Mechanism of the inhibiting action of electrolytes on the micellar effect in alkaline hydrolysis of *p*-nitrophenyl ethyl chloromethylphosphonate

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The influence of KCl, KBr and sodium salicylate (NaSal) on the micellar effect of cetylpyridinium bromide in the alkaline hydrolysis of *p*-nitrophenyl ethyl chloromethylphosphonate has been studied and the effects of electrolytes on the rate constant and surface potential compared; based on the data obtained, it can be concluded that the reaction inhibition is determined both by a change in the structure and properties of the micellar aggregates and by a decrease in the concentration of the nucleophile in the micelles due to a decrease in the surface potential.

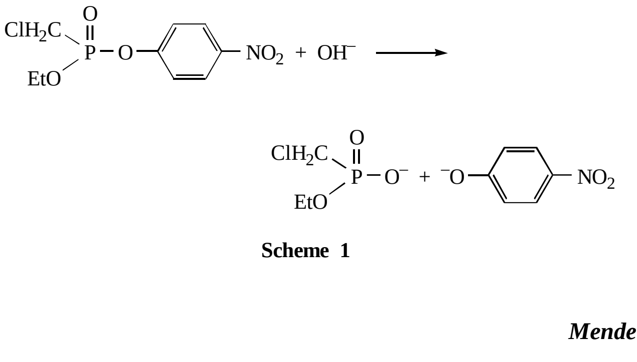
Alkaline hydrolysis reactions of organophosphorus compounds are accelerated by micelles of cationic surfactants and retarded by micelles of anionic surfactants.[1] The concentration (or separation in the case of inhibition) of reagents in the micellar pseudo-phase is the main reason for micellar catalysis.[1] A substrate is completely or partially (depending on the structure) solubilized by micelles, and the concentration of the hydroxide ion in the micellar pseudo-phase is determined by the surface potential. Additives which change the potential, such as electrolytes,[2] alcohols[3] and other co-surfactants,[4] exert an effect on micellar catalysis.

In addition, the structure and properties of a micellar system change under the action of electrolytes, which is due to a decrease in the surface potential of the micelles. As the electrolyte concentration increases to a certain value C_{cr}, the micellar transition sphere–cylinder is observed.[5] Although the pseudo-phase model of micellar catalysis does not take into account the geometry of the aggregates, it can be assumed that the micellar transition sphere–cylinder also exerts an effect on the reaction rates in micelles.

In this work, we address the problems involved in investigating the factors which determine the nature of the effect of electrolytes on micellar catalysis. The potential of the micellar surface, which affects both the concentration of nucleophile and the structure of micelles, is considered to be the main factor. We therefore studied the effect of cetylpyridinium bromide (CPB) micelles on the rate of alkaline hydrolysis of *p*-nitrophenyl ethyl chloromethylphosphonate **1** (see Scheme 1) over a wide concentration range of salts KCl, KBr and NaSal. This concentration range covers the regions of both spherical and cylindrical micelles.

Compound **1** was obtained according to the literature procedure.[6] A sample of CPB was precipitated twice from ethanol using diethyl ether. The reaction kinetics were studied by spectrophotometry on a Specord UV-Vis instrument by monitoring the change in the optical density of solutions at 400 nm (formation of the *p*-nitrophenolate anion). The observed rate constants were calculated using the least-squares method.

A *ca.* 20-fold acceleration of the reaction studied was observed in CPB micelles in the absence of electrolytes. Inorganic anions with different hydrophilicities (Br^- and Cl^-) and an organic anion Sal^-, whose behaviour in micellar solutions differs strongly from that of other hydrophobic counterions,[7] were used in the experiment.



