The salt effect in the alkaline hydrolysis of O-ethyl O-(p-nitrophenyl) chloromethylphosphonate catalyzed by cetylpyridinium bromide*

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The alkaline hydrolysis of O-ethyl O-(p-nitrophenyl) chloromethylphosphonate catalyzed by the micelles of cetylpyridinium bromide is inhibited on addition of KCl, KBr, or sodium salicylate (NaSal). This is caused by both a decrease in the nucleophile concentration in micelles owing to a reduction in the surface potential and a change in the micellar structure and properties.

Key words: kinetics, rate constant, micellar catalysis, hydrolysis, counterion, surface potential, electrolytes.

The alkaline hydrolysis of esters of phosphorus acids is catalyzed by micelles of cationic surfactants and inhibited by micelles of anionic surfactants.^{1,2} The main cause of micellar catalysis of bimolecular reactions is the concentration or, in the case of inhibition, separation of reagents in the micellar pseudophase.³ Depending on the hydrophobicity, a substrate is completely or partially solubilized by micelles, and the concentration of the hydroxide ion in the micellar pseudophase is determined by the surface potential. Additives that change the potential influence micellar catalysis. Electrolytes,⁴ alcohols,⁵ and co-surfactants⁶ are among these additives.

The problem of the influence of an electrolyte on the catalytic effect of ionic micelles is attracting much attention among researchers. In micellar systems, the nature and the concentration of electrolytes substantially affect the rate of chemical reactions. Thus, one can observe the growth of micelles, an increase in the degree of binding of counterions, and, when the concentration of electrolytes reaches a certain value, $C_{\rm cr}$, the sphere—cylinder micellar transformation.⁷ Earlier, we have studied the influence of the concentration of an ionic reagent,⁸ buffer solutions,⁹ and inorganic and organic salts¹⁰ on the efficiency of micellar catalysis and found critical salt concentrations corresponding to the transformation of spherical micelles into cylindrical ones.

The goal of the present work is to study the influence of electrolytic additives on the potential of the micellar surface in micellar catalysis. For this purpose, the effect of cetylpyridinium bromide (CPB) on the rate of alkaline hydrolysis of O-ethyl O-(p-nitrophenyl) chloromethylphosphonate (1) (Scheme 1) was studied in a wide range of the KCl, KBr, and NaSal concentrations, which covers the area of both spherical and cylindrical micelles.



Experimental

Compound 1 was obtained according to the known procedure.¹¹ Chemically pure CPB twice reprecipitated from ethanol with ether was used. The kinetics of reaction was monitored by spectrophotometry on a Specord UV-Vis instrument from changes in the optical density of solutions at a wavelength of 400 nm (formation of the *p*-nitrophenoxide anion). The initial concentration of the substrate was $5 \cdot 10^{-5}$ mol L⁻¹. Alkaline hydrolysis was carried out in 0.005 N NaOH solutions. Salt concentrations (C_s) varied in the range 0–1 mol L⁻¹. The observed rate constants were determined from the dependence ln ($D_{\infty} - D$) = $-k_{obs}t$ + const, where D and D_{∞} are the optical density of the solution at a moment t and upon completion of the reaction, respectively. The k_{obs} values were calculated using the least-squares method.

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The influence of KCl, KBr, NaBr, and NaSal on the catalytic effect of CPB in the alkaline hydrolysis of compound 1 was studied. Twenty-fold acceleration of the reaction is observed in the presence of CPB. Electrolytes were selected with consideration of the nature of counterions. Inorganic ions of different hydrophilicity, Br⁻ and Cl⁻, and the organic anion, Sal⁻, whose behavior in micellar solutions strongly differs from other hydrophobic counterions,¹² were used in the experiment.

In the series of Cl^- , Br^- , and Sal^- counterions, only the salicylate anion was found to be active as a nucleophile with regard to the substrate, although its activity was several orders of magnitude lower than that of the hydroxide ion. That is why the contribution of the reaction of Sal⁻ with compound 1 to the observed rate constant was further neglected.

