Hydrolysis of bis(4-nitrophenyl) ethyl phosphate in micellar solutions of dicationic surfactants

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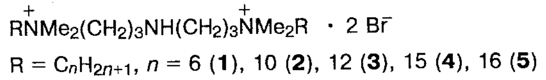
The effect of dicationic surfactants on the hydrolysis of bis(4-nitrophenyl) ethyl phosphate in a borate buffer is studied. The presence of long-chain surfactants results in a significant (up to 50-fold) increase in the observed rate constant (k_{obs}) of the process. The catalytic effect of micelles increases with increasing alkyl chain length due to the strengthening of binding of the reagents by micelles. The presence of two cationic centers in the surfactant molecule enhances the catalytic properties of micelles. The dependence of k_{obs} of hydrolysis of the substrate on the borate buffer concentration is studied. Alkaline hydrolysis is more sensitive to the added surfactant than the reaction involving borate ions.

Key words: micellar catalysis; hydrolysis; dicationic surfactants; buffer.

One of the methods for enhancement of the catalytic effect of the cationic surfactants is the introduction of a second cationic center into the surfactant molecule.[1,2] Dicationic surfactants: $RN^+Me_2(CH_2)_nN^+Me_2R \cdot 2Br^-$ ($R = C_{16}H_{33}$, n = 4, 6) easily form micelles and are 2—5 times stronger catalysts in the reactions of hydroxyl ions with chloro- and fluoro-2,4-dinitrobenzene and hydroxyl and fluoride ions with 4-nitrophenyl diphenyl phosphate than cetyltrimethylammonium bromide (CTAB).[1]

To clarify the features of the catalytic effect of the dicationic surfactant on hydrolysis of an organophosphorus substrate and to find the dependence of the surfactant catalytic effect on its structure and on the presence of a buffer we studied the hydrolysis of bis(4-nitrophenyl) ethyl phosphate (BNEP) ($3 \cdot 10^{-5}$ mol L^{-1}) in aqueous micellar solutions of surfactants **1—5** in borate buffer (borax concentration, C_b = 0.05 mol L^{-1}, pH 9.07, 40 °C).



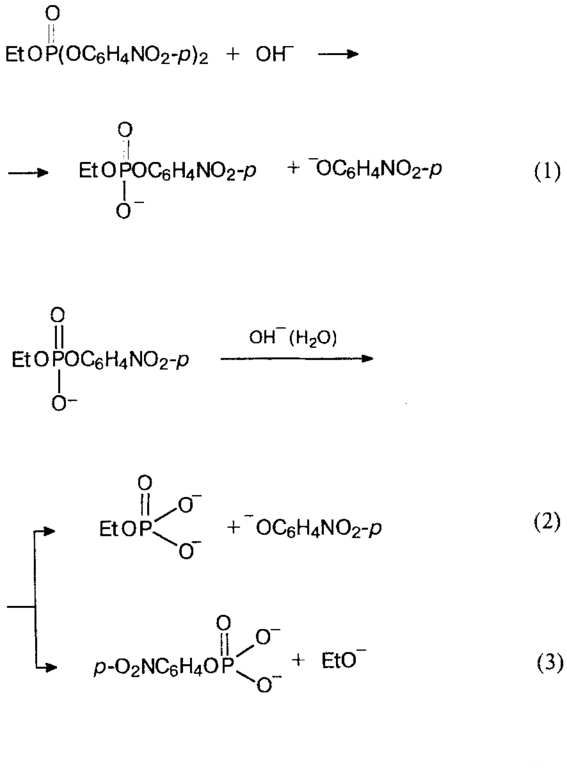
$$R\overset{+}{N}Me_2(CH_2)_3NH(CH_2)_3\overset{+}{N}Me_2R \cdot 2\,Br^-$$

$R = C_nH_{2n+1}$, n = 6 (**1**), 10 (**2**), 12 (**3**), 15 (**4**), 16 (**5**)

For comparison we used the dicationic surfactant: $C_{12}H_{25}N^+Me_2(CH_2)_3N^+H_2C_{12}H_{25} \cdot 2Br^-$ (**6**) and CTAB.