Scheme 1

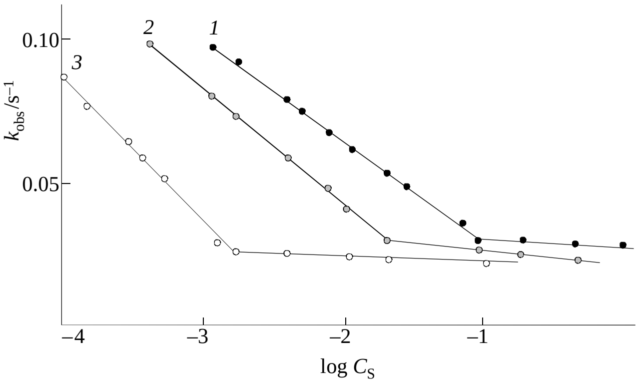


Figure 1 The dependence of the observed rate constant for the hydrolysis of **1** in CPB micelles on the logarithm of the concentration of KCl (*1*), KBr (*2*) and NaSal (*3*) (25 °C, 0.001 M CPB, 0.005 M NaOH).

In the series of Cl^-, Br^- and Sal^- counterions studied, only the salicylate anion exhibits nucleophilic activity with respect to the substrate, although this is, however, several orders of magnitude lower than for the hydroxide ion. Therefore, we subsequently neglect the contribution of the reaction of Sal^- with compound **1** to the observed rate constant. The primary salt effect in the reaction of alkaline hydrolysis of **1** in the absence of surfactants was observed only for the salicylate ion: the observed rate constant decreases *ca.* 5-fold (from 0.02 to 0.004 s^{-1}) as the concentration of NaSal increases from 0.05 to 0.5 M. In the presence of KCl and KBr, the rate of alkaline hydrolysis of **1** in the absence of micelles remains unchanged over a wide range of salt concentrations (0–2 M).

The addition of electrolytes to the micellar solution decreases the catalytic effect of micelles to the extent of complete suppression of micellar catalysis in the region of high salt concentration (~1 M). The experimental data were analysed in semilogarithmic coordinates similarly to ref. 8 (see Figure 1). As can be seen from the plot, the k_{obs} *vs.* log C_S dependence for each counterion contains two linear regions with different

Table 1 The values of K_S and k_m for the reaction of basic hydrolysis of **1** in micellar solutions of CPB in the presence of KBr (25 °C, 0.001 M CPB, 0.005 M NaOH).

C_{KBr}/M	K_b/M^{-1}	k_m/s^{-1}	k_m/k_{aq}^a
0.002	350	0.36	18
0.003	380	0.26	13
0.005	410	0.22	11
0.01	550	0.13	6.5
0.02	890	0.054	2.7
0.05	1022	0.052	2.6
0.1	1262	0.047	2.4
0.2	1312	0.036	1.8
0.3	—	0.028^b	1.4

[a] $k_{aq} = 0.02\ s^{-1}$. [b] The values of k_m, corresponding to the plateau of k_{obs} *vs.* C_{surf} plot.

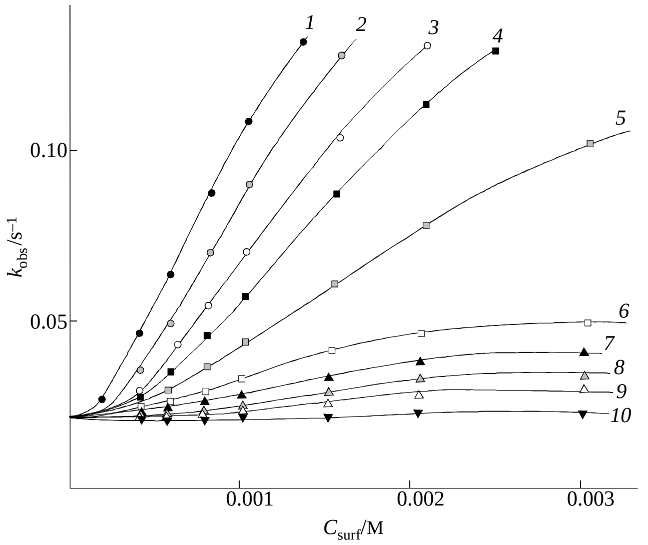


Figure 2 The dependence of the observed rate constant for the hydrolysis of **1** on CPB concentration: (*1*) 0, (*2*) 0.002, (*3*) 0.003, (*4*) 0.005, (*5*) 0.01, (*6*) 0.02, (*7*) 0.05, (*8*) 0.1, (*9*) 0.2, (*10*) 0.3 M KBr.

