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Catalysis of the hydrolysis of phosphorus acids esters by the mixed micelles of long-chain amines and cetylpyridinium bromide

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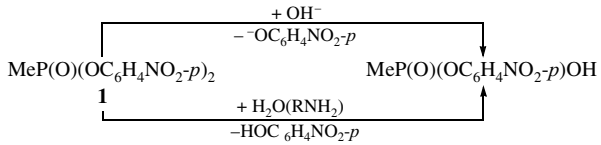
Self-association of long-chain amines and formation of mixed micelles, including cetylpyridinium bromide, influence the rate and the direction of the *O*,*O*-(bis-*p*-nitrophenyl)methylphosphonate hydrolysis; characteristic parameters of the micellar aggregates have been obtained by kinetic methods and ^{1}H NMR spectroscopy.

The ability of long-chain amines to self-associate leads to essential changes in their basicity and nucleophilicity compared with short-chain analogues.[1–3] In the presence of surfactants, long-chain amines form mixed micelles which have some quite new properties.[4,5] The influence of the mixed micelles formation in the presence of amines on their reactivity has not been practically studied up to now.

The main goal of this work was to investigate the catalytic activity of primary long-chain *n*-alkylamines in water and aqueous solutions of cetylpyridinium bromide (CPB). For this purpose, the kinetics of hydrolysis of *O*,*O*-(bis-*p*-nitrophenyl)-methylphosphonate **1** has been studied, and a set of characteristic parameters of the mixed micelles formed in the systems have been obtained by independent physical techniques.

Esters of phosphorus acids in the presence of amines in aqueous solutions undergo alkaline hydrolysis as well as hydrolysis due to the general base mechanism[3,6]



The contribution of the aminolysis in the case of primary amines is rather small.[3,7] The effect of the general base catalysis in aqueous solutions is proportional to the basicity of the nucleophile. The dependence of the observed rate constants (k_{obs}) on the concentration of hydrophilic short-chain amines is linear in a rather wide range.[3] In the case of amines with hydrophobic radicals, the process becomes more complicated because of aggregation phenomena.

The kinetics of hydrolysis of **1** in aqueous solutions of partially protonated decylamine or octylamine as monitored under pseudo-first-order conditions by optical spectroscopy based on an increase in the absorbance due to the liberation of *p*-nitrophenolate (λ = 400 nm). The dependence of the rate constants on the concentration of decylamine (C_{DA}) reflects changes in the system under study (Figure 1, curve *4*). The first linear portion corresponds to a pre-micellar state. The changes in the curvature of $k_{obs} = f(C_{DA})$ are connected with micelles formation. The plateau is due to saturation of the micelles by substrate molecules. The linearity of the dependences of k_{obs} on the octylamine concentration up to 0.015 mol dm^{-3} (pH 9.4–10 .4) gives evidence of the absense of octylamine associates in this range. The bimolecular rate constant (k_2) is equal to 0.7 dm^3 mol^{-1} s^{-1} .

The fact of micelle formation by long-chain amines has been confirmed by measuring the surface tension of aqueous solutions. The values of the critical micelle concentration (CMC) for decylamine are essentially lower as compared with octylamine (for example, in the point of half-protonization, the CMC values at

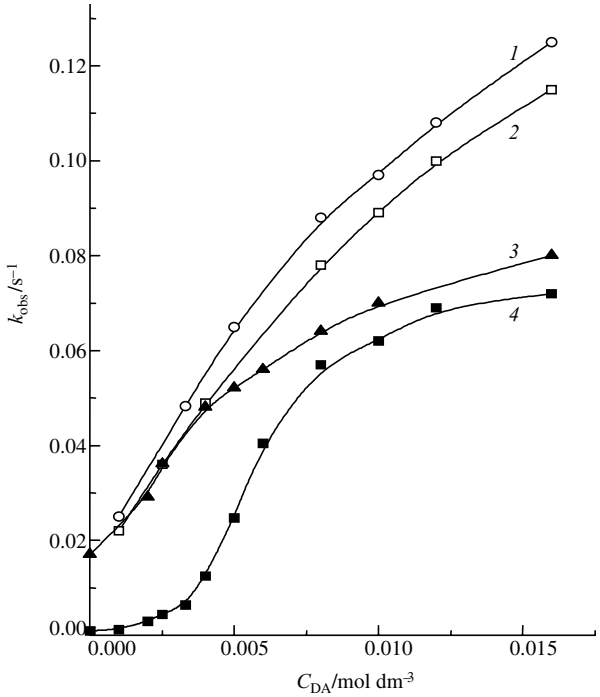


Figure 1 Observed rate constants for the hydrolysis of **1** as functions of decylamine concentration (25 °C). (*1*) C_{CPB} = 0.05 and (*2*) 0.02 mol dm^{-3} at varied pH; (*3*) C_{CPB} = 0.015 mol dm^{-3} at pH 9.4; (*4*) C_{CPB} = 0 at pH 9.4.

