## Catalysis of the hydrolysis of esters of phosphorus acids by *n*-decylammonium chloride/*n*-decylamine mixed micelles

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The effect of n-decylammonium chloride/n-decylamine mixed micelles on the rate of hydrolysis of aryl esters of acids of four-coordinate phosphorus was studied spectrophotometrically. The shape of the concentration curves is characteristic of the micellar catalysis reactions. The binding constants of the substrate, critical micelle concentrations, and the rate constants in the micellar phase were determined. A specific effect of the structure of substrates on these parameters was shown.

Key words: esters of phosphorus acids, hydrolysis, rate constants, *n*-decylamine, *n*-decylammonium chloride, micellar catalysis.

The micellar catalysis of solvolysis and aminolysis of esters of carboxylic acids by micelles containing an amino group capable of a nucleophilic attack was studied in detail by a number of investigators<sup>1</sup> in order to clarify the effect of hydrophobic and electrostatic interactions between the substrate and the micelle on the reaction rate. The electrostatic interactions significantly affect catalysis of reactions of substrates devoid of high hydrophobicity.<sup>2,3</sup> The presence of both hydrophobic and charged substituents in substrates leads to a specific orientation of the substrate in the micelle.<sup>2</sup> As follows from the studies on the effect of hydrophobic interactions between the reactants on the reaction rates in the model systems based on higher amines, 4-8 the approach of the reactants associated with the hydrophobic interaction results in an appreciable acceleration of reactions (up to 10-fold) due to the entropy factor.<sup>6</sup>

Previously<sup>9</sup> we showed that mixed micelles consisting of protonated and nonprotonated forms of *n*-decylamine were formed in aqueous solutions of partly protonated *n*-decylamine at various ratios *n*-decylammonium chloride (DAC)/*n*-decylamine (DA). When the degree of protonation of an amine is less than 0.5, it is the neutral form of higher amines that participates in the micellar catalysis of hydrolysis of esters of phosphorus acids.<sup>10</sup>

The aim of this work was the study of the catalytic effect of mixed micelles DAC/DA in the reaction of hydrolysis of esters of acids of four-coordinate phosphorus 1-8.

## Experimental

The substrates were obtained using the known procedures,  $^{11-13}$  and their melting and boiling points are in agree-



**7:** 
$$R = C_6H_4NO_2-\rho$$
;  $R' = R'' = OC_6H_4Cl-\rho$ ;  
**8:**  $R = C_6H_4NO_2-\rho$ ;  $R' = OC_6H_4NO_2-\rho$ ;  $R'' = OPh$ 

ment with the published data. *n*-Decylamine (Fluka) was dried over alkali and then distilled.

The kinetics of hydrolysis of substrates in the micellar solutions was investigated at the constant degree of protonation of *n*-decylamine,  $\alpha = C_{DAC}/(C_{DA} + C_{DAC}) = 0.42$ . The reactions were carried out in quartz cuvettes at constant temperature ( $25\pm0.5$  °C) at the initial concentrations of the substrates of  $8 \cdot 10^{-5}$  mol L<sup>-1</sup>. The reaction kinetics was investigated spectrophotometrically on a Specord UV-VIS instrument by monitoring the increase in the optical density of solutions (*D*) at 400 nm for the *p*-nitrophenyl esters and at 290 nm for the phenyl ester. The observed first-order rate constants  $k_{obs}$  were determined from the equation

$$\ln(D_1 - D_t) = -k_{obs} \cdot t + \text{const},$$

where  $D_1$  and  $D_t$  are the optical densities after the completion of the reaction and at time *t*, respectively. The rate constants for reactions catalyzed by *n*-butylamine as well as those for alkaline hydrolysis of certain substrates were determined follow-

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ing an analogous procedure. The bimolecular rate constants for the reaction catalyzed by *n*-butylamine were calculated from the formula  $k = k_{obs}/C_{Bu}n_{NH_2}$  taking into account the degree of protonation of the amine.

## **Results and Discussion**

The influence of micelles on the rate of organic reactions is often determined by binding of the substrates with the micelles and distribution of reagents between the micelles and water. Usually, hydrophobic substrates are more sensitive to micellar catalysis or inhibition,<sup>1</sup> which reflects an important role of hydrophobic interactions in binding of the substrates with



Fig. 1. The dependence of the observed rate constants  $(k_{obs})$  for the hydrolysis of esters 1-5 on  $C_0$  in the DAC/DA/H<sub>2</sub>O system.



