied spectrophotometrically on a Specord UV-VIS instrument at 25 °C. The course of the processes was followed by changes in the optical density of solutions at 400 nm (accumulation of *p*-nitrophenolate anion). The initial concentration of the substrate was $5 \cdot 10^{-5}$ mol L^{-1}, and the degree of conversion was higher than 90%. The required pH values were attained by adding HCl solutions and recorded by a pH-340 instrument.

The observed pseudo-first-order rate constants (k_{obs}) were determined from the dependence:

$$\log(D_\infty - D_\tau) = -0.434 k_{obs}\tau + \text{const},$$

where D_τ and D_∞ are the optical densities of solutions at the moment τ and after completion of the reaction, respectively. The k_{obs} values were calculated by the least squares method, and the second-order rate constants (k_2) were calculated from linear dependences of k_{obs} on the amine concentration (C_{am}) using the following equation:

$$k_2 = k_{obs} + k_0/C_{am} \cdot \alpha,$$

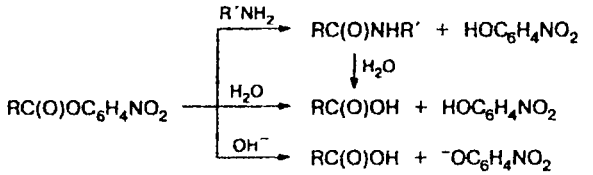
where k_0 is the rate constant of alkaline hydrolysis of the substrate determined at a specified pH, and α is the portion of neutral amine form under conditions of the kinetic experiment. The α values were determined from pK_a values of the amines using the formula: $\alpha = K_a/(K_a + [H]^+)$.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1333–1338, July, 1998.

1066-5285/98/4707-1296 $20.00

Results and Discussion

Aminolysis is the main process in the splitting of carboxylic acid esters in aqueous solutions in the presence of primary amines; however, alkaline and neutral hydrolyses can also occur in parallel.[6]



The contribution of side reactions to the k_{obs} value is rather small, but it should be taken into account, in particular, at pH > 10. In the absence of surfactant, the dependences of k_{obs} on the amine concentration in the reactions between *n*-butylamine and *n*-heptylamine and PNPA at pH 10.6 are linear in a wide range of concentrations (up to 0.02 mol L^{-1}), whereas the dependence of k_{obs} for the reaction between PNPA and decylamine is nonlinear because of its tendency to self-association.[7]

The k_2 values for the reactions between for *n*-butylamine and for *n*-heptylamine and PNPA at 25 °C calculated taking into account the contribution of alkaline hydrolysis and the portion of the reactive (neutral) form are equal to 10.0 mol^{-1} L s^{-1} and 12.0 mol^{-1} L s^{-1}, respectively. They are close to the k_2 values for ethylamine and *n*-decylamine in the pre-micellar region and are approximately equal to 9.0 mol^{-1} L s^{-1} (see Ref. 7). In the absence of surfactant, the pK_a values for *n*-butylamine and *n*-heptylamine in the concentration interval from 0.002 to 0.020 mol L^{-1} are equal to 10.7—10.9 and 10.9—11.1, respectively. The effect of the amine concentration on pK_a (an increase in pK_a as the amine content increases) is likely due to a change in the ionic strength of the solution. The pK_a value for decylamine is considerably lower than 10.[7]

The behavior of alkylamines with different lengths of alkyl radicals in micellar solutions of cationic surfactants is significantly different. Acid-base equilibria are known to be shifted in aqueous micellar solutions of surfactants.[8,9] The acidity of compounds increases in cationic micelles, whereas the proton affinity decreases in anionic surfactants. These effects are due to the selective solubilizing ability of micelles toward acidic and basic forms of compounds; for ionogenic surfactants they are governed mainly by the surface potential of a micelle. The dependence of the observed constant of acid-base dissociation ($K_{a,obs}$) on the concentration is described by Eq. (1):[9]

$$K_{a,obs} = [(1 + K_B C_{surf})/(1 + K_A C_{surf})] \cdot K_{a,w}, \quad (1)$$

where $K_{a,w}$ is the constant of acid-base dissociation in water; K_B and K_A are binding constants of basic and acidic forms of compounds, respectively, and C_{surf} is the concentration of surfactant.

The effect of ionic micelles on the acid-base equilibrium can be divided into nonelectrostatic and electrostatic components:[10]

$$pK_{a,m} = pK_{a,i} - \psi F/(2.3RT), \quad (2)$$

where $pK_{a,m}$ is the apparent pK_a value in the micellar phase, $pK_{a,i}$ is the nonelectrostatic component of pK_a shift in the micelles that characterizes the effect of medium, ψ is the surface potential (mV), F is the Faraday constant, and R is the universal gas constant.

