The influence of micellization of *n*-decylamine on its basicity and reactivity toward carboxylic acid esters

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Micellization of *n*-decylamine in aqueous solution leads to substantial decrease in its pK_a and increase in its reactivity in the nucleophilic substitution of *p*-nitrophenylic esters of carboxylic acids (up to 70 times compared to ethylamine which forms no micelles). The influence of cetylpyridinium bromide on the acid-base properties of *n*-decylamine and its reactivity was investigated. It was found that the reaction with *n*-decylamine can be accelerated or retarded depending on the hydrophobicity of the esters. The quantitative characteristics of the micellar catalytic processes were estimated.

Key words: *n*-decylamine; esters of carboxylic acids; cetylpyridinium bromide, micellization, basicity, nucleophilic substitution.

The use of surfactants is one of the most important ways of affecting the reactivity of organic compounds. Micellar catalysis is based on several factors: on the reagents concentrating in the micellar pseudophase and on changes in solvation and orientation of reacting molecules, shifts in their pK_a due to different solubilization of particles participating in acid-base equilibria, salt effects.[1,2] Of particular interest are surfactants, which are reagents themselves.[3,4]

In the present work the effects on micellization on the basicity of *n*-decylamine in aqueous solutions and its reactivity in interactions with *p*-nitrophenyl esters (PNPE) were studied. Esters differing in hydrophobic properties — *p*-nitrophenylacetate (PNPA), *p*-nitrophenylbutyrate (PNPB), *p*-nitrophenylcaprylate (PNPC) — were chosen as substrates.

Experimental

The amines and PNPE used were purified by conventional techniques. Specimens of chemically pure cetylpyridinium bromide (CPB) were precipitated twice by ether from its ethanol solution.

Values of pK_a were determined by potentiometric titration of amines on a "pH-340" instrument. Solutions with the amine concentration from 0.001 to 0.0075 mol L^{-1} were used; solutions of 0.1 and 0.02 *N* HCl were titrants. The CPB concentration was varied from 0 to 0.02 mol L^{-1}.

The reaction kinetics was studied by the spectrophotometric technique using a "Specord UV-Vis" instrument at 25 °C. The course of the process was followed by changes in the optical density of solutions at the wavelength 400 nm (formation of the *p*-nitrophenolate anion). The initial concentration of the substrate was $5 \cdot 10^{-5}$ mol L^{-1}, the transformation extent was 90—95 %. The required pH values were attained by adding HCl solutions. The rate constants observed (k_{obs}) were determined from the relation

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

where D and D_∞ are optical densities of solutions at the moment t and after the reaction completion, respectively. The k_{obs} values were calculated by the least squares method.

Results and Discussion

The aminolysis of PNPE in aqueous solutions is a complicated process, even in the absence of surfactants, since other processes can proceed in parallel with the main process, for instance, the aqueous and alkaline hydrolyses and formation or decomposition (the limiting stage) of the tetrahedral intermediate.[5] A simplified reaction scheme is represented below (Scheme 1).

The specific behavior of hydrophobic amines and, in particular, that of *n*-decylamine is associated with their tendency to association, which can reflect in their acid-base properties and reactivity.[6,7]

We showed that pK_a of *n*-decylamine in aqueous solutions is lower than that of its short-chain analogs because of aggregation and depends on its concentration. The pK_a value decreases with increasing the *n*-decylamine concentration in solution, which, at a constant pH, increases the portion of the neutral reactive form (α) (Table 1) and must result in increasing reactivity of *n*-decylamine in its interaction with PNPE.

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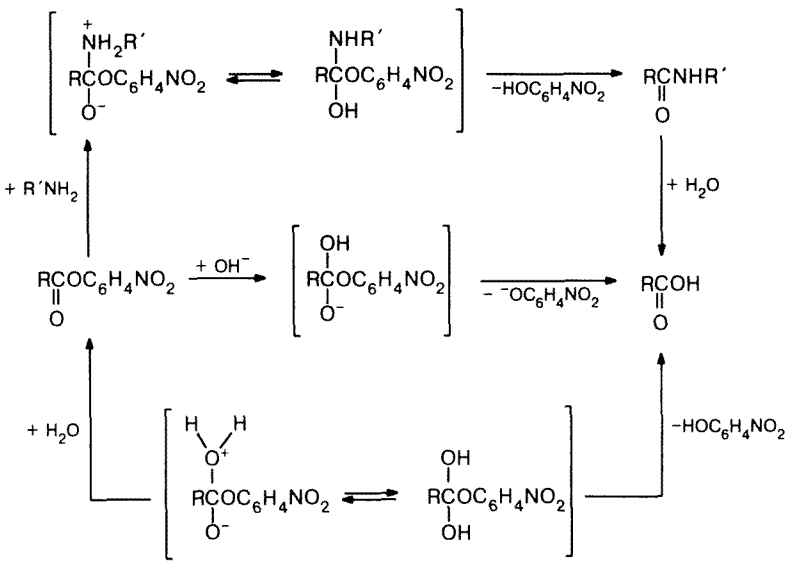
Scheme 1



