Kinetics of alkaline hydrolysis of esters of phosphorus acids in micellar and hexagonal phases in the cetyldimethylethylammonium bromide—NaOH—water system

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The influence of micellar (Mi) and hexagonal (E) mesophases of the cetyldimethylethylammonium bromide—NaOH—water system (I) on the rates of alkaline hydrolysis of O-p-nitrophenyl-O, O-diethyl phosphate (2), O-p-nitrophenyl-O-ethylethyl phosphonate (3), and O, O-di(p-nitrophenyl)methyl phosphonate (4) was studied by UV spectrophotometry. The binding constants of the substrates, critical micelle concentrations, and rate constants of reactions in the micellar phase were determined. In micellar solutions of system I, a tenfold increase in the rates of alkaline hydrolysis of 2-4 was observed. An increase in the degree of medium ordering during the formation of the E-phase results in a twofold acceleration of alkaline hydrolysis of 2 and 3 and in the inhibition of this process in the case of 4.

Key words: micellar catalysis, esters of acids of tetracoordinated phosphorus, lyomesophases, kinetics.

Many biologically significant systems are arranged according to the type of liquid crystals^{1,2} exhibiting such properties as "order and mobility" and capability of "acting through arrangement."¹ The regularities of chemical processes in thermotropic liquid crystals are well studied;³ at the same time, there are only few data on the effect of lyotropic liquid crystals (LLC) on the rates and selectivity of chemical reactions.

The formation of supramolecular associates (micelles) from amphiphilic molecules with the cation-active head group results in the acceleration of nucleophilic substitution at the tetracoordinated phosphorus atom with the participation of anionic nucleophiles.^{4,5} A change in the reactivity of substrates due to an increase in the arrangement and ordering of the medium on going from micelles to LLC has been studied for several examples.6 - 10The formation of nematic LLC in the myristyltrimethylammonium bromide-n-decanol-water-NH₄Br system results in a 1000-fold increase in the rate constant of iodosobenzoic acid-catalyzed hydrolysis of esters of phosphonic acids as compared to the discotic mesophase.⁶ The formation of the lamellar mesophase in the cetyltrimethylammonium bromide (CTAB)n-hexanol-NaOH-water system results in a change in the mechanism of decomposition of O-p-nitrophenyl-O, O-dimethylthiophosphate (1) as compared to the micellar pseudo-phase.⁸ In the micellar pseudo-phase and lamellar mesophase of the n-decylammonium chloride*n*-decylamine—water system, the dealkylation of substrate 1 occurs with similar rates dependent on the fraction of the active nucleophile on the associate surface.^{9,10}

In this work, we studied the effect of the molecular arrangement and ordering in the cetyldimethylethylammonium bromide (CDAB)—NaOH—water system (I) on the kinetics of alkaline hydrolysis of esters of acids of tetracoordinated phosphorus (EATP) 2-4 (Scheme 1).



 $\begin{aligned} R &= p \text{-NO}_2 C_6 H_4; \ R' &= R'' = \text{EtO (2)}; \ R' &= \text{Et, } R'' = \text{EtO (3)}; \\ R' &= p \text{-NO}_2 C_6 H_4 O, \ R'' &= \text{Me (4)} \end{aligned}$

Experimental

Substrates were synthesized by known procedures,¹¹ their melting and boiling points corresponded to the published values. The CDAB sample (Sigma) was recrystallized from ethanol. Bidistilled water deaerated by refluxing was used for preparing solutions. Samples of the liquid-crystalline mesophases

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were obtained by mixing a weighed amount of the surfactant with a solution of NaOH followed by storage for 2 days. To determine the type of the mesophase, samples of solutions were interposed between the slide and cover glasses and glued to avoid evaporation of the solvent. The type of the mesophase and the region of its existence were determined by polythermal polarization microscopy using a RNMK 0.5 observation device and a Boetius heating table. Mesophases were identified by the textures that appeared, using the known procedure.¹² To record spectra of 2 and 3 in heptane, methanol, and water, concentrated solutions of the substrates in these solvents were preliminarily prepared and added to a cell with the corresponding solvent. Prior to recording spectra, solutions of the substrates in micellar and liquid-crystalline media were preliminarily stored at 25 °C for 2 days to achieve equilibrium. The cell length was varied in such a way that the optical density (D) was >0.5. Saturated solutions were used in the case of substrate 4.