Hydrolysis of BNEP in the absence of surfactants follows the Scheme 1.

Scheme 1



In the first stage of the process, alkaline hydrolysis of BNEP occurs with elimination of 4-nitrophenolate ion and with the formation of 4-nitrophenyl ethyl phosphate anion (reaction (1)). In the second stage, in parallel to reaction (2), dealkylation (reaction (3)) can occur with the formation of 4-nitrophenyl phosphate dianion. However, the observed rate constant (k_{obs}) of the second stage is two—three orders lower than that of the first stage.[3] Therefore, the discussion to follow will concern the first stage of the process.

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Experimental

Dicationic surfactants **1—5** were synthesized by interaction of tetramethyldipropylenetriamine with the corresponding alkyl halide in a molar ratio 1 : 2. After preliminary purification, the reagents were combined and stirred for 2—3 days at *ca.* 20 °C. The degree of reaction was determined by potentiometric titration, which allowed us to calculate the amount of unchanged amine. After completion of the reaction, the products were recrystallized twice from absolute ethanol and were characterized by elemental analysis data. Melting points of the surfactants **2—5** were: 45 °C, 57 °C, 75 °C, and 90 °C, respectively. Surfactant **1** is a viscous product. Surfactant **6** (m.p. 185 °C) was synthesized by interaction of *N,N,N',N'*-tetramethyltrimethylenediamine with dodecyl bromide in a molar ratio 1 : 2 by the method described above. CTAB (Chemapol) was reprecipitated from ethanol with ether. BNEP (m.p. 140 °C), 4-nitrophenyl ethyl chloromethylphosphonate (NECP) (b.p. 165—170 °C/0.01 Torr, n_D^{24} 1.5430), and 4-nitrophenyl bis(chloromethyl)phosphinate (NCP) (m.p. 87 °C) were synthesized as described earlier.[4—6] The reaction kinetics was monitored spectrophotometrically (Specord UV-VIS) by following the appearance of the absorbance band at 400 nm due to the 4-nitrophenolate ion. ^{31}P NMR spectra were recorded on a Bruker MSL-400 (161.6 MHz) at 35 °C. Concentrations of NECP and NCP were 0.0185 and 0.00625 mol L^{-1}, respectively.

Results and Discussion

The observed rate constant hydrolysis of BNEP (k_{obs}) is not changed in the presence of surfactant **1**, which does not form micelles in the solution, while with dicationic surfactants **2—5** with longer chains k_{obs} increases significantly (up to 50 times) (Fig. 1).

The substantial increase in k_{obs} of the reaction can be a result of micellization of surfactants **2—5**. The shape of the dependence of k_{obs} *vs.* surfactant concentration (C_S) with a drastic increase at the initial part of the curve, followed by passing through a maximum, confirms this assumption.

To determine the parameters of the micellar-catalyzed reaction, namely, the constants of substrate (K_A) and nucleophile (K_B) binding with the micelle and the rate constants for the reaction in a micellar phase (k_m) we used the equation[7]

$$k_{obs} = \frac{(k_m/V)K_A K_B C + k_0}{(1 + K_A C)(1 + K_B C)} ,$$

where C is the overall surfactant concentration after subtraction of the critical micellar concentration, V is the surfactant molar volume, k_0 is the reaction rate constant in a solution. The thus calculated constants of reagent binding and the reaction rate constants in micellar phase are given in Table 1. The lengthening of the hydrocarbon radical is accompanied by a decrease in the ratio k_m/V and by an increase in K_A and K_B (see Table 1). The increase in micellar catalytic effect, $(k_{obs}/k_0)_{max}$, of the surfactants under study can be explained by strengthening the reagent binding by micelles.