The obtained data on the effect of CPB micelles on the amine pK_a values are presented in Table 1. The surfactant affects most strongly the pK_a value of decylamine ($\Delta pK \approx 1$) which is associated with its higher hydrophobicity as compared to other amines. The surfactant has no effect on the pK_a value of *n*-butylamine, which is the most hydrophilic of the amines studied.

According to the data published previously,[11] we used the pK_a values of the corresponding amines in solutions of the nonionogenic surfactant (Triton X-100), where micelles have an uncharged surface, as the model for quantitative determination of $pK_{a,i}$. The $pK_{a,i}$ values of the amines in the presence of nonionogenic surfactant are presented in Table 2.

Table 1. The amine pK_a values in aqueous solutions of CPB at different amine concentrations

C_{CPB} /mol L^{-1}	pK_a at C_{am}/mol L^{-1}							
	0.0025	0.0025	0.005	0.010	0.0025	0.005	0.010	0.0025
	n-Butylamine	*n*-Heptylamine			*n*-Octylamine			*n*-Decylamine
0	10.70	10.85	10.95	10.95	10.55	10.73	10.78	10.27
0.00025	10.70	10.80	10.65		10.50	10.60		
0.00125	10.65	10.65	10.59	10.70	10.40	10.47	10.65	10.05
0.0025	10.70	10.52	10.50	10.6	10.20	10.40	10.52	9.80
0.004		10.45	10.40	10.50		10.22		9.70
0.005	10.65	10.36		10.45	10.00	10.10	10.30	9.63
0.006		10.30	10.35	10.42	9.95			9.55
0.0075	10.65	10.30	10.30	10.38	9.85	10.05	10.15	9.50
0.010	10.65			10.35	9.80	10.0	10.10	9.40

Table 2. The K_B, $pK_{a,m}$, and ψ values in aqueous micellar solutions of CPB at different amine concentrations

Amine	C_{am}[a]	$pK_{a,i}$[b]	K_B[c]	$pK_{a,m}$	ψ/mV
n-Heptylamine	0.0025	10.60	402	8.2	139
n-Heptylamine	0.0050	10.60	320	8.4	128
n-Heptylamine	0.01	10.60	290	8.48	125
n-Octylamine	0.0025	10.50	530	7.8	156
n-Octylamine	0.0050	10.50	420	8.1	142
n-Octylamine	0.01	10.50	380	8.2	138
n-Decylamine[d]	0.0025	10.00	660	7.4	150
n-Decylamine[d]	0.0050	10.05	330	7.7	140

[a] C_{am} are given in mol L^{-1}. [b] The amine pK_a values determined at given amine concentrations in aqueous solutions of Triton X-100 (the content of nonionogenic surfactant was 0.05 and 0.01 mol L^{-1}). [c] K_B are given in mol^{-1} L. [b] According to Ref. 7.

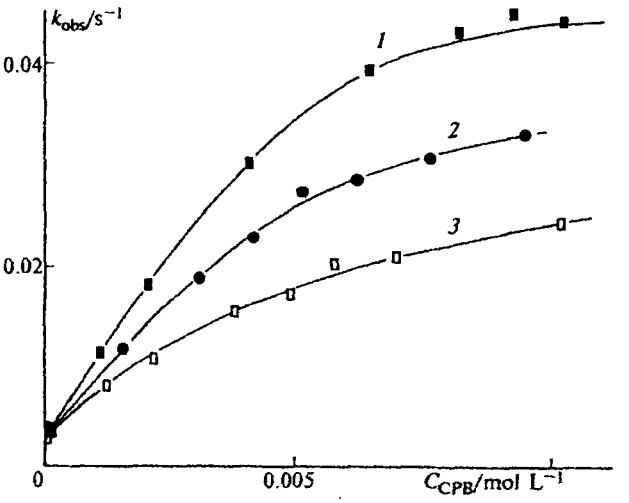


Fig. 1. Dependences of the observed rate constants (k_{obs}) for reactions between PNPA and amines on the CPB concentration (C_{am} = 0.0025 mol L^{-1}, 25 °C): *1*, *n*-cetylamine, pH 9.0; *2*, *n*-decylamine, pH 9.0; *3*, *n*-octylamine, pH 9.5.