The primary salt effect in the basic hydrolysis of 1 in the absence of a surfactant was observed only for the salicylate anion: when the concentration of NaSal increases from 0.05 to 0.5 mol L^{-1} , the observed rate constant decreases by a factor of 5 (from 0.02 to 0.004 s⁻¹). In the presence of KCl or KBr, the rate of the noncatalyzed basic hydrolysis of 1 remains unchanged in a wide range of salt concentrations (0-2.0 mol L^{-1}).

Introduction of electrolytes into the micellar solution reduces the catalytic effect of a surfactant up to its complete suppression in the region of high salt concentrations (~1 mol L^{-1}). Experimental data are plotted in semilogarithmic coordinates in Fig. 1. For each counterion, the k_{obs} —log C_s dependence has two linear segments with different slopes. The equations of the straight lines and the C_{cr} values at the break point are given in Table 1. In accordance with the literature data,¹⁰ the C_{cr} values were interpreted by us as the concentrations of counterions corresponding to the sphere—cylinder transformation of CPB micelles. The cation does not affect the rate constant, and the inhibitive action of an electrolyte depends on the nature and the concentration of the counterion.

The activity row of the counterions studied in the alkaline hydrolysis of 1 is $Cl^- < Br^- < Sal^-$ and coincides with lyotropic series obtained earlier.¹³ It is agreed that this row reflects an increase in the ionic affinity to the micellar surface. However, as noted earlier, ¹⁴ hydrophilicity seems to be the primary factor, and, as a result, less hydrated ions (Br⁻ and Sal⁻) effectively bind to the micellar surface, thus neutralizing the micellar charge, at concentrations lower than those of the chloride ions.

It should be noted that the C_{cr} values for chloride and bromide ions, found for CPB,¹⁴ were virtually the same as similar values for cetyltrimethylammonium bromide (CTAB) obtained by us earlier.¹⁰ Taking into account the closeness of the values of critical micel-



Fig. 1. The dependence of the observed rate constant (k_{obs}) of the basic hydrolysis of 1 in CPB micellar solutions on the logarithmic concentration of (1) KCl, (2) KBr, and (3) NaSal (25 °C, 0.005 N NaOH, 0.001 mol L⁻¹ of CPB); inset: the dependence of the rate constant of the alkaline hydrolysis of 1 in the micellar phase (k_m) on the logarithmic concentration of (1) KCl and (2) KBr (under the same conditions).

Table 1. The $C_{\rm cr}$ values and the equations of straight lines, describing the dependence $k_{\rm obs} - \log C_{\rm s}$ in the concentration range (A) below and (B) above $C_{\rm cr}$

Counterion	$C_{ct}/mol \ L^{-1}$	Equation				
CI-	0.1	A: $k_{obs} = -0.039 \log C_s - 0.0099$				
		n = 8, r = 0.99				
CI-	0.1	B: $k_{obs} = -0.019 \log C_s + 0.0184$				
		n = 4, r = 0.999				
Br-	0.02	A: $k_{\rm obs} = -0.045 \log C_{\rm s} - 0.044$				
		n = 6, r = 0.98				
Br ⁻	0.02	B: $k_{obs} = -0.010 \log C_s + 0.016$				
		n = 5, r = 0.999				
Sal	0.0015	A: $k_{obs} = -0.051 \log C_s - 0.11$				
		n = 7, r = 0.99				
Sal	0.0015	B: $k_{obs} = -0.0019 \log C_s + 0.029$				
		n = 5, r = 0.99				

lization concentration (CMC) for CTAB and CPB, such a coincidence may be considered regular and a conclusion can be drawn that the phase and structural transformations in micellar solutions depend, above all, on the size of the hydrophobic fragment of a surfactant, and the nature of the head group is of secondary importance.