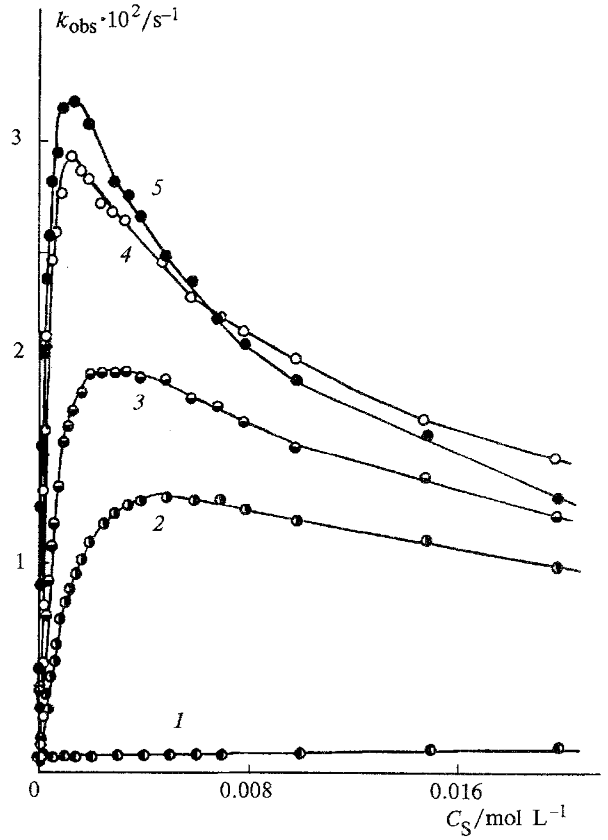

Fig. 1. The dependence of the observed rate constants for hydrolysis of BNEP (k_{obs}) *vs.* concentration of surfactants **1** (*1*), **2** (*2*), **3** (*3*), **4** (*4*), and **5** (*5*) (C_b = 0.05 mol L^{-1}, pH 9.07, 40 °C).

The presence of the NH group in the molecules of surfactants **2—5** can lead to the manifestation of functional micellar catalysis. However, the independence of k_{obs} on the concentration of surfactant **1**, which does not form micelles (see Fig. 1), and the weaker catalytic effect of surfactant **3** in comparison with surfactant **6**, which does not comprise the NH group (30- and 40-fold increase in k_{obs}, respectively, see Table 1 and Fig. 2),

Table 1. Parameters of micelle-catalyzed reaction of hydrolysis of BNEP in aqueous surfactant solutions (C_b = 0.05 mol L^{-1}, pH 9.07, 40 °C)

Surfactant	$(k_m/V)\cdot10^4$ /s^{-1}	K_A /mol^{-1} L	K_B /mol^{-1} L	$(k_{obs}/k_0)_{max}$*
2	4.1	630	52	20 (0.0045)
3	3.8	810	89	30 (0.0025)
4	3.3	2260	130	46 (0.0015)
5	3.1	1720	180	50 (0.0015)
CTAB	4.4	1370	70	33 (0.003)

* k_{obs} = 6.4·10^{-4} s^{-1}; in parenthesis the values of $C_{S(max)}$/mol L^{-1} are given.