Processing of experimental dependences $pK_{a,obs} = f(C_{CPB})$ using Eqs. (1) and (2) made it possible to calculate the binding constants of neutral forms of the amines (K_B), the $pK_{a,m}$ values, and the potentials of micellar surfaces (see Table 2). The binding constants of protonated forms of the amines, K_A, are not larger than 1 mol^{-1} L due to electrostatic repulsion from similarly charged micellar surfaces.

As can be seen from the data obtained, the binding of the neutral form of the amine increases as its hydrophobicity increases. The K_B value of the amine decreases as its concentration increases due to saturation of micelles. Along with this, a decrease in the surface potential of CPB micelles occurs, which may be due to solubilization of the neutral form of the amine by micelles leading to their loosening and a decrease in the charge density.

The ψ value in the system "CPB—water—*n*-heptylamine" is somewhat smaller than those in the systems with *n*-octylamine and *n*-decylamine (see Table 2). It is known that amines and alcohols with chains of medium length (C(5)—C(7)) are used as co-surfactants, for instance, in preparation of microemulsions,[12] and that their behavior differs from that of short- and long-chain homologs. At low concentrations, the molecules of these compounds are localized behind the head groups of micelles in the so-called palisade layer[13] and decrease the surface potential.[14] The more hydrophobic *n*-octylamine and *n*-decylamine form mixed micelles with CPB; they have qualitatively different character and somewhat higher potentials than that of *n*-heptylamine. The ψ values we calculated for CPB are in rather good agreement with the literature data.[11] This confirms the validity of using the amines as probes for characterization of the surface potential of micelles.

Table 3. The observed rate constants (k_{obs}/s^{-1}) for PNPA aminolysis at different CPB concentrations and pH (C_{am} = 0.0025 mol L^{-1}, 25 °C)

C_{CPB}	k_0/s^{-1},	k_{obs}/s^{-1} at pH					
/mol L^{-1}	10.6*	10.6	9.4	9.7	10.1	10.4	10.6
		n-Butylamine	*n*-Heptylamine				
0	0.0032	0.0095	0.0025	0.0029	0.0058	0.010	0.013
0.001	0.0035	0.013	0.0042	0.0060	0.0095	0.0205	0.027
0.0016		0.012	0.0055	0.0075	0.0125		0.029
0.0020	0.0036	0.014	0.0060	0.0088		0.030	
0.0033			0.0070	0.0117	0.018	0.038	0.0475
0.0040			0.0076	0.0125	0.019	0.043	0.0532
0.0050	0.0038	0.15	0.00814	0.014	0.023	0.048	0.060
0.0060		0.017				0.050	0.0625
0.0075		0.014	0.0092	0.016	0.027	0.054	0.065
0.010	0.0042	0.015	0.096		0.029		

* The pH value.

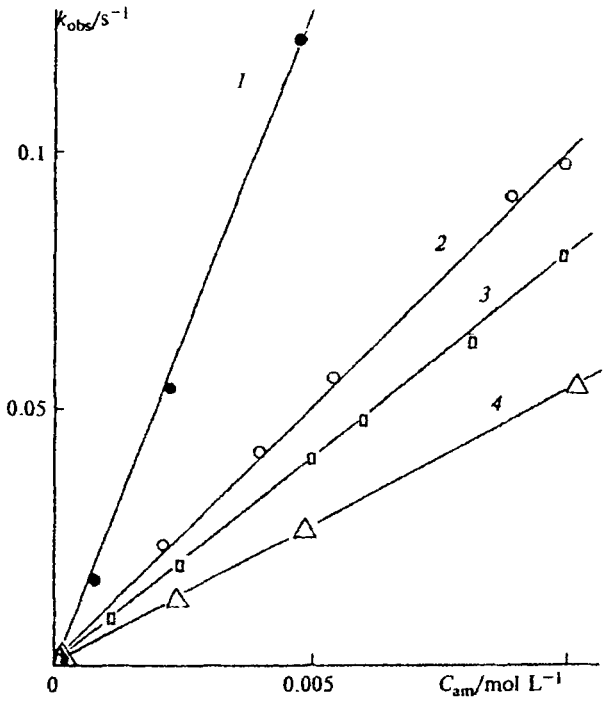


Fig. 2. Dependences of the observed rate constants (k_{obs}) of PNPA aminolysis on the amine concentrations at a constant CPB concentration (0.01 mol L^{-1}, 25 °C): *1*, *n*-decylamine, pH 9.4; *2*, *n*-heptylamine, pH 10.4; *3*, *n*-octylamine, pH 9.5; *4*, *n*-butylamine, pH 10.4.