With the aim of carrying out a systematic investigation, we studied a series of the k_{obs} - C_{surf} dependences at different concentrations of KBr and KCl (data for KBr as an example are presented in Fig. 2). The results obtained were analyzed within the framework of the



Fig. 2. The dependence of the observed rate constant (k_{obs}) of the alkaline hydrolysis of 1 on the CPB concentration; C_{KBr} /mol $L^{-1} = 0$ (*I*), 0.002 (*I*), 0.003 (*I*), 0.005 (*I*), 0.01 (*I*), 0.02 (*G*), 0.05 (*I*), 0.1 (*B*), 0.2 (*P*), 0.3 (*IO*) (25 °C).

 Table 2. Micellar parameters of the basic hydrolysis of 1 in aqueous CPB micellar solutions in the presence of KCl and KBr

C _s	K _b /mol ^{−1} L		$k_{\rm m}/{\rm s}^{-1}$		$k_{\rm m}/k_{\rm w}^*$	
/mol L ⁻¹	KCI	KBr	KCI	KBr	KCI	КВг
0.002		350		0.36		18
0.003	460	380	0.30	0.26	15	13
0.005	470	410	0.27	0.22	13.5	11
0.01	470	550	0.23	0.13	11.5	6.5
0.02	570	890	0.16	0.054	8.0	2.7
0.05	950	1022	0.078	0.052	3.9	2.6
0.1	1100	1262	0.054	0.047	2.7	2.4
0.2	1300	1312	0.048	0.036	2.4	1.8
0.3	1650		0.045	0.028**	2.2	1.4

Note. The conditions of hydrolysis: 0.005 N NaOH,

0.001 mol L⁻¹ of CPB, 25 °C.

* $k_{\rm w} = 0.02 \, {\rm s}^{-1}$.

** The k_{obs} value corresponding to the point where the dependence k_{obs} — C_{surf} flattens out.

pseudophase model of micellar catalysis according to the equation¹⁵

$$k_{\rm obs} = \frac{k_{\rm w} + k_{\rm ni} K_{\rm b} C_{\rm surf}}{1 + K_{\rm b} C_{\rm surf}},$$

where k_w and k_m (s⁻¹) are the rate constants in the aqueous and the micellar phase, respectively; K_b (mol⁻¹ L) is the effective constant of binding of the substrate; and C_{surf} is the surfactant concentration minus CMC. The results of mathematical processing are summarized in Table 2. As the salt concentrations increases, the constant of binding of the substrate in-

creases as well. This is due to the salting out action of inorganic ions. It is known that a change in the shape of micelles can also change the area of localization and the constants of binding of a solubilizate.¹⁶ The calculated $k_{\rm m}$ values were analyzed in the semilogarithmic coordinates $k_{\rm m}$ -log $C_{\rm s}$ (see Fig. 1, inset).

The data given in Table 2 show that in the presence of KBr, the efficiency of micellar catalysis where spherical micelles exist is reduced by a factor of ~7, whereas for the region of cylindrical micelles it is only halved. The $C_{\rm cr}$ values are equal to 0.022 and 0.092 mol L⁻¹ for the bromide and the chloride ions, respectively, which is in quite good agreement with the data presented in Table 1. A higher angular coefficient in the case of KBr (equation of the straight line as far as the $C_{\rm cr}$ point: $k_{\rm m} = -0.29 \log C_{\rm s} - 0.45$) compared to KCl ($k_{\rm m} =$ $-0.18 \log C_{\rm s} - 0.15$) may reflect a higher degree of binding of the bromide ions than that of the chloride ions.

To clear up the mechanism of action of electrolytes on the micellar catalytic effect, we calculated the change in the micellar surface potential (Ψ) as the concentrations of KCl and KBr increase. Earlier,⁶ it has been shown that the surface potential and CMC are linked by a Nernst type relationship:

$$d|\Psi|/d\log CMC = 59.16 \text{ mV.}$$
(1)

Using our own data on measurements of the surface tension of CPB micellar solutions in the presence of salts as well as the semiempirical expression (see Ref. 17), we calculated the CMC values at the different concentrations of KBr and KCl and then, using Eq. (1), the Ψ values (Tables 3).