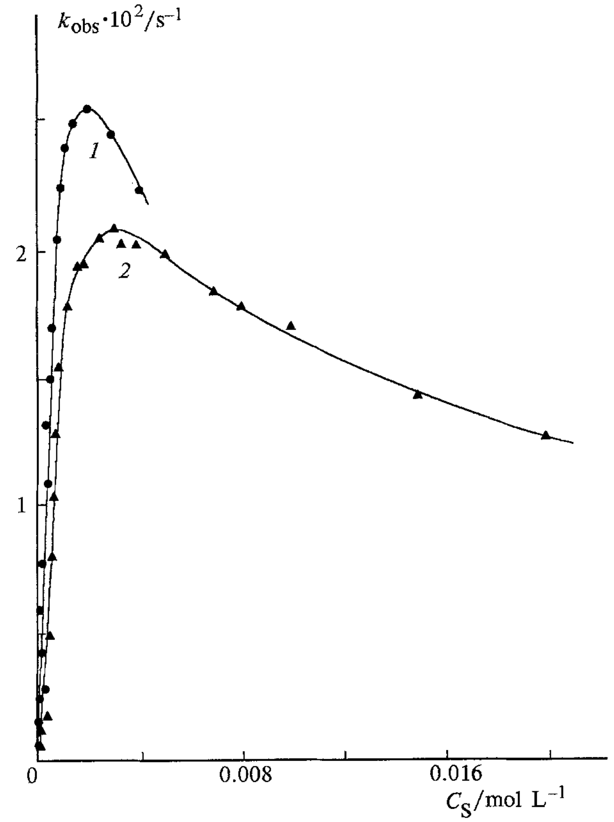

Fig. 2. The dependence of the observed rate constants for hydrolysis of BNEP (k_{obs}) *vs.* concentration of surfactant **6** (*1*) and CTAB (*2*) (conditions as in Fig. 1).

attest to the absence on contribution of aminolysis to the overall reaction. The products of aminolysis were also not found in the processes with other phosphorus-containing substrates. In the course of decomposition of NECP in 0.01 *M* solution of NaOH and decomposition of NCP in aqueous micellar 0.01 *M* solution of surfactant **4,** the signals were only observed for the product of alkaline hydrolysis of the substrate in ^{31}P NMR spectra (δ 14.2 and 27.5, respectively).[8]

The presence of two cationic centers in the surfactant molecule slightly enhances the micellar catalytic effect. The catalytic activity of surfactant **5** is somewhat higher than that of CTAB. This is a result of stronger binding of the reagents by micelles of dicationic surfactant (see Table 1).

It is worth noting that the reaction carried out in buffer solutions has some specific features, because the determined rate constants account for the course of the overall process, which comprises, in addition to alkaline hydrolysis, the reaction with the buffer component of the solution. To clarify the role of buffer in the reaction under study we determined the dependences of k_{obs} of hydrolysis of BNEP on the borax concentration in solution.

The results given in Tables 2 and 3 indicate that k_{obs} tends to a definite limit value at high borax concentrations in solutions of surfactants **2—6** and CTAB. This is, probably, a result of partial neutralization of the positive micelle charge when they bind the buffer anions. Extrapolation of k_{obs} to the zero buffer concentration gives the rate constant of hydrolysis of BNEP in a micellar phase ($k_{m(1)}$). The insignificant contribution of spontaneous hydrolysis in the value of k_{obs} at the pH of the borax buffer solutions[9] allows us to refer $k_{m(1)}$ to alkaline hydrolysis of the substrate. For the aqueous phase, the value of $k_{aq(1)}$ is calculated from literature data[10] and is equal to $1.8 \cdot 10^{-5}$ s^{-1} at 40 °C.

From the tangent of the slope of the initial parts of the dependences of k_{obs} on the buffer concentration (Fig. 3, see Tables 2 and 3) the bimolecular rate constants for the reaction with borate ions in aqueous

Table 2. The observed rate constants for hydrolysis of BNEP in buffer micellar solutions of surfactants **2**, **4—6**, and CTAB at 40 °C

C_b /mol L^{-1}	$k_{obs} \cdot 10^2$ /s^{-1}								
	2		**4**		**5**		**6,**	CTAB	
	0.0004 *M*	0.0045 *M*	0.0004 *M*	0.0015 *M*	0.0004 *M*	0.0015 *M*	0.00042 *M*	0.0004 *M*	0.003 *M*
0*	0.13	0.31	1.0	1.1	1.2	1.2	0.7	—	0.96
0.005	0.18	0.45	1.2	1.4	1.4	1.5	—	—	1.2
0.01	0.24	0.63	1.5	1.8	1.6	2.0	0.89	0.14	1.4
0.015	0.27	0.74	1.6	2.0	1.9	2.1	—	—	1.6
0.02	0.32	0.89	1.7	2.2	2.1	2.3	1.1	0.34	1.8
0.03	0.33	1.0	—	—	—	—	1.2	0.54	1.9
0.04	0.36	1.1	1.8	2.6	2.1	2.6	1.4	0.70	2.1
0.05	—	—	—	—	—	—	1.5	0.79	2.1
0.06	0.39	1.3	1.9	2.7	2.1	2.8	1.5	0.83	2.1
0.08	0.41	1.4	1.8	2.8	2.2	2.9	1.6	0.94	2.1
0.10	0.43	1.4	1.9	2.7	2.2	2.9	1.7	1.0	2.1

* The values of k_{obs} are obtained by extrapolation to C_b = 0.