A nonlinear dependence of the rate constant of the PNPE decomposition on its concentration in aqueous solutions (Fig. 1) can be explained by aggregation of the *n*-decylamine molecules. Kinetic measurements were carried out at pH 9.4 when formation of mixed micelles, consisting of neutral and protonated *n*-decylamine molecules, is possible. The catalysis in the presence of *n*-decylamine associates is analogous to the catalysis in the presence of cationic surfactants. A sharp rise and flattening of the (k_{obs}) curve depending on the *n*-decylamine concentration (C_{DA}) in catalyzed processes make themselves evident for PNPC at C_{DA} ~0.006 mol L^{-1}, while for PNPA and PNPB the concentration exceeds 0.01

Table 1. Values of pK_a and α at different concentrations of *n*-decylamine (pH 9.4)

C_{DA} /mol L^{-1}	pK_a	α
0.001	10.30	0.11
0.0025	10.27	0.12
0.0035	10.20	0.14
0.0045	10.15	0.15
0.005*	10.10	0.17
0.006	10.05	0.17
0.0075	9.96	0.22
0.008	9.90	0.24
0.009	9.80	0.29
0.01**	9.65	0.36

* pK_a of ethylamine at a 0.005 mol L^{-1} concentration is 10.80.
** *n*-Decylamine is poorly soluble in water at concentrations >0.01 mol L^{-1}.

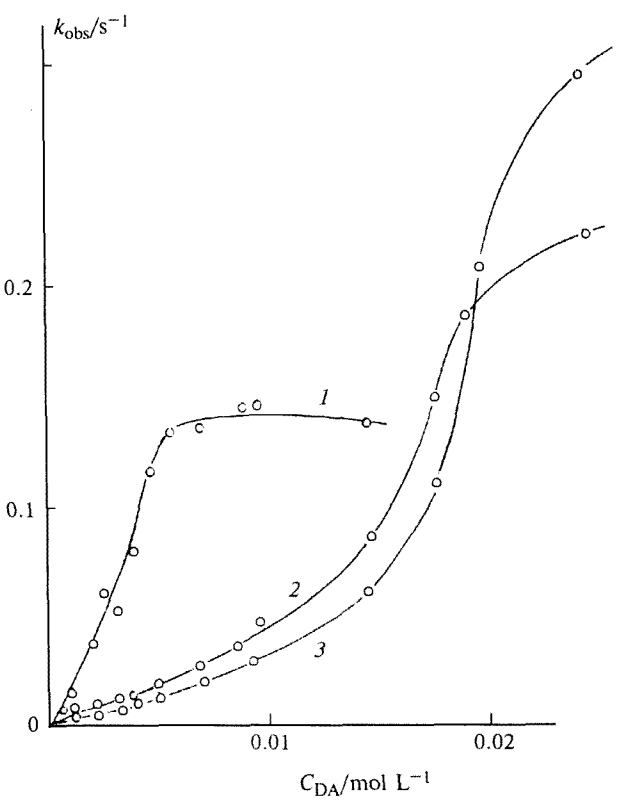


Fig. 1. Dependence of the rate constants of aminolysis of PNPC (*1*), PNPB (*2*), and PNPA (*3*) on the concentration of *n*-decylamine in aqueous solution (pH 9.4, 25 °C).

mol L^{-1}. It can be suggested that the substrate affects the aggregation in the system.