slopes. According to ref. 8, the values of salt concentrations at the inflection points of C_{cr} were interpreted as the concentrations of counterions corresponding to the sphere–cylinder transition of the CPB micelles. For Cl^-, Br^- and Sal^-, C_{cr} are equal to 0.1, 0.02 and 0.0015 M, respectively. The replacement of the cation (K^+ by Na^+) has no effect on the rate constant. Thus, the activity series for the counterions studied as a function of the extent of their action on the rate of alkaline hydrolysis of **1** is the following: $Cl^- < Br^- < Sal^-$, and this coincides with the lyotropic series obtained previously.[9] It is noteworthy that the C_{cr} values for chloride and bromide ions found in this work for CPB coincided with the analogous values for cetyltrimethylammonium bromide micelles obtained previously.[8]

Despite the fact that ion-molecular reactions of nucleophilic substitution in the presence of electrolytes has been studied previously, the mechanism of this phenomenon remains unclear. The question of the effect of the shape of the aggregates on the reactivity of compounds has not yet been answered. To compare the mechanism of the inhibition effect of electrolytes in spherical and cylindrical micelles, we studied a series of k_{obs}–log C_{surf} dependences at different concentrations of KBr covering the regions of both spherical and cylindrical micelles (see Figure 2). The data obtained were analysed in terms of the pseudo-phase model of micellar catalysis by equation (1):[10]

$$k_{obs} = \frac{k_{aq} + k_m K_b C_{surf}}{1 + K_b C_{surf}} \quad (1)$$

where k_{aq} and k_m/s^{-1} are the rate constants in aqueous and micellar phases, respectively; K_b/M^{-1} is the reduced binding constant of the substrate; and C_{surf} is the concentration of the surfactant minus CMC. The results of mathematical processing are presented in Table 1. As the concentration of the salts increases, the binding constant of the substrate increases due to the salting-out effect of inorganic ions with respect to the hydrophobic compound. It is also known that the site of localization and binding constant of the solubilizate can change depending on the shape of the micellar particles.[11]

The calculated values of k_m were analysed in the semilogarithmic coordinates (see Figure 3). The character of the dependence obtained is similar to that of the plot presented in Figure 1. The values of the Br^- concentration in the inflection point are $C_{cr} = 0.02$ M, which coincides with C_{cr} in Figure 1. It is noteworthy that the slopes of the linear dependence before the inflection point (equation of line before the point C_{cr}: $k_m = -0.29 \log C_S - 0.45$) and after it (equation of line after the point C_{cr}: $k_m = -0.039 \log C_S - 0.008$) differ strongly. This indicates that the inhibition of the micellar effect by the

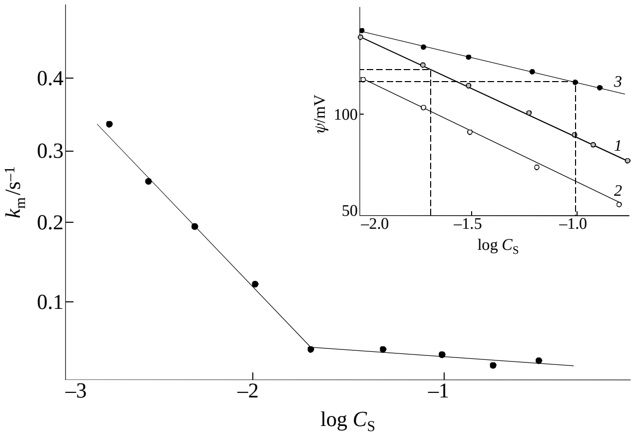


Figure 3 The dependence of the rate constant in the micellar phase on the logarithm of the concentration of KBr (insertion: the dependence of the surface potential on the logarithm of the concentration of KBr: (*1*) calculated from equation (2), (*2*) data from ref. 13, (*3*) on the logarithm of KCl concentration).

