Aminolysis of 4-nitrophenyl esters of phosphorus acids in reversed micelles of 2-hydroxyethyldimethylpentadecylammonium bromide

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The reactions of *n*-cetyl- and *n*-hexylamines with 4-nitrophenyl esters of tetracoordinated phosphorus acids in chloroform in the presence of 2-hydroxyethyldimethylpentadecylammonium bromide and the influence of the latter on the acid—base equilibrium of the bromphenol blue dye (BPB) were studied by the spectrophotometric method. In the presence of reversed micelles of the cationic surfactant, the observed rate constant of aminolysis increases by more than two orders of magnitude. The catalytic efficiency of the micelles increases as the concentration of the long-chain amine decreases and on going from the latter to a short-chain amine. The acid—base equilibrium of BPB in micellar solutions is shifted due to the formation of a complex between the surfactant and the BPB dianion.

Key words: micellar catalysis; surfactant; alkylamine; esters of phosphorus acids; acid-base equilibrium.

Cationic surfactants containing the 2-hydroxyethyl group are effective catalysts for many reactions in aqueous solutions, including nucleophilic substitution of esters of tetracoordinated phosphorus acids.¹ The catalytic effect of 2-hydroxyethyl surfactants in alkaline media is explained by the simultaneous micellar and nucleophilic catalysis involving the dissociated 2-hydroxyethyl group.^{2,3} The effect of reversed micelles of this type of surfactant on processes involving esters of phosphorus acids is almost unstudied.⁴

In this work, we studied the reactions of *n*-cetylamine (CA) and *n*-hexylamine (HA) with 4-nitrophenylbis(chloromethyl)phosphinate (1) and 4-nitrophenylethylchloromethylphosphonate (2) in chloroform in the presence of 2-hydroxyethyldimethylpentadecylammonium bromide (HDPB).

Experimental

Esters 1 and 2 were synthesized as described previously.^{5,6} HDPB was obtained by quaternization of 2-dimethylaminoethanol by pentadecylammonium bromide.⁷ *n*-Hexylamine (purity grade) was stored over NaOH and distilled prior to use. *n*-Cetylamine (Loba-Chemie) was used without additional purification. Chloroform was purified by a standard method.⁸

The kinetics of the reactions were studied by the spectrophotometric method on Specord UV-VIS and SF-26 spectrophotometers by measuring the intensities of absorption bands of 4-nitrophenol (PNP) at 318.5 nm in the absence of a surfactant and 4-nitrophenolate ion at 403.2 nm (for CA) and 430 nm (for HA) in the presence of a surfactant. The values of the observed first-order rate constants (k) were calculated by the least-squares method on an Elektronika DZ-28 microcomputer. The concentration of substrates in all experiments was $1 \cdot 10^{-4}$ mol L⁻¹.

The solubilization of the bromphenol blue (BPB) dye by solutions of the surfactant in chloroform was studied by UV spectroscopy on a Specord UV-VIS spectrophotometer. The volume of a HDPB solution saturated with the dye $(V/\mu L)$, for which the optical density of the bands of BPB at 423.7 nm and 609.8 nm lies within 0.1–1.0, was added with a microsyringe to a quartz cell (optical path length 1 cm) containing 2 cm³ of a solution of the cationic surfactant with the specified concentration. The change in the optical density of the surfactant solution, when 1 μ L of a HDPB solution saturated with the dye was added, was used as a function dependent on the surfactant concentration.

Results and Discussion

In the absence of the surfactant, the dependences of the observed first-order rate constants of the reactions of CA and HA with 1 on the amine concentration (C_A) are nonlinear (Fig. 1). This can be due to the formation of aggregates of the reversed-micelle type⁹ or the assistance from the second amine molecule.⁵

In the presence of HDPB, the rate constants of the reactions of 1 with amines increase by more than two orders of magnitude (Fig. 2). As the surfactant concentration increases, the retardation of the increase in the rate constants (with a tendency to reach a plateau) is observed, which is characteristic of micellar systems.

The effect of micelles on the aminolysis of ester 1 also manifests itself as a change in the character of the

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Fig. 1. Dependences of the observed rate constant of aminolysis of 1 on the concentration of CA (1) and HA (2) in chloroform at 25 °C.