Fig. 2. The dependence of the observed rate constants  $(k_{obs})$  for the hydrolysis of esters 6-8 on  $C_0$  in the DAC/DA/H<sub>2</sub>O system.

micelles. However, in addition to the concentration of reagents in micelles and the difference in the reaction rates in the bulk solution and in the micellar pseudophase, micellar catalysis is also affected by other factors, which make it difficult to interpret experimental results and lead to manifestation of the substrate specificity of micellar catalysis.<sup>1,14-16</sup>

We investigated catalytic hydrolysis of esters of phosphorus acids, viz., of phosphates, phosphonates, and phosphinates at a constant ratio of DAC/DA and variable overall *n*-decylamine concentration in the DAC/DA/H<sub>2</sub>O system. The dependences of the observed rate constants  $k_{obs}$  on the overall concentration of *n*-decylamine in the system ( $C_0 = C_{DAC} + C_{DA}$ ) are presented in Figs. 1 and 2.

The concentration dependences of  $k_{obs}$  for phosphonates and phosphinate reach a plateau (see Fig. 1) with an increase in  $C_0$ , while those for phosphates pass through a maximum (see Fig. 2). The difference in the character of the concentration dependences is probably due to the difference in the solubilization region of substrates in the micelles. Phosphonates (2-5) and phosphinate (1), which have higher basicity, can form hydrogen bonds with the protonated form of the amine being located at the micellar surface. Solubilization of less basic phosphates (6-8) can, probably, occur in the hydrophobic nucleus of the micelle.

The pseudophase model of the micellar catalysis<sup>14</sup> was used for a quantitative description of the concentration dependences of substrates 1-5 (see Fig. 1). First, the micelle solubilizes the substrate, and the latter is then subjected to catalytic hydrolysis following a general base mechanism<sup>10</sup> with the participation of the neutral form of the amine. The hydrolysis of the substrates under study is slow; therefore the equation for the micellar catalysis<sup>14</sup> in the form given below can be applied to the observed rate constant  $k_{obs}$ .

$$k_{\rm obs}/(k_{\rm m} - k_{\rm obs}) = K_{\rm s}(C_0 - {\rm CCM}),$$
 (1)

where  $k_{\rm m}$  is the reaction rate constant in the micellar pseudophase,  $K_{\rm s}$  is the binding constant of the substrate with the micelle, and CCM is the critical concentration of micelle formation.

The values of  $k_m$ ,  $K_s$  and CCM calculated from the concentration dependences for substrates 1-5 are listed in Table 1. The rate constants for hydrolysis of the substrates catalyzed by *n*-butylamine and for alkaline hydrolysis in the absence of micelles are also given therein.

A comparison of the  $k_m$  values with the catalytic constants for *n*-butylamine (which cannot form micelles) indicates that the structure of the substrate has a specific effect on the reaction rate constants in micelles.

The acceleration of hydrolysis (P) in the DAC/DA/H<sub>2</sub>O system was evaluated as the ratio of the maximum observed rate constant to the first-order rate constant in the presence of *n*-butylamine at the same concentrations of amines (see Table 1). The P value

**Table 1.** The kinetic parameters for the hydrolysis of esters 1-5 in the presence of mixed micelles DAC/DA, the rate constants for alkaline hydrolysis of substrates 1-8, and the rate constants for hydrolysis in the presence of *n*-butylamine

Subst-	ССМ	Ks	k <sub>m</sub>	k <sub>BunNH2</sub>	k <sub>OH</sub> -	Р
rate	/mol L <sup>-1</sup>	/L mol <sup>-1</sup>	/s <sup>-1</sup>	/L mol	-1 s <sup>-1</sup>	
1	0.0030	64	0.0670	0.550	69	4
2	0.0055	30	0.0070	0.0133	4.0	9
3	0.0045	55	0.00182	0.0082	3.53*	55
4	0.0015	21	0.950	0.121	28	133
5	0.0045	82	0.214	0.110	27	60
6				0.0052	0.32	400
7				0.0043	1.44*	2270
8				0.0080	2.5	3820

\* Determined in this work at 25 °C in KOH solutions, other values were taken from Ref. 17. *P* values for the substrates 6-8 were estimated analogously to those for substrates 1-5 in the presence of mixed micelles in the DAC/DA/H<sub>2</sub>O system, 25 °C.