The apparent pK_a shift can make a considerable contribution to the micellar kinetic effect by changing the concentration of reactive form of the reagents. The CPB micelles increase substantially the α values of the amines (in particular, at high pH) and it is the pK_a shift of alkylamines that is the reason for the effect of cationic surfactant on the reactivity of nucleophiles in the processes studied. However, the micellar effect of CPB governs not only the influence on the acid-base properties of reagents. For instance, the α values for *n*-heptylamine at pH 9.7, for octylamine at pH 9.5, and for decylamine at pH 9.0 are nearly equal; at the same time, the reactivity of *n*-decylamine is considerably higher than those of *n*-octylamine and *n*-heptylamine at these pH in micellar CPB solutions (Fig. 1 and Table 3).

The linear dependences of k_{obs} on the amine concentrations (up to 0.01 mol L^{-1}) in micellar solutions with a CPB content of 0.01 mol L^{-1}, *i.e.*, in the region where no changes in α are observed, are shown in Fig. 2. The calculated k_2 value for *n*-butylamine is approximately equal to 12 mol^{-1} L s^{-1}, which is close to k_2 value in water, and is independent of the surfactant concentration (see Table 3). The CPB micelles do not solubilize *n*-butylamine because of its good solubility in water; for this reason, the process virtually occurs in the aqueous phase even in the presence of a detergent. It was found from the linear dependences (see Fig. 2) that the k_2 values for *n*-heptylamine and *n*-octylamine are approximately equal to 19 mol^{-1} L s^{-1} and 28 mol^{-1} L s^{-1}, respectively. These values are considerably higher than the corresponding values in water and reflect an effective increase in k_2, which characterizes the process in both the aqueous phase and micellar pseudophase. The calculation for *n*-decylamine becomes more complicated since the α value changes substantially in the studied interval of amine concentrations.

The dependences of k_{obs} values for the reactions between PNPA and alkylamines on the CPB concentration are shown in Fig. 1 and listed in Table 3. The flattened profiles of the concentration curves of the reactions between the amines studied (except for *n*-butylamine) and PNPA are typical of micelle-catalyzed processes, which confirms the binding of the reagents by CPB micelles and makes it possible to use the equation of pseudophase model (3) that relates k_{obs} to the parameters of the processes in the micellar phase:[2]

$$k_{obs} = (k_0 + k_m K_{bond} C_{surf})/(1 + K_{bond} C_{surf}), \quad (3)$$

Table 4. The k_m, K_{bond}, and CMC values for reactions between alkylamines and PNPA at different pH (C_{am} = 0.0025 mol L^{-1}, 25 °C)

Amine	pH	α′ *	k_m /s^{-1}	k_m/α'	K_{bond} /mol L^{-1}	KKM /mol^{-1} L	k_0 /s^{-1}	k_m/k_0
n-Heptylamine	9.0	0.034	0.00576	0.17	320	0.0006	0.002	~3
n-Heptylamine	9.4	0.082	0.0121	0.15	306	0.0002	0.0025	5
n-Heptylamine	9.7	0.151	0.240	0.16	230	0.0003	0.0029	8
n-Heptylamine	10.1	0.308	0.0420	0.14	200	0.0006	0.005	8
n-Heptylamine	10.4	0.471	0.072	0.15	210	0.0002	0.01	7
n-Heptylamine	10.6	0.585	0.0975	0.17	250	0.0004	0.013	7
n-Octylamine	9.5	0.185	0.0345	0.19	250	0.0001	0.0025	14
n-Decylamine	9.0	0.2	0.0617	0.31	140	0.0001	0.002	24
n-Cetylamine	9.0	0.25	0.0856	0.34	140	0.0006	0.002	43

* The portion of nonprotonated amine form at a CPB concentration of not less than 0.01 mol L^{-1}, *i.e.*, in the region where its maximum effect on pK_a amines is attained and remains nearly unchanged with further increase in the surfactant content.