Table 3. The observed rate constants for hydrolysis of BNEP in buffer micellar solutions of surfactant **3**

C_b /mol L^{-1}	$k_{obs} \cdot 10^2$ /s^{-1}								
	C_S = 0.0004 mol L^{-1}			C_S = 0.0025 mol L^{-1}			C_S = 0.01 mol L^{-1}		
	40 °C	55 °C	65 °C	25 °C	40 °C	55 °C	25 °C	40 °C	55 °C
0*	0.43	1.3	2.2	0.17	0.52	2.3	0.14	0.35	0.92
0.005	0.51	1.5	2.4	0.23	0.79	2.9	0.18	0.52	1.7
0.01	0.59	1.6	2.6	0.31	1.0	3.4	0.22	0.71	2.5
0.015	0.65	1.7	2.8	0.33	1.3	4.0	0.26	0.88	3.0
0.02	0.74	1.8	3.0	0.44	1.4	4.2	0.30	1.1	3.4
0.03	0.76	1.9	3.1	0.49	1.7	4.8	0.35	1.3	4.1
0.04	0.81	2.0	3.2	0.54	1.9	5.2	0.39	1.4	4.5
0.05	—	2.1	3.3	0.56	1.9	5.4	0.41	1.5	5.1
0.06	0.87	2.1	3.3	0.59	2.0	5.7	0.45	1.6	5.2
0.08	0.92	2.3	3.4	0.59	2.1	5.8	0.47	1.8	5.5
0.10	0.96	2.4	—	0.59	2.1	6.0	0.51	1.8	6.0

* The values of k_{obs} are obtained by extrapolation to C_b = 0.

($k^b_{aq(2)}$) and micellar ($k^b_{m(2)}$) phases were calculated (Table 4). The bimolecular rate constant for alkaline hydrolysis in the micellar phase ($k^{OH}_{m(2)}$) was determined by dividing the $k_{m(1)}$ by concentration of the hydroxyl ions.

A comparison of ratios $k^{OH}_{m(2)}/k^{OH}_{aq(2)}$ and $k^b_{m(2)}/k^b_{aq(2)}$ (see Table 4) indicates that alkaline hydrolysis of BNEP is more sensitive to the effect of the surfactant than the reaction involving borate ions. The catalytic effect of micelles of the dicationic surfactants in the former case achieves two or more orders of magnitude. However, high concentrations of the buffer components and a rather strong enhancement by surfactant micelles of the bimolecular rate constants for the reaction with participation of borate ions by micelles (see Table 4) allow us to draw conclusions that in micellar solutions, in addition to the attack of hydroxyl ions at the substrate, the hydrolysis catalyzed by the buffer contributes significantly. The fraction of alkaline hydrolysis in the overall process can vary with a change in alkalinity of the medium. This results in the shape of the dependence of k_{obs} of hydrolysis of BNEP in micellar solutions on pH (Fig. 4). The weak dependence of k_{obs} on pH at the region close to neutral is followed by a drastic increase in the rate constants at pH > 8.5. This fact can be the result of the increasing contribution of