Table 2. The kinetic parameters of alkaline hydrolysis of the phosphates in the presence of mixed micelles DAC/DA

Subst- rate	CCM · 10 <sup>3</sup> /mol L <sup>-1</sup>	$\frac{K_{\rm s}}{/\rm L}$ r	K <sub>b</sub> nol <sup>-1</sup>	k · 10 <sup>3</sup> ∕s <sup>−1</sup>	k <sub>m</sub> /k <sub>OH</sub>	A	P <sub>1</sub>
6	4.0	628	11	1.84	60	24	1492 (1440)*
7	3.5	194	32	6.5	50	46	2749 (2310)*
8	2.5	291	33	1.47	61	50	4299 (3233)*

\*  $(k_m/K_{OH}) \cdot A$ , V was taken as 0.35 L mol<sup>-1</sup>.  $P_1$  is the ratio of the maximum  $k_{obs}$  to  $k_{OH}$  (pH 9.32,  $k_{OH}$  values, L mol<sup>-1</sup> s<sup>-1</sup>, were taken from Table 1).

increases with the lengthening of the hydrocarbon radicals in the alkoxy groups of the substrates (*cf.* 2 and 3 in Table 1).

According to the previous investigations,<sup>14</sup> the shape of the concentration dependences for phosphates 6-8(see Fig. 2) is characteristic of bimolecular processes in micelles under strong binding of the substrate and nucleophile. Evidently, in the case of phosphates 6-8, a change in the mechanism of catalysis occurs, and the hydroxide ion becomes the second reactant. This can result from the low basicity of phosphates and the presence of three hydrophobic phenyl groups; as a consequence, the phosphates 6-8 are solubilized in the hydrophobic nucleus of the micelle locating the phosphoryl group in the Stern layer,<sup>18</sup> where hydroxide ions can also be present. In the system under study  $(DAC/DA/H_2O)$  at  $\alpha = 0.42$  (pH 9.32), the maximum rates for the substrates 6-8 are observed at  $C_{max} =$ 0.0123, 0.012, and 0.011 mol  $L^{-1}$ , respectively.

The concentration of the reacting ion in the Stern layer can be far higher than that in the aqueous phase due to the ion exchange between counterions and the reacting ion.<sup>19</sup> As a result, the concentrations of the substrate and hydroxide ion can be comparable, thus determining the shape of the concentration dependences in Fig. 2. The latter can be described by the Berezin equation<sup>14</sup> written in the form

$$k_{\rm obs} = \frac{k_{\rm m} K_{\rm s} K_{\rm b} (C_0 - {\rm CCM})}{V[1 + K_{\rm s} (C_0 - {\rm CCM})][1 + K_{\rm b} (C_0 - {\rm CCM})]}, \qquad (2)$$

where  $k_{\rm m}$  is the rate constant in the micellar pseudophase,  $C_0$  is the overall concentration of decylamine, and  $K_{\rm b}$  is the binding constant of the hydroxide ion. The values of  $k_{\rm m}$ ,  $K_{\rm s}$ , and  $K_{\rm b}$  for the phosphates **6**-**8** are presented in Table 2.

The optimum concentrations of the surfactants estimated<sup>14</sup> as  $C_{opt} = (K_s K_b)^{-0.5}$  are close to the values of  $C_{DA}$  at their maximum and are equal to 0.0133, 0.0126 and 0.01 mol L<sup>-1</sup> for substrates **6**-**8**, respectively. We also calculated<sup>14</sup> the reaction acceleration effects due to the accumulation of the reactants in the micelle  $A = K_s K_b / [V(K_s^{0.5} + K_b^{0.5})^2]$ , and due to an increase in the reactivity upon the transfer of reactants from water into the micelle,  $k_m/k_{OH}$ . These values are close to the experimental values of the accelerations ( $P_1$ ) for the micellar catalysis of the alkaline hydrolysis of phosphates **6**-**8**. It is interesting to note that a correlation was found between the rate constants for the reaction catalyzed by n-butylamine and those for alkaline hydrolysis of the substrates. The following regression equation can be written:

$$\log (k_{\text{BunNH}_2}) = 0.944 \cdot \log (k_{\text{OH}^-}) - 2.31$$
  
(r = 0.937, s = 0.29, n = 8).