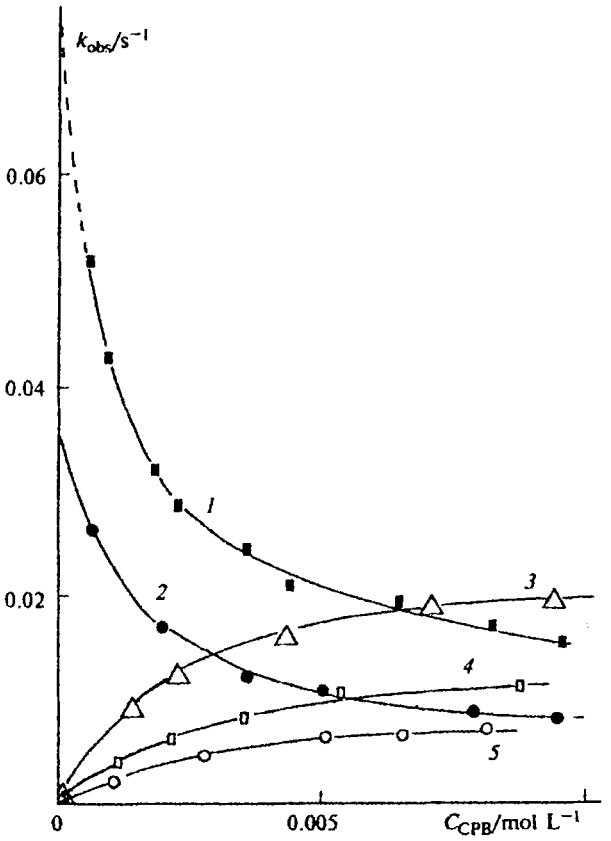


Fig. 3. Changes in the observed rate constants (k_{obs}) for reactions between PNPC and amines (C_{am} = 0.0025 mol L^{-1}, 25 °C) and OH^- ion depending on the CPB concentration: *1*, *n*-cetylamine, pH 9.0; *2*, *n*-decylamine, pH 9.0; *3*, *n*-butylamine, pH 10.4; *4*, *n*-heptylamine, pH 10.4; *5*, alkaline hydrolysis at pH 10.4.

where C_{Surf} is the surfactant concentration corrected for the critical micelle concentration (CMC), k_0 and k_m are the rate constants in the absence of surfactant and in the micellar phase, respectively, and K_{bond} is the binding constant of substrate.

As can be seen in Table 3, CPB virtually has no effect on the reaction between *n*-butylamine and PNPA and on the alkaline hydrolysis of PNPA. Using Eq. (3) and the data in Fig. 1 and Table 3, we found the K_{bond} values for the substrates and the k_m and CMC values for the reactions between alkylamines and PNPA at different pH (Table 4).

The data in Table 4 indicate that the K_{bond} values of the substrate are small (150—300 mol^{-1} L) and decrease somewhat as pH of the medium increases. The dependence $k_m = f(\alpha')$ for *n*-heptylamine is linear and can be described by Eq. (4):

$$k_m = 0.1617\alpha' - 0.0017 \qquad n = 7,\ r = 0.9946, \qquad (4)$$

where α' is the protion of nonprotonated amine.

In contrast to PNPA solutions, the alkaline hydrolysis of PNPC in micellar CPB solutions is accelerated by about an order of magnitude (Fig. 3, Table 5). The data in Table 5 indicate a rather good binding of PNPC by CPB micelles (K_{bond} ~ 1000—2000 mol^{-1} L). This provides the concentration of the substrate molecules and nucleophiles in the micellar pseudophase. Reactions of PNPC aminolysis in aqueous micellar solutions of cationic surfactants are specific: either catalysis or inhibition of the process can occur depending on the nucleophile hydrophobicity. The changes in the observed rate constants for the reactions between PNPC and alkylamines depending on CPB concentration are shown in Fig. 3. The K_{bond}, k_m, and CMC values found using Eq. (3) are listed in Table 5.

The reactions between *n*-butylamine and *n*-heptylamine and PNPC in micellar solutions of surfactants are accelerated by factors of 15 to 30. It should be noted that the observed rate constants at pH 10.4 are effective quantities involving the processes of alkaline hydrolysis and aminolysis of PNPC enhanced by CPB micelles. We attempted to separate a portion of the aminolysis process out from k_2, which made it possible to determine the parameters K_{bond}, k_m, and CMC for the reaction between *n*-butylamine and PNPC and to show that if the process of alkaline hydrolysis is accelerated by an order of magnitude, then aminolysis is accelerated approximately by a factor of 65 (see Table 5).