The kinetics of hydrolysis of substrates in micellar solutions was studied in thermostatted quartz cells (I = 1 cm) at initial concentrations of substrates of $1 \cdot 10^{-4}$ mol L⁻¹. In the case of the hexagonal (E) phase, a solution with a substrate was thoroughly stirred for 20 min prior to use. The reaction kinetics was studied using spectrophotometry on a Specord UV-VIS instrument from the increase in optical density at 400 nm. The observed first-order rate constants (k_{obs}/s^{-1}) were determined by the regression method from the equation

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

where D_1 and D_t are the values of the optical density when the reaction is stopped and at moment t, respectively. Parameters of micelle-catalyzed reactions were determined from Eqs. (1) and (2) (see below) by the weighed root-mean-square method using original programs for a PC/AT 486DX2.

The surface tension was measured by the ring detachment method using a Denouy tensiometer.

Results and Discussion

The micelle formation results in changes in the short-range order structure of the system. Self-arrangement of components to form LLC leads to the appearance of the long-range orientation order.¹³ It is known that an increase in the order in the system on going from isotropic to thermotropic liquid crystals can affect the rate and selectivity of reactions.³ Studying the effect of LLC on the reactions of nucleophilic substitution in EATP, one should take into account that micelles are structural units of lyomesophases. Since mono- and bimolecular reactions can occur in spherical micelles, the concentration dependences of k_{obs} should be analyzed to determine the rate constants in the micellar pseudo-phase.¹⁴ The microstructure of the LLC surface with packing is similar.¹⁵ It can be divided into three zones. The first zone consists primarily of hydrocarbon chains, along which a minor number of water molecules is distributed. In the second surface zone, relatively mobile head groups of a surfactant are localized. The latter interact with solvents and counterions to stabilize the mesophase in a solution. The third zone is formed by external water molecules and counterions. Micelles have a similar microstructure of the surface.¹⁴



Fig. 1. Dependence of the surface tension (σ) on the concentration of CDAB in the CDAB-NaOH-water system (I) at 25 °C. CMC = $5 \cdot 10^{-4}$ mol L⁻¹.

The critical micelle concentration (CMC) of CDAB in the CDAB-water system (II) was determined by the break in the dependence of the surface tension $(\sigma/dyne \ cm^{-2})$ on the surfactant concentration and was equal to $5.2 \cdot 10^{-4}$ mol L⁻¹ (Fig. 1), which is somewhat lower than that for the CTAB-water system (III) $(9 \cdot 10^{-4} \text{ mol } \text{L}^{-1})$.¹⁶ We showed by polythermal polarization microscopy that at $C_{CDAB} = 0.1 \text{ mol } L^{-1}$ system II exists in the metastable (monotropic) liquidcrystalline state, whereas at $C_{CDAB} = 0.4 \text{ mol } L^{-1}$ the stable E-phase is formed, which follows from the appearance of the "angular" texture similar to that described previously.¹² The latter fact implies that the solution is structured to form a hexagonal packing of cylinders of amphiphilic CDAB molecules. It is known that the E-phase is also formed in system III when the surfactant concentration increases to 0.72 mol L⁻¹.¹⁶

lons OH⁻⁻, which are reagents in the hydrolysis reaction under study, are concentrated in micelles and LLC (due to Coulomb forces) in the region of positively charged tetraalkylammonium groups, *i.e.*, in the Stern layer in micelles¹⁴ and in the second (surface) zone in LLC. The site of localization of substrates in supramolecular associates depends on their structure, and the local microenvironments of hydrophilic and hydrophobic groups of the substrate can be different.

In order to determine the local microenvironment of the substrates studied in the micellar and E-phases of system II, we studied their electronic absorption spectra and determined the spectral parameters of absorption bands in these phases as well as in heptane, methanol, and water. The values of wave numbers for maxima of the absorption bands (ν/cm^{-1}), extinctions (ε), and half-widths of the bands ($\Delta v_{1/2}/cm^{-1}$) are presented in Table 1.