Fig. 2. Dependences of the observed rate constants of the reactions of CA (1, 2, 4, 5) and HA (3) with 1 on the concentration of HDPB in chloroform at 25 °C (1-3), 40 °C (4), 50 °C (5) and $C_{\rm A} = 0.01$ (1, 4, 5), 0.05 mol L⁻¹ (2, 3).

dependence of k of the reaction on the amine concentration. For example, in HDPB solutions, this dependence has a linear character in the studied region of amine concentration (Fig. 3) and is described by the following equation:

$$k = k_1 \cdot C_A,\tag{1}$$

where k_1 for the aminolysis of 1 at 25 °C in chloroform in the presence of 0.04 *M* HDPB is equal to 0.29 and 0.21 L mol⁻¹ s⁻¹ for HA and CA, respectively, and in the presence of 0.09 *M* HDPB, 0.61 and 0.45 L mol⁻¹ s⁻¹. Equation (1) likely reflects a change in the microenvironment of the amine due to bonding of the nucleophile by



Fig. 3. Dependences of the observed rate constants of the reactions of CA (I, 3) and HA (2, 4, 5) with 1 (1-4) and 2 (5) in the presence of HDPB on the amine concentration in chloroform at 25 °C and $C_{\text{HDPB}} = 0.04$ (1, 2), 0.09 (3, 4), and 0.25 mol L⁻¹ (5).

HDPB micelles. At higher concentrations of the amine, the dependence of k on C_A has another form (Fig. 3, curve 5) likely due to substantial differences in the composition of the medium.

The reaction parameters were obtained by processing the kinetic data (see Fig. 2) using the least-squares method by the equation 10

$$(k - k_0)/(k_m - k) = K_{\text{bond}} \cdot (C_{\text{surf}} - \text{cmc})$$

 $(k_0 \text{ and } k_m \text{ are the rate constants of the reaction in the solvent bulk and micellar phase, <math>K_{\text{bond}}$ is the bonding constant of the substrate and surfactant micelles, and cmc is the critical micelle formation concentration (Table 1)).

According to previous studies,¹¹ the catalytic effect of micelles on chemical reactions is related to concentrating the reagents when the latter are transferred from the solvent bulk to the micellar aggregates and to the

Table 1. Parameters of the HDPB-catalyzed reactions of *n*-cetyl- and *n*-hexylamine with 1 in chloroform

Amine	T	C _A	cmc • 10 ³	$k_{\rm m} \cdot 10^2$	Kbond	$k_0 \cdot 10^5$	$k_{\rm m}/k_0$
	/°C	r	nol L ⁻¹	/s ⁻¹	/L mol ⁻¹	/s ⁻¹	
CA	25	0.01	3.4	2.6	2.3	6.3	413
	25	0.05	4.8	4.8	7.1	36	133
	40	0.01	4.7	2.7	4.8	9.7	278
	50	0.01	9.8	4.8	4.3	12	400
HA	25	0.05	3.2	16	3.2	35	457

Table 2. Activation energy and entropy of the HDPBcatalyzed reaction of n-cetylamine with 1 in chloroform

C _{HDPB} /mol L ⁻¹	$E_{a,eff}$ /kJ mol ⁻¹	$-\Delta S_{\text{eff}}^{\star}$ /J K ⁻¹ mol ⁻¹	
0	17.0	276	
0.05	29.3	204	
0.1	31.3	193	
0.15	32.8	185	
0.2	31.3	189	
0.25	30.4	191	
0.3	29.6	193	

influence of the micellar microenvironment on the transition state. It can be seen from the data presented in Table 1 that ester 1 is characterized by low values of the bonding constant of the substrate with the surfactant micelles, which is typical of the solubilization of esters of phosphorus acids by reversed micelles. 12-14 In addition, a sharp increase in k_m as compared to k_0 is observed. This means that in the case under question, the reaction rate constant mainly increases not due to concentrating the reagents, as is commonly accepted,¹⁵ but due to an increase in the rate constant in the micellar phase. The k_m/k_0 value for the aminolysis of 1 in chloroform in the presence of HDPB micelles increases as the length of the hydrocarbon radical in the amine molecule and the CA concentration increase (see Table 1). The latter effect is related to the fact that the concentration of CA affects k_0 more strongly than k_m .