Reactions of PNPC aminolysis with *n*-decylamine and *n*-cetylamine (pH 9.0) are inhibited by CPB mi-

Table 5. The k_m, K_{bond}, and CMC values of reactions between alkylamines and PNPC at different pH (C_{am} = 0.0025 mol L^{-1}, 25 °C)

Reagent	pH	k_0/c^{-1}	k_m/c^{-1}	K_{bond}[a]	KKM[b]	k_m/k_0
OH^-	10.4	0.0005	0.0059	1070	0.0002	10.0
n-Butylamine	10.4	0.0007	0.0202	910	0.00007	30.0
n-Butylamine[c]	10.4	0.0002	0.0130	1100	0.00005	65.0
n-Heptylamine	10.4	0.0007	0.0105	690	0.00005	15.0
n-Decylamine	9.0	0.039	0.0060	1090	0.00005	0.15
n-Decylamine	9.4	0.07	0.0161	1990	0.00045	0.23
n-Cetylamine	9.0	0.06	0.0097	750	0.0001	0.16

[a] K_{bond} are given in mol L^{-1}. [b] CMC are given in mol L^{-1}. [c] Data for the aminolysis process.

celles by factors of 4 to 6 (see Table 5). The fact that CPB micelles inhibit reactions between PNPC and decylamine and cetylamine is in contrast to the increasing binding of neutral forms of these amines, *i.e.*, with the increasing portion of reactive forms. It can be assumed that *n*-decylamine and *n*-cetylamine, which are prone to micellization, form mixed micellar aggregates with CPB and PNPC, in which the amine and PNPC are localized in different regions, which hampers their interaction to inhibit the process. In addition, inhibition of the reactions may indicate that they occur inside a low-polarity micelle, where the polar transition state of S_N2-process is destabilized.

Thus, marked substrate specificity as well as the effect of the amine radical hydrophobicity on the aminolysis process, which can be either accelerated or slowed, are observed in micellar solutions of cationic surfactants in reactions between primary aliphatic amines and *n*-nitrophenyl carboxylates. It was shown that this process occurs by a complex mechanism of micellar catalysis involving a shift of the acid-base equilibrium of a nucleophile. In addition, functionalization of micelles occurs in the case of higher amines capable of micellization (such as *n*-octylamine, *n*-decylamine, and *n*-cetylamine), which makes an additional contribution to the catalytic properties of these systems. The quantitative parameters characterizing the structure and properties of micellar aggregates were determined on the basis of kinetic experiments performed and studies of the acid-base equilibria in CPB solutions.

References

1. C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1986, **22**, 425.
2. C. A. Bunton, *Adv. Chem. Sos.*, 1987, 425.
3. C. A. Bunton, F. Nome, F. Quina, and L. S. Romsted, *Acc. Chem. Res.*, 1991, **24**, 357.
4. V. S. Pshezhetskii and A. P. Luk'yanova, *Bioorg. Khim.*, 1976, **2**, 110 [*Bioorg. Chem.*, 1976, **2** (Engl. Transl.)].
5. R. F. Bakeeva, L. A. Kudryavtseva, V. E. Bel'skii, S. B. Fedorov, and B. E. Ivanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1429 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **31**, 1297 (Engl. Transl.)].
6. W. P. Jencks, *Catalysis in Chemistry and Enzymology*, McGraw-Hill Book Company, New York, 1969.
7. A. B. Mirgorodskaya, L. A. Kudryavtseva, and B. E. Ivanov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 336 [*Russ. Chem. Bull.*, 1996, **45**, 351 (Engl. Transl.)].
8. S. Harada, H. Ocada, T. Sano, T. Yamashita, and H. Yano, *J. Phys. Chem.*, 1990, **94**, 7648.
9. I. V. Berezin, K. Martinek, and A. K. Yatsimirskii, *Usp. Khim.*, 1973, **42**, 1729 [*Russ. Chem. Rev.*, 1973, **42** (Engl. Transl.)].
10. N. Funasaki, *J. Colloid Interface Sci.*, 1978, **64**, 46.
11. N. O. Mchedalov-Petrosyan, L. P. Loginova, and V. N. Kleshchevnikova, *Zh. Fiz. Khim.*, 1993, **67**, 1649 [*Russ. J. Phys. Chem.*, 1993, **67** (Engl. Transl.)].
12. *Microemulsions: Structure and Dynamics*, Eds. S. E. Friberg and P. Bothorel, CRC Press Inc., Boca Raton, Florida, 1987.
13. R. Zana, S. Yiv, C. Strazielle, and P. Lianos, *J. Colloid Interface Sci.*, 1981, **80**, 208.
14. J. Kibblewhite, C. J. Drummond, F. Grieser, and T. W. Healy, *J. Phys. Chem.*, 1987, **91**, 4658.

Received July 10, 1997;
in revised form October 10, 1997