The absorption spectra of substrates 2 and 3 in heptane, methanol, and water somewhat differ. In the micellar (Mi) and hexagonal (E) mesophases of system II, the spectral parameters are close to those in water (see Table 1), which can be due to adsorption of water-

Solvent	2			3						
	v	Δ٧	3	v	Δν	3	٧	Δν	ε	
	cm ⁻¹		cm ⁻¹			cm ⁻¹				
n-Heptane	37200	5300	13420	36800	6200	10620	37000			
Methanol	37040	7100	12258	36600	7800	9670	37000	6300	15420	
Water	36240	7500		35800	8000	7800	36600	8400		
Micelles	36200	7500	6020	35800	7800	8700	33000*			
E-phase	36440	7200		35900	7200	9375	33000*			
Vaseline							36800			
							35800 sh			

Table 1. Effect of solvents on the position of the maximum of the band of the electron $\pi \rightarrow \pi$ -transition in EATP 2, 3, and 4

* Imaginary shift of the band; for explanations, see text.

solvated substrates on the surface of supramolecular aggregates. The absorption spectra of substrate 4 in heptane, methanol, and water differ insignificantly (see Table 1). The spectra of the Mi- and E-phases of system II exhibit an unusual apparent long-wave shift of the absorption band of substrate 4 to 33000 cm^{-1} , and the value of the shift and absorption intensity increase when the substrate is stored in these phases for several days. The spectrum of substrate 4 changes in time, due, on the one hand, to its gradual dissolvation and, on the other hand, to partial spontaneous aqueous hydrolysis accelerated by the Mi- and E-phases of II to form p-nitrophenol instead of the p-nitrophenolate anion (PNPA) and the resulting superposition of three spectra of the substrate (p-nitrophenylmethyl phosphonate anion, and p-nitrophenol). Due to this, the position of the maximum of the absorption band of the substrate can be determined only approximately, which does not allow one to estimate the polarity of the microenvironment of this substrate.

For system I, we performed a comparative analysis of the kinetic features of the alkaline hydrolysis of EATP observed when the degree of arrangement and ordering of the system increase. It is established that alkaline hydrolysis occurs in the Mi- and E-phases, and one equivalent of PNPA is formed in the case of substrates 2 and 3. There is a possibility for substrate 4 to eliminate two *p*-nitrophenoxyl groups; however, the rate of elimination of the second group is considerably lower than that of the first group, and the observed rate constant is related to the elimination of the first group. The first reaction order with respect to the substrates studied at the ratio C_{OH} : $C_S \approx 10-20$ was retained until the end of the reaction.

Figures 2--4 present the dependences of the observed rate constants of hydrolysis of substrates 2--4 on the CDAB concentration in system I in the region of micelle existence and during the formation of the E-phase. For all the substrates, k_{obs} reach a plateau in the Mi-phase and decrease as the degree of ordering in the system increases on going from the Mi-phase to the E-phase. For the quantitative description of the concentration dependences in the Mi-phase, we used the pseudo-phase model of



Fig. 2. Dependences of the observed rate constant (k_{obs}) of alkaline hydrolysis of *O*-*p*-nitrophenyl-*O*, *O*-diethyl phosphate (2) on C_{CTAB} in micellar (1) and hexagonal (2) phases of the CDAB-NaOH-H₂O system (I) at 25 °C. $C_{NaOH} = 0.008$ mol L⁻¹.



Fig. 3. Dependences of the observed rate constant (k_{obs}) of alkaline hydrolysis of *O-p*-nitrophenyl-*O*-ethylethyl phosphonate (3) in micellar and hexagonal phases of the CDAB-NaOH-water system (1) at 25 °C on C_{CDAB} (*1-3*) and C_{NaOH} (4-6) at $C_{NaOH} = 0.08$ (1), 0.008 (2), and 0.001 (3) mol L⁻¹, $C_{CTAB} = 0.002$ (4), 0.005 (5), and 0.6 (6) mol L⁻¹, as well as k_{m} at different C_{NaOH} (7).



Fig. 4. Changes in the observed rate constant of alkaline hydrolysis of O, O-di(*p*-nitrophenyl)methyl phosphonate (4) in micellar and hexagonal media of the CDAB-NaOH-water system (I) at 25 (1) and 17 (2) °C. $C_{NaOH} = 0.001$ mol L⁻¹.