The existence of this correlation attests to the similarity of the mechanisms of two reactions that are compared and the similar effect of substituents at the phosphorus atom on the reaction center. In contrast to this, in the micelle-catalyzed hydrolysis of substrates, no correlation was observed between  $k_m$  and rate constants for the alkaline hydrolysis of substrates, or between those for the reaction catalyzed by *n*-butylamine. Such behavior of  $k_m$  indicates a certain substrate specificity of the micellar catalysis in the hydrolysis of substrates 1-5 catalyzed by nonprotonated amino groups of mixed micelles according to the general base mechanism.

A more significant manifestation of the substrate specificity for phosphates 6-8 is the change in the reaction mechanism in the micellar pseudophase, a transition to the micelle-catalyzed alkaline hydrolysis.

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## References

- J. H. Fendler and E. J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975, 545.
- 2. T. C. Bruice, J. Katzhendler, and L. R. Fedor, J. Am. Chem. Soc., 1968, 90, 1333.
- 3. M. Chevion, J. Katzhendler, and S. Sorel, Isr. J. Chem., 1972, 10, 975.

- 4. D. G. Oakenfull, J. Chem. Soc., Perkin Trans. 2, 1973, 1006.
- 5. D. G. Oakenfull and D. E. Fenwick, Austral. J. Chem., 1974, 27, 2149.
- 6. C. A. Blyth and J. R. Knowles, J. Am. Chem. Soc., 1971, 93, 3021.
- 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, 32, 1297 (Engl. Transl.)].
- R. F. Bakeeva, V. E. Bel'skii, L. A. Kudryavtseva, S. B. Fedorov, and B. E. Ivanov, *Izv. Akad. Nau<sup>1</sup> SSSR, Ser. Khim.*, 1984, 1475 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, 33, 1356 (Engl. Transl.)].
- R. F. Bakeeva, S. B. Fedorov, L. A. Kudryavtseva, V. E. Bel'skii, and B. E. Ivanov, *Kolloidn. Zh.*, 1984, 46, 755 [*Colloid J. USSR*, 1984, 46 (Engl. Transl.)].
- R. F. Bakeeva, L. A. Kudryavtseva, S. B. Fedorov, V. E. Bel'skii, and B. E. Ivanov, *Zh. Obshch. Khim.*, 1982, 52, 2503 [J. Gen. Chem. USSR, 1982, 52 (Engl. Transl.)].
- 11. H. J. Brass and M. L. Bender, J. Am. Chem. Soc., 1972, 94, 7421.
- C. A. Bunton, S. J. Farber, and E. J. Fendler, J. Org. Chem., 1968, 33, 29.
- Houben-Weyl, Methoden der Organischen Chemie, Thieme, Stuttgart, 1964, 12/2, 685.
- I. V. Berezin, K. Martinek, and A. K. Yatsimirskii, Usp. Khim., 1973, 42, 1729 [Russ. Chem. Rev., 1973, 42 (Engl. Transl.)].
- E. Kiirend, Eesti NSV Teaduste Acadeemia Tumetisted, 1983, 32, 52.
- 16. S. B. Fedorov, V. E. Bel'skii, L. A. Kudryavtseva, E. P. Tishkova, and B. E. Ivanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 530 [Bull. Acad. Sci. USSR, Div. Chem. Sci., 1984, 33, 486 (Engl. Transl.)].
- V. E. Bel'skii, L. A. Kudryavtseva, O. M. Il'ina, and B. E. Ivanov, Zh. Obshch. Khim., 1979, 49, 2470 [J. Gen. Chem. USSR, 1979, 49 (Engl. Transl.)].
- C. A. Bunton and L. Robinson, J. Org. Chem., 1969, 34, 773.
- L. S. Romsted, in *Micellization, Solubilization and Microemulsions*, Ed. K. L. Mittal, Plenum Press, New York, 1977.

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