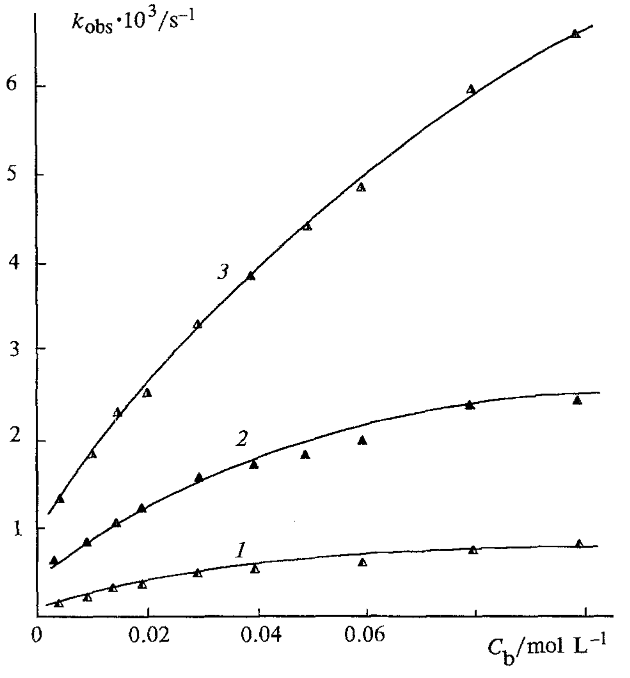

Fig. 3. The dependence of the observed rate constants for hydrolysis of BNEP (k_{obs}) *vs.* borax concentration at 40 °C (*1*), 55 °C (*2*), and 65 °C (*3*).

Table 4. Bimolecular rate constants for hydrolysis of BNEP with the participation of hydroxyl and borate ions in water and in micellar solution in borate buffer (pH 9.07, 40 °C)

Surfactant	C_S /mol L^{-1}	$k^b_{m(2)}$ /mol^{-1} L s^{-1}	$\frac{k^b_{m(2)}}{k^b_{aq(2)}}$ *	$\frac{k^{OH}_{m(2)}}{k^{OH}_{aq(2)}}$ **
2	0.0004	0.095	6.4	74
	0.0045	0.29	19.5	170
3	0.0004	0.16	10.0	240
	0.0025	0.51	34.0	295
	0.01	0.35	23.5	200
4	0.0004	0.50	34.0	565
	0.0015	0.64	43.0	625
5	0.0004	0.53	36.0	650
	0.0015	0.67	45.0	680
6	0.0004	0.17	11.0	400
CTAB	0.003	0.45	30.0	540

* $k^b_{aq(2)}$ = 0.015 mol^{-1} L s^{-1}.
** $k^{OH}_{aq(2)}$ = 1.5 mol^{-1} L s^{-1} (*cf.* Ref. 10).

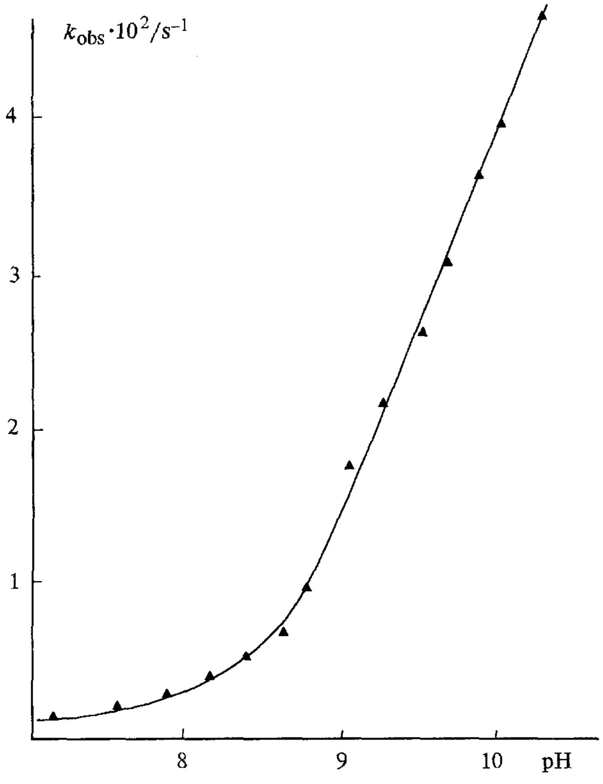

Fig. 4. The dependence of the observed rate constant for hydrolysis of BNEP (k_{obs}) in micellar solutions of surfactant **3** *vs*. pH (C_b = 0.05 mol L^{-1}, C_S = 0.0025 mol L^{-1}, 40 °C).

alkaline hydrolysis of the substrate, sensitive to the micellar effect.

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