micellar catalysis,^{4,14} assuming that the substrate is first solubilized by a micelle and then undergoes alkaline hydrolysis. Prior to the micelle formation (in the region of surfactant concentrations lower than CMC), the k_{obs} value corresponds to k_{OH} in water, which indicates the absence of catalytically active pre-micellar associates. To determine the parameters of the micelle-catalyzed processes, we used Eqs. (1) and (2):⁴

$$(k_{\rm obs} - k_{\rm OH})/(k_{\rm in} - k_{\rm obs}) = K_{\rm S}(C_{\rm surf} - \rm CMC), \qquad (1)$$

$$\frac{1/(k_{obs} - k_{OH})}{K_{S}(C_{surf} - CMC)} = \frac{1/[(k_{m} - k_{OH}) \times k_{C}(k_{m} - k_{OH})]}{1/(k_{m} - k_{OH})},$$
 (2)

where k_{OH}/s^{-1} is the constant of alkaline hydrolysis in water under experimental conditions, k_m/s^{-1} is the reaction rate constant in the micellar pseudo-phase, K_S/L mol⁻¹ is the binding constant of the substrate and micelle divided into the aggregation number (N), and CMC/mol L⁻¹ is the critical micelle concentration.

The calculated values of the parameters of the micelle-catalyzed processes are presented in Table 2. The



Fig. 5. Dependences of E_a (1) and ΔS^{*} (2) on the CDAB concentration for micelle-catalyzed alkaline hydrolysis of O, O-di(p-nitrophenyl)methyl phosphonate (4).

values of an increase in the alkaline hydrolysis rates in micellar solutions of CDAB estimated as $P_1 = k_m/k_{OH}$ are close in the case of substrates 2 and 3. Despite the fact that substrate 4 is characterized by a higher K_S value $(1.8 \cdot 10^4 \text{ L mol}^{-1})$ than substrates 2 and 3 (see Table 2), its P_1 value is only 18. The high value of the binding constant has been also obtained previously⁴ for O, O-di(p-nitrophenyl)phenyl phosphonate (5) in the reaction of alkaline hydrolysis catalyzed by CTAB micelles. The strong binding of these substrates can probably be explained by specific interactions of the π -electronic system of benzene rings of their *p*-nitrophenoxyl groups with head groups of cationic micelles (" π -cation"-interaction¹⁸). Thus, according to the data obtained, the micellar catalysis by CDAB of the alkaline hydrolysis of the EATP studied is characterized by weakly pronounced substrate specificity. The strong binding of substrate 4 by CDAB micelles does not correspond to a considerable increase in its reactivity.

The changes in the activation parameters for the alkaline hydrolysis reaction of substrate 4 in system I were estimated from the temperature dependence of k_{obs} on the CDAB concentration (Fig. 5). This estimate shows that the observed energy and activation entropy

Table 2. Parameters of micelle-catalyzed reactions in the CDAB-NaOH-water system

Sub- strate	<i>т</i> /°С	C _{N₃OH} /mol L ^{−1}	k _{OH} * · 10 ³ /c ⁻¹	CMC · 10 ⁴ /mol L ⁻¹	$\frac{k_{\rm m}\cdot 10^2}{10^2}$	$\frac{k_{\rm E}^{**} \cdot 10^3}{{\rm s}^{-1}}$	K _S /L mol ⁻¹	Pi	P ₂	P ₃
2	25	0.0080	0.08	5.0±0.8	0.10±0.01	0.15±0.02	910±100	12.5	6.7	1.9
3	25	0.0010	0.15-	4.4±0.8	0.36±0.05	0.21±0.03	1030±240	24	17	1.4
	25	0.0080	1.20	4.3±0.8	1.86±0.20	2.9±0.6	940±190	15.5	6.4	2.4
	25	0.0800	12.0	1.2±0.1	12.9±0.15	20.1±3.0	700±100	11	6.5	1.7
4	25	0.0010	27	7.0±0.8	48.0±1.5	16.6±2.0	18600±2300	18	29	0.6
	17	0.0010	17.8	7.7±0.7	27.0±2.0	5.0±0.70	16200±2000	15	54	0.37

* $k_{\text{OH}} = k_2 \cdot C_{\text{OH}}$, where k_2 is the bimolecular rate constant of alkaline hydrolysis of substrates (L mol⁻¹ s⁻¹): 0.01 (2), 0.015 (3), and 27 (4).¹⁷

** The rate constants of hydrolysis of substrates in the E-phase ($k_{\rm E}/s^{-1}$) were determined at $C_{\rm CDAB} = 0.6$ mol L⁻¹.