20 °C are 0.0013 mol dm^{-3} for decylamine and 0.010 mol dm^{-3} for octylamine). The CMC data confirm that the conditions of our kinetic experiments in the case of octylamine correspond to the pre-micellar range, whereas for decylamine they cover the range of the micelle formation. This is reflected in the specific pattern of the dependence of k_{obs} on the amine concentration.

Table 1 Micellar parameters for the hydrolysis of **1** in CPB solutions in the presence of primary *n*-alkylamines (25 °C).

Amine	C/mol dm^{-3}	pH	K_{bond}/ dm^3 mol^{-1}	CMC[a]/ mol dm^{-3}	k_m/s^{-1}	k_m/k_0'[b]
Octylamine	0.0025	9.4	195	0.00012	0.031	77
	0.005	9.4	267	0.00021	0.033	82
	0.01	9.4	364	0.00012	0.039	96
	0.02	9.4	350	0.00010	0.041	98
Decylamine[c]	0.001	9.4	80	0.00010	0.060	150
	0.0018	9.4	92	0.000098	0.083	206
	0.0025	9.4	87	0.00007	0.12	300
OH$^-$[d]		10.4	330	0.00060	0.20	

[a]For CPB in aqueous solutions, the CMC is equal to 0.0006 mol dm^{-3} .[18] [b]k_0' is the constant of alkaline hydrolysis at pH 9.4 in the absence of CPB. [c]In the absence of CPB at pH 9.4, for decylamine: K_{bond} = 46 mol^{-1} dm^3, CMC = 0.001 mol dm^{-3} and k_m = 0.21 s^{-1} . [d]In a dilute NaOH solution.

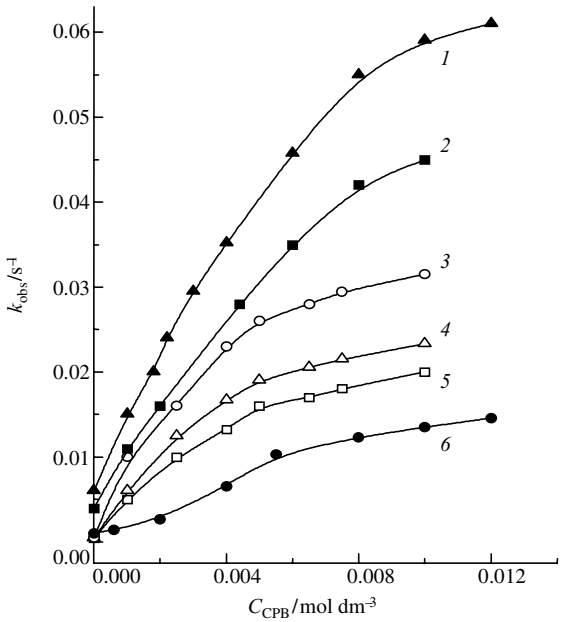


Figure 2 Observed rate constants for the hydrolysis of **1** in the presence of *n*-alkylamines (pH 9.4, 25 °C) as functions of CPB concentration. Decylamine C_{DA} = (*1*) 0.0025, (*2*) 0.0018 and (*6*) 0.001 mol dm^{-3}; octylamine C_{OA} = (*3*) 0.02, (*4*) 0.005 and (*5*) 0.0025 mol dm^{-3}.

In the decomposition of **1** in aqueous solutions in the presence of CPB and a long-chain amine, one can expect the acceleration of alkaline hydrolysis as well as of the process catalysed by the general base mechanism. First of all, it is induced by solubilization of the substrate and the amine by micelles because of hydrophilic interactions. Hydroxide ions are also concentrated at the positively charged micellar surface due to electrostatic attraction. This concentration of reagents in the micellar pseudophase, which in turn is accompanied by changes in the microenvironment, solvation and orientation of reacting species, is the reason of micellar catalytic effects observed in aqueous surfactant solutions.[8–10] The influence of CPB on the hydrolysis rate of **1** (Figure 1, curves *1–3*) with increasing quantities of decylamine is related to an increase in the pH of solutions (from 9 up to 11) as well as to an increase in the concentration of the nucleophile. The latter 'activates' water molecules which participate in the degradation of ester bonds. To estimate the influence of amines on the rate of the process, the kinetic experiment should be performed at fixed pH values, which were attained by adding HCl.

The relationship obtained for the hydrolysis of **1** in the presence of octylamine in an aqueous solution of CPB at pH 9.4 was slightly changed by varying the amine concentration in the reaction media (Figure 2). This is evidence of the alkaline hydrolysis prevalence under the mentioned conditions. The amine acts here only as a buffer.