Analyzing these data, one can suppose that the inhibitive action does not depend on the nature of the counterion, which determines only the $C_{\rm cr}$ value. For all electrolytes studied, $k_{\rm obs}$ decreased to a value equal to the rate constant in water. The micellar surface potential

Table 3. Quantitative relationships between the electrolyte concentration, CMC, and the CPB micellar surface potential

C _s /mol L ⁻¹	CMS/mmol L ⁻¹		Ψ/mV	
	KCI	KBr	KCI	KBr
0	0.80*	0.80*	140**	140**
0.01	0.79	0.75	139	137
0.02	0.64	0.46	134	124
0.03	0.57	0.34	131	116
0.04	0.52	0.28	129	111
0.05	0.49	0.24	128	107
0.07	0.44	0.19	125	101
0.1	0.41	0.15	123	95
0.2	0.32	0.09	117	82
0.3	0.27	0.069	112	75
0.5	0.24	0.048	110	66

* According to the literature data.¹⁸

** According to the literature data.19

150

100

-2.0



-1.0

 $\log C$

Fig. 3. The dependence of the CPB micellar surface potential (Ψ) on the logarithmic concentration of KBr: I, according to the data from Table 3; 2, according to the literature data;¹⁸ 3, on the logarithmic concentration of KCl (see Table 3); the dotted lines indicate the critical values of the salt concentration and the surface potential.

-1.5

is nonzero when the catalytic effect is completely suppressed $(k_{obs} = k_w)$. The inhibitive action of electrolytes is due to a simultaneous decrease in the micellar surface potential and replacement of reactive counterions in the Stern layer by nonreactive ones. When the hydroxide ions are completely displaced from the micellar surface by nonreactive anions, the catalytic effect is completely suppressed, although the potential of the Stern layer is nonzero.

While the $k_{obs} - \log C_s$ plot includes two linear segments, the dependence $\Psi - \log C_s$ is linear over the entire range of electrolyte concentrations (Fig. 3) and is expressed by the equations

 $\Psi = -41.6 \log C_{\rm s} + 53.2$ n = 11; r = 0.999 for KBr $\Psi = -17.52 \log C_{\rm s} + 104$ n = 11; r = 0.999 for KCl

A similar linear dependence was obtained by plotting the data from the earlier published paper,²⁰ where the potential values of CTAB micelles were determined in the study of the acid-base equilibrium of indicators in the presence of KBr. The slope values of the corresponding straight lines, obtained by us and the authors of the paper under discussion,²⁰ virtually coincide (the angular coefficient value for different indicators varies in the range 43-49).

The presence of a break in the dependence $k_{obs} - \log C_s$ may mean that the suppression of the concentration factor occurs differently in spherical and cylindrical micelles as the surface potential decreases, or attest to the existence of additional mechanisms of inhibitive action that are not related to the concentration effect. It is conceivable that in cylindrical micelles, the influence of the micellar microenvironment becomes decisive. This influence does not depend directly on the surface potential and only slightly change upon addition of salts. Indeed, there is information in the literature on changes in the degree of binding of counterions,²¹ in the localization area of solubilizates, and the solubilizability of micelles¹⁶ in passing from sphere to cylinder. In addition, the fact that surfactant molecules in cylindrical micelles are packed more closely than in spherical ones can cause a change in the substrate microenvironment, its orientation and mobility and, consequently, its reactivity.

Of special interest is the fact that the C_{cr} values for Br⁻ and Cl⁻ correspond to the same surface potential value (-124 and -123 mV, respectively) (see Fig. 3). Apparently, this value is characteristic of CPB micelles, i.e., one can discuss not only the critical concentration of electrolytes but also the critical potential value that controls the structural transformations of CPB micelles.

Thus, the main factor determining the inhibitive action of electrolytes on the catalytic effect of ionic surfactants is the micellar surface potential. There is a critical potential value independent of the nature of the counterion at which the mechanism of the micellar inhibitive action changes. This change is likely due to the sphere-cylinder transformation of micellar aggregates.

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