The change in temperature weakly affects the k value (see Fig. 2) and parameters of the micelle-catalyzed reaction (see Table 1). It is seen from the data in Table 2 that in the presence of the surfactant, the activation energy increases and the absolute value of the activation entropy decreases, *i.e.*, the acceleration of aminolysis in solutions of HDPB is caused by the favorable change in the entropy factor.

The solubilization of reagents in reversed micelles can affect their spectral properties. It is known that in the presence of amines, PNP can form in a solution a complex with the hydrogen bond and an ion pair, whose equilibrium in solvents with a low ($\varepsilon = 2-7$) dielectric constant

is shifted to the formation of a nonionic structure. However, even in chloroform, the spectrum of PNP contains the characteristic band at 400 nm, which is evidence for the formation of the ion pair.¹⁶ The data in the change in the optical density (D) of the complex of *n*-cetylamine with PNP in the presence of HDPB are presented in Fig. 4. In reversed HDPB micelles, as the surfactant concentration increases, an intense absorption band appears at 400-410 nm and the optical density of the band at 318 nm decreases. This indicates that in a micellar solution of HDPB in chloroform, the CA



Fig. 4. Dependences of the optical density of the absorption band of the CA complex with BPB in chloroform in the presence of HDPB on the surfactant concentration at $\lambda =$ 318.5 (1, 2), 403.2 (3), and 408.2 nm (4), 25 °C, $C_{CA} =$ 0.01 (2, 3) and 0.05 mol L⁻¹ (1, 4); $C_{BPB} = 10^{-4}$ mol L⁻¹, d = 1 cm.

complex with PNP is in the polar microenvironment. Some change in the D value of the complex in the presence of the surfactant when the CA concentration increases (see Fig. 4) can be due to an increase in the degree of bonding of the substrate (see Table 1) and the possible variation of the polarity of the micelles when they solubilize the long-chain amine.

Thus, the results of the kinetic studies indicate that the cationic surfactant HDPB forms micelles in chloroform at cmc = $3.4 \cdot 10^{-3} - 9.8 \cdot 10^{-3}$ mol L⁻¹ (see Table 1). This is supported by the data on solubilization of the acid dye bromphenol blue in solutions of HDPB. For example, in the region of surfactant concentrations less than $4 \cdot 10^{-3}$ mol L⁻¹, the absorption spectrum of the solution of HDPB in chloroform saturated with the dye contains an absorption band with a maximum at 423.7 nm (Fig. 5), which can be assigned to a complex between the dye monoanion HR⁻ and the cationic surfactant:

$$[HR^{-}-surf.] = [R^{2}-surf.] + H^{+}.$$
(2)

An increase in the concentration of HDPB results in the appearance of a new absorption band at 609.8 nm (see Fig. 5) and retardation of an increase in the optical density of the band at 423.7 nm (Fig. 6). This fact attests to a partial shift of equilibrium (2) to the formation of a complex between the surfactant and the BPB dianion and to a substantial change in the dye microenvironment in a solution of the surfactant, which can be explained by its transfer from the bulk of the solvent to the polar core of the micelle. The region of surfactant concentration in which the absorption band at 609.8 nm appears (0.004 mol L^{-1} , see Fig. 6) coincides with the cmc values determined by the kinetic method (see Table 1). The increase in the $\Delta D/V$ ratio for the absorp-



Fig. 5. Absorption spectrum of BPB in a solution of HDPB in chloroform at $C_{\text{HDPB}} = 0.0025$ (1), 0.008 mol L^{-1} (2), d = 1 cm, 18 °C, V = 0.06 (1), 0.01 mL (2).



Fig. 6. Change in the optical density of the absorption band of BPB in a solution of HDPB on the concentration of the surfactant in chloroform at 18 °C, $\lambda = 423.7$ (*I*) and 609.8 nm (2).

tion band at 423.7 nm and some decrease in this indication for the absorption band at 609.8 nm when the surfactant concentration is greater than 0.008 mol L^{-1} are likely related to the rearrangement of the structure of micellar aggregates, which has different effects on the bonding constants of mono- and dianions of the dye.¹⁷

The data presented indicate that reversed micelles of the cationic surfactant are efficient catalysts for the reactions of esters of tetracoordinated phosphorus acids with n-alkylamines, affecting the reactivity of the solubilized reagents and the equilibrium of the complexes formed in the system. This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09277).

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