In the concentration range up to 0.01 mol L^{-1} $k_{obs} = f(C_{DA})$ is nearly linear for PNPA and PNPB. The second-order rate constant (k_2), calculated for the linear portion of the curve (see Fig. 1) from the relation $k_2 = (k_{obs} - k_{OH})/C_{DA} \cdot \alpha$, where k_{OH} is the rate constant of the alkaline hydrolysis at a specified pH, is equal to ~9 mol^{-1} L s^{-1} for PNPA and ~11 mol^{-1} L s^{-1} for PNPB. The obtained values can be correlated with k_2 (mol^{-1} L s^{-1}, 25 °C) for ethylamine: in the reaction with PNPA $k_2 = 9.0$ (*cf.* 9.65 according to literature data[8]), $k_2 = 8.7$ for PNPB. Thus, the kinetic effect of micellization of *n*-decylamine in its interaction with PNPA and PNPB manifests at relatively high concentrations of *n*-decylamine ($C_{DA} > 0.01$ mol L^{-1}). For this concentration range, it is reasonable to use Eq. (1) relating k_{obs} with micellar phase parameters[1]:

$$k_{obs} = \frac{k_m K_b C_{surf} + k_0}{1 + K_b C_{surf}}, \quad (1)$$

where C_{surf} is the concentration of micellized substance corrected for the critical concentration of micellization (CCM)); k_0 and k_m are the rate constants in the absence of surfactant and in the micellar phase, respectively; K_b is the substrate binding constant.

The results of calculations are given in Table 2. As is seen from the data obtained, the substrate binding by the *n*-decylamine micelles increases with increasing the substrate hydrophobicity. A sharp drop in CCM for PNPC gives evidence for the substrate effect on the micellization process. The order of the change in k_m values for PNPE studied coincides with the change in their stability under the conditions of alkaline hydrolysis (k_0). However, the k_m/k_0 ratio for PNPC is higher nearly by a factor of 10 compared to that for PNPA.

One can conclude that the reactivity of micellizing amines in their reaction with PNPE is much higher than those of their short-chain analogs. For instance, the rate constant of the interaction of *n*-decylamine with PNPC, estimated at $C_{DA} = 0.006$ mol L^{-1}, is 138 mol^{-1} L s^{-1}, which exceeds the rate constant of the reaction of the substrate with ethylamine ($k_2 = 2.05$ mol^{-1} L s^{-1}) by a factor of 70.

We studied the effect of a cationic surfactant, cetylpyridinium bromide (CPB), on the reaction of

Table 2. Parameters of micellarly catalyzed reactions of interaction between PNPE and *n*-decylamine (pH 9.4, 25 °C)

Substrate	k_0/s^{-1}	k_m/s^{-1}	CCM / mol L^{-1}	K_b / mol L^{-1}	k_m/k_0
PNPA	0.00027	0.530	0.0147	130	1960
PNPB	0.00015	0.295	0.0139	290	2000
PNPC	0.000013	0.168	0.0022	780	13000

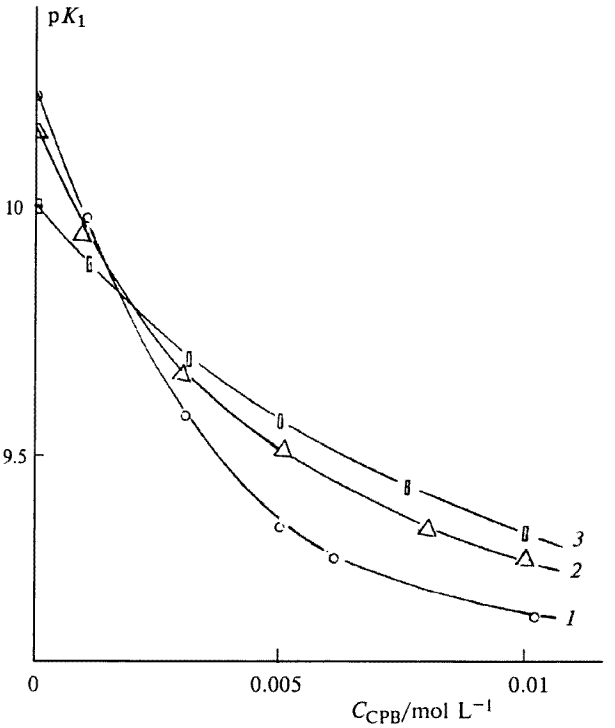


Fig. 2. Effect of the CPB concentration on pK_1 of *n*-decylamine, C_{DA}/mol L^{-1}: 0.001 (*1*); 0.0025 (*2*); 0.005 (*3*).

n-decylamine with PNPE. In this case, mixed micelles containing both *n*-decylamine and CPB molecules can form. The amine groups in the micelles of cationic surfactants are shielded from water molecules by hydrophobic radicals, which results in a sharp decrease of their pK_a.[6,9] If the amine is distributed between the aqueous and micellar phases, its basicity, in specific cases, can be characterized by two pK_a values.[9]