 $(E_a \text{ and } \Delta S^{*})$ increase in the Mi-phase as compared to the aqueous medium. A similar increase in E_a has been observed previously⁴ for catalysis of the alkaline hydrolysis of substrate 1 by CTAB micelles. For an aqueous alkaline solution, $E_a = 34 \text{ kJ mol}^{-1}$, $\log A = 7.39$, ¹⁷ $\Delta H = 31.5 \text{ kJ mol}^{-1}$, and $\Delta S^{*} = -117 \text{ J mol}^{-1} \text{ K}^{-1}$. The high negative value of ΔS^{*} for alkaline hydrolysis indicates that the reagents should be ordered to form the transition state. For micellar catalysis, the activation entropy is shifted to positive values, most likely due to the favorable overall change in the entropy factors for the processes determining the reaction rate, the formation of a pentacoordinated intermediate and its decomposition to the starting and final products.

The activation parameters in the hexagonal mesophase at $C_{\rm CDAB} = 0.6 \text{ mol } L^{-1}$ have the following effective values: $E_a = 152 \text{ kJ mol}^{-1}$, $\log A = 25$, $\Delta H =$ 149 kJ mol}⁻¹, and $\Delta S^{*} = -225 \text{ kJ mol}^{-1}$. Their unusually high values are probably caused by the superposition of several factors: the contribution of the reaction itself, the contribution of solubilization of the substrate, and the change in the parameters of the liquid-crystalline structure with change in temperature.³

A smooth decrease in k_{obs} is observed for all substrates during the phase transition $Mi \rightarrow E$, *i.e.*, as the degree of ordering increases and anisotropy appears in the reaction medium (see Fig. 2-4). This can be explained by the transformation of spherical micelles into cylindrical micelles followed by their removal and formation of the E-phase of them similarly to the process in the CTAB- H_2O system ¹⁶ Thus, the kinetics of alkaline hydrolysis of EATP is sensitive to slight fluctuations of ordering appearing in the phase transition $Mi \rightarrow E$, which has been observed previously³. For substrate 4 with two p-nitrophenoxyl groups and a high value of $K_{\rm S}$, a decrease in k_{obs} is observed at lower concentrations of surfactants than that for 2 and 3. This is the result of its more efficient binding with CDAB micelles and more efficient promotion of the growth of cylindrical micelles.19

The effect of the degree of ordering in system I on the reactivity of EATP can be estimated by the values of $P_2 = k_{\rm m}/k_{\rm E}$ and $P_3 = k_{\rm E}/k_{\rm OH}$ (k_E is the reaction rate constant in the E-phase), which characterize the ordering effects in comparison with the micellar and aqueous alkaline solutions, respectively. For substrates 2 and 3, the P_2 values indicate a -7-17-fold decrease in the reaction rate in the E-phase as compared to that in the micellar phase (see Table 2). As shown above, these substrates are adsorbed on the surface of supramolecular associates of spherical micelles; therefore, a decrease in the reactivity of the substrates is caused most likely by a decrease in the diffusion mobility of substrates 2 and 3 rather than by a change in the polarity of the microenvironment of the substrates during the formation of the E-phase.3

The P_3 values indicate an approximately twofold increase in alkaline hydrolysis of substrates 2 and 3 in

the E-phase as compared to the aqueous phase, which can be explained as follows. As known, substrates fall in an aqueous layer between the cylinders in the E-phase and are oriented in a certain way under the action of the anisotropic potential of intermolecular interactions.³ When the orientation of the reagents is favorable, they can approach each other, and their reactivity increases as compared to the isotropic solutions.

The P_2 and P_3 values for substrate 4 indicate the strong inhibition of alkaline hydrolysis as compared to both the micellar solution (by 30-50 times) and aqueous solution (by 2-3 times). Structural ordering of the liquid-crystalline phase can restrict the molecular and conformational mobility of reagents.³ The orientation of substrate 4 is most likely unfavorable for the reaction and, hence, its reactivity becomes substantially lower. It cannot be ruled out that the inhibition can be due to the separation of the substrate and nucleophile, because the first of them is immersed in the hydrocarbon region of cylindrical micelles of the E-phase due to its two hydrophobic p-nitrophenyl groups. For bimolecular processes at the interface or near the interface surface, the influence of the ordered medium is caused by the action of several reagents rather than one on the localization, orientation, and mobility.

Thus, the formation of LLC, which is evidence for the order in system I, results in an increase in the substrate specificity as compared to that in the micellar pseudo-phase. The substrate specificity in micellar catalysis is manifested as the influence of the nature of the substrate on the binding constant and extent of acceleration of the reaction. The effect of the E-phase differs by the character of the influence rather than by the extent: acceleration of alkaline hydrolysis for substrates 2 and 3 and inhibition of the same reaction for substrate 4.

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