electrolytes in these regions occurs to different extents and, probably, *via* different mechanisms. The data on the change in the catalysis value k_m/k_{aq} presented in Table 1 agree with this assumption. In the region of existence of spherical micelles, the efficiency of micellar catalysis in the presence of KBr decreases by ~7 times but only twice in the region of cylindrical micelles.

To elucidate the mechanism of action of electrolytes on the micellar effect, we calculated the change in the potential of the micellar surface (ψ) as the salt concentration increases. It is shown[4] that a Nernst correlation exists between the surface potential and CMC, equation (2).

$$d|\psi|/d\log \text{CMC} = 59.16 \text{ mV} \quad (2)$$

Using our data from measuring the surface tension of micellar solutions of CPB in the presence of salts, and the semi-empirical expression presented in ref. 12, we calculated CMC values at different concentrations of KBr and KCl and then ψ values from equation (2) (see Figure 3). Analysing the data presented in Figures 1 and 3, we may draw the following conclusions concerning the mechanism of inhibiting action of electrolytes in micellar catalysis.

The value of the inhibition action is independent of the nature of the counterion. For all electrolytes studied, we observed a decrease in k_{obs} to the value equal to the rate constant in water. The surface potential of micelles upon complete suppression of the micellar effect ($k_{obs} = k_{aq}$) is not zero. This is related to the fact that the inhibiting action of electrolytes is caused by the simultaneous decrease in the surface potential of the micelles and displacement of reactive counterions from the Stern layer by unreactive counterions. When hydroxide ions are completely displaced from the micellar surface by unreactive anions, the micellar effect is completely suppressed, although the potential in the Stern layer differs from zero.

The k_m–log C_S and k_{obs}–log C_S plots consist of two linear regions, whereas the ψ–log C_S dependence is linear over the whole range of electrolyte concentrations (Figure 3) and can be expressed by the equation $\psi = -41.6 \log C_S + 53.2$ ($n = 11$, $r = 0.999$). A similar linear dependence was obtained when the data from ref. 13 were plotted.

It is of special interest that the C_{cr} values for Br^- and Cl^- correspond to the same values of the surface potential (124 and 123 mV, respectively) (see Figure 3). This indicates that there is a critical value of the surface potential at which the mechanism of electrolyte action changes sharply. This ψ_{cr} value is most likely the characteristic one for CPB micelles and results in micellar transitions.

The presence of a break in the k_{obs}–log C_s dependence implies that in spherical and cylindrical micelles the factor of concentration with a decrease in the surface potential is suppressed to different extents or this indicates the existence of additional mechanisms of inhibition action, which are not associated with the concentration effect. Perhaps the effect of the micellar microenvironment, which does not depend directly on the surface potential, becomes determining in cylindrical micelles and changes insignificantly when salts are added. In fact, published data exist on the change in the degree of counterion binding,[11] the site of localization of reagents and the solubilizing capability of micelles[14] for the sphere–cylinder transition. In addition, a denser packing of surfactant molecules in cylindrical micelles as compared to spherical micelles can lead to a change in the microenvironment of the substrate, its orientation and mobility and, as a consequence, its reactivity. An alternative explanation for the existence of the break is the assumption that two main inhibiting factors act before the C_{cr} point: a decrease in the surface potential and displacement of reactive counterions, while after C_{cr}, only the first factor acts, which results in weakening of the inhibition effect.

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Received: Moscow, 17th December 1997
Cambridge, 27th February 1998; Com. 8/00197J