Two jumps of the potential are recorded if *n*-decylamine is titrated in the presence of CPB, *i.e.* there are two pK_a values: the first, pK_1, corresponds to the basicity of the molecules in aqueous solution or in the micellar surface layer; the second, pK_2, is responsible for the basicity of the amine molecule in the micelle. Changes in CPB and *n*-decylamine concentrations have little effect on pK_2, it does not change and is 8.0±0.1;

Table 3. Parameters of micellar catalyzed reactions between PNPE and *n*-decylamine in the presence of CPB (pH 9.4, 25 °C)

Substrate	C_{DA} / mol L^{-1}	k_0/s^{-1}	k_m/s^{-1}	CCM / mol L^{-1}	K_b / mol L^{-1}	k_m/k_0
PNPA	0.001	0.0013	0.0209	0.00102	474	20.5
PNPA	0.0025	0.00307	0.0668	0.000144	296	21.7
PNPA	0.005	0.0082	0.185	<0.0001	230	22.5
PNPB	0.005	0.0095	0.0579	<0.0001	500	6.1
PNPC	0.0025	0.060	0.0097	0.001	750	0.16
PNPC	0.005	0.116	0.031	0.00085	1090	0.27

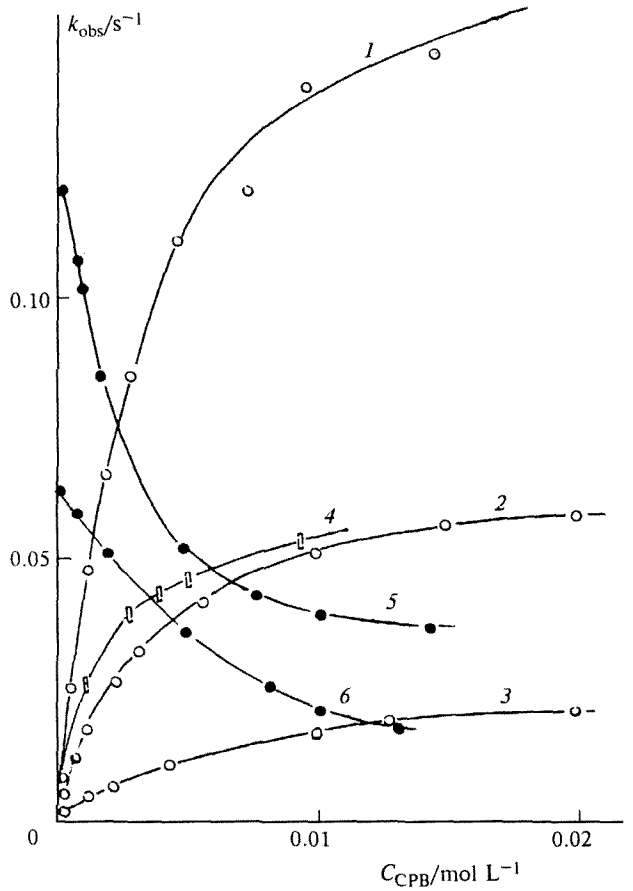


Fig. 3. Dependence of the rate constants of the interaction between PNPE and *n*-decylamine on the concentration of CPB (pH 9.4, 25 °C): *1*, PNPA, C_{DA} = 0.005 mol L^{-1}; *2*, PNPA, C_{DA} = 0.0025 mol L^{-1}; *3*, PNPA, C_{DA} = 0.001 mol L^{-1}; *4*, PNPB, C_{DA} = 0.005 mol L^{-1}; *5*, PNPC, C_{DA} = 0.005 mol L^{-1}; *6*, PNPC, C_{DA} = 0.0025 mol L^{-1}.

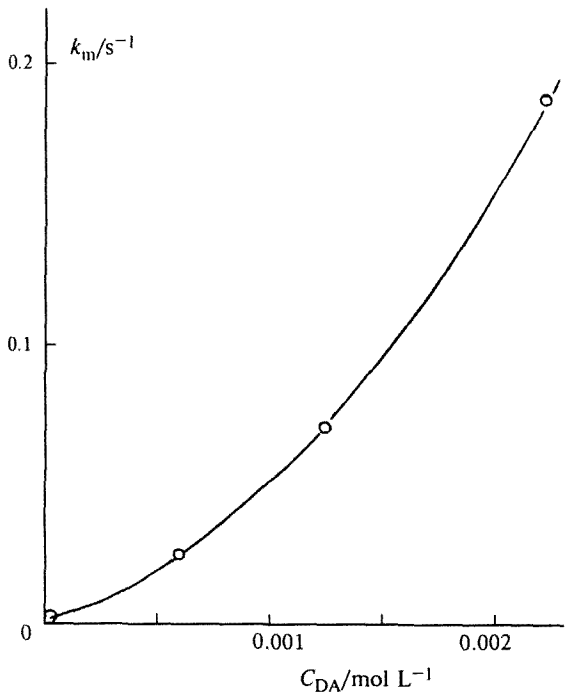


Fig. 4. Dependence of the rate constant in the micellar phase of the reaction between PNPA and *n*-decylamine in CPB aqueous solution on the concentration of the neutral form of amine (pH 9.4, 25 °C).

pK_1 essentially decreases with increasing the concentration of surfactant (Fig. 2), which results in an increase of the fraction of nonprotonated amine under the conditions of kinetic measurements at pH 9.4.