At the same time, the rate of hydrolysis of **1** in the micellar solution of CPB in the case of decylamine significantly depends on the amine concentration (Figure 2). This allows us to assume that decylamine acts not only as a buffer but also as a general base catalyst.

The data were analysed in terms of the pseudophase model of micellar catalysis,[8,9] which was successfully used for mixed micelles,[11,12] by the equation:

$$k_{obs} = \frac{k_m K_{bond} C_{det} + k_0}{1 + K_{bond} C_{det}}, \quad (1)$$

where k_0 and k_m are the rate constants in aqueous and micellar phases, respectively, K_{bond} is the reduced binding constant of the substrate, C_{det} is the concentration of the detergent minus CMC.

As one can see in Table 1, hydrophobic amines enhance the micelle formation of CPB and reduce the CMC values. This is characteristic of the formation of mixed aggregates.[13] The effect of amines on the substrate bonding is more significant in the presence of decylamine and reflects the decrease of K_{bond}. Nevertheless, the efficiency of the micellar catalysis (k_m/k_0') in the hydrolysis process of **1** in CPB solutions is higher in the case of decylamine as compared with octylamine (Table 1). This is due to the increasing contribution of general base catalysis.

Thus, the peculiarities of the decylamine kinetic behaviour in the presence of CPB can be explained by the formation of mixed micelles in these systems. We tried to confirm the kinetic data by ^{1}H NMR spectroscopy with the Fourier transform and pulsed-gradient spin echo (FT-PGSE). This technique allowed us not only to obtain the spectra of chemical ingredients of micellar systems but also to determine the self-diffusion coefficients (D) of the components.[14,15] The self-diffusion measurements were performed using a modified TESLA-BS 576A NMR spectrometer (100 MHz) equipped with home-built field-gradient units producing a field gradient up to 50 G cm^{-1}, according to the procedure described earlier.[14] Water used for the NMR experiments was prepared from 95% (v/v) of deuterium oxide (Ferak) and 5% of twice-distilled water; the concentration of CPB was 0.05 mol dm^{-3}. The self-diffusion data and the results of calculation are presented in Table 2.

The lines from the $(-CH_2-)_n$ groups of CPB and decylamine (1.2 ppm) and from water (4.78 ppm) are most suitable for self-diffusion measurements in ^{1}H NMR spectra. The diffusive decay of the methylene line cannot be divided into the fractions from CPB and decylamine. It is very difficult to imagine that two substances which differ in molecular weight and micelle-forming properties diffuse equally. We can suppose that both CPB and decylamine move as components of a single structural aggregate. Using the modified Stokes–Einstein equation,[16] we estimated (see Table 2) the effective micelle radius R as

$$R = (1 - 2\phi)kT/6\pi\eta D, \quad (2)$$

where ϕ is the volume fraction of the dispersed phase and η = = 1.033 N s m^{-2} is taken equal to the viscosity of D_2O at 30 °C. Up to a certain concentration of decylamine, one can see only a little increase of the aggregates effective radius as compared with the pure CPB system (mole fraction $X_{DA} = 0$). When the molar ratio between CPB and decylamine is approximately 3:1, the aggregate size is dramatically increased, or changes in the micelle shape from spheroid to cylinder occur.

Another confirmation of the formation of mixed micelles is broadening of all lines in the NMR spectra except that of water when decylamine is added to the CPB solution (Table 2). The increase in the line width ($f_{1/2}$) indicates that there is a reduction in the intramicelle molecular motion[17] as a result of penetration of decylamine into the CPB micelles.

Hence, by means of the kinetic method and ^{1}H NMR spectroscopy, the existence of mixed micelles formed by decylamine and CPB was confirmed. Their catalytic properties as well as the influence on the mechanism of hydrolytic decomposition of phosphorus acid esters were estimated. Several characteristic parameters of mixed aggregates such as critical micelle concentrations, self-diffusion coefficients and effective hydrodynamic radii of mixed micelles were obtained.

Table 2 Parameters of the mixed micelles, measured by ^{1}H NMR spectroscopy[a] at different ratios between CPB[b] and decylamine (X_{CPB} + XDA = 1).

X_{DA}	$D/10^{-11}$ m^2 s^{-1}	R_m/Å	$f^c_{1/2}$/Hz
0.0	5.15	42.1	4.8
0.091	5.11	43.1	5.5
0.169	4.99	44.1	7.0
0.219	4.95	44.3	9.8
0.306	4.04	54.2	12.0
0.338	2.97	73.7	14.0
0.389	2.61	83.6	16.5
0.656	1.50		125.0

[a]Measurements were performed at 30±0.5 °C, the accuracy of measurements is ≤ 4%. [b]C_{CPB} = 0.05 mol dm^{-3}, (the concentration of CPB in the experiments remained constant). [c]The width of the $(-CH_2-)_n$ line (1.2 ppm).

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