The fraction of micellarly bound *n*-decylamine (β) is determined from the ratio $\beta = C'_{DA}/C_{DA}$, where C'_{DA} is concentration of amine in the micelle, C_{DA} is the overall amine concentration, which, in their turn, are determined from the positions of jumps on the curves of potentiometric titration. The values of β are almost independent of the CPB concentration and decrease with increasing C_{DA} (mol L^{-1}) in solution: β = 0.56; 0.51; 0.45; 0.34 at C_{DA} = 0.001, 0.0025, 0.005, 0.0075, respectively.

In contrast to *n*-decylamine, surfactants do not affect the acid-base properties of ethylamine. Because of its weak binding in the micelles, changes in the CPB concentration from 0 to 0.02 mol L^{-1} lead to a decrease in the ethylamine pK_a by 0.1.

Effect of the CPB on the reactivity of ethylamine toward PNPE is also insignificant. A change in the CPB content in solution at the ethylamine concentration 0.005 mol L^{-1} has no practical effect on the k_{obs} value in the reaction with PNPA – at C_{surf} from 0 to 0.01 mol L^{-1} k_{obs} = 0.0018 s^{-1} (±10 %). In the case of PNPC the effect is somewhat stronger: k_{obs} = 0.00045 s^{-1} in the absence of surfactant and k_{obs} = 0.001 s^{-1} at C_{surf} = 0.01 mol L^{-1}.

On the contrary, the CPB additives substantially increase the rate of interaction of *n*-decylamine with PNPA. The dependences of k_{obs} on the CPB concentration have a flattened shape, which is typical of micellar analysis (Fig. 3). Calculations using Eq. (1) allow us to obtain parameters of the micellar catalyzed reaction, which are listed in Table 3.

As follows from the data of Table 3, PNPA is effectively solubilized by the CPB micelles, the smaller K_b value being characteristic of more concentrated solutions; this can be due to a decrease in the polarity of micelle because of the intrusion of non-polar *n*-decylamine molecules into the micelles. The rate constant in the micellar pseudophase formed with the participation of CPB is higher than the corresponding rate constants of the reaction of *n*-decylamine in water by about a factor of 20. It increases with increasing amine concentration. This allows one to suggest that the reagents are localized in the same domain of the micelle,

the most probable on its surface, which favors their interaction.

The dependence of k_m on the concentration of *n*-decylamine in the micellar pseudophase ($C_{DA} \cdot \beta$) has a nonlinear character (Fig. 4), which is evidence for a contribution of catalytic processes to the reaction.

The binding constant of PNPB is higher than that of PNPA; however, the micellar effect in the interaction with *n*-decylamine is lower: $k_m/k_0 \sim 6$. The alkyl radical can be suggested to be drawn deep into the micelle carrying away the carbonyl carbon atom, which results in a steric hindrance of its attack on the amine

Unlike the reactions of PNPA and PNPB with *n*-decylamine, the corresponding reaction with PNPC is inhibited by CPB micelles (see Fig. 3). The micellar parameters of the reaction are given in Table 3. The K_b values obtained allow one to conclude that PNPC is bound by the surfactant micelles to a greater extent than PNPA and PNPB. The rate constants in the micellar pseudophase are essentially lower than in water (the process retarded by a factor of 3–5). In the absence of CPB, PNPC favors the formation of the *n*-decylamine micelles which catalyze the reaction with PNPC, to accelerate essentially the process (see Fig. 1). Adding CPB into the system results in the rearrangement of the micelles and formation of a new highly organized system, *viz.*, mixed aggregates of different composition. The neutral molecules of *n*-decylamine and substrate, included in the micelle, are apparently separated and unfavorably oriented, which hampers their interaction and results in the inhibition of the process. In addition, the retardation of the reaction can evidence that the process proceeds inside a micelle of low polarity, and in this case destabilization of transition state of the S_N2-reaction is possible.

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