# Kinetics of alkaline hydrolysis of ethyl *p*-nitrophenyl ethylphosphonate in the reverse micellar system: sodium dodecyl sulfate—hexanol—water

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The kinetics of alkaline hydrolysis of ethyl *p*-nitrophenyl ethylphosphonate in the reverse micellar system sodium dodecyl sulfate—hexanol—water was studied. At high pH and low water content, the process occurs at the surface layer and can satisfactorily be described by the pseudo-phase model equation.

**Key words:** reverse micelles, pseudo-phase, catalysis, alkaline hydrolysis, ethers of tetracoordinate phosphorus acids.

Reverse micelles are biomimetic structures with a mechanism of catalytic action similar in many respects to that governing the operation of biomembranes.<sup>1</sup> New experimental data in this area are important to verify the reliability of the pseudo-phase model<sup>2</sup> and compare the factors determining the efficiency of catalysis in reverse micellar media and normal micelles. Unlike the reverse micellar sodium bis(2-ethylhexyl) sulfosuccinate (AOT)\*-alkane-water system.<sup>2-4</sup> little is known concerning the ternary sodium dodecyl sulfate (SDS)-hexanol-water system.<sup>5</sup>

This work is aimed at studying the features and mechanism of the catalytic action of the reverse micellar system SDS-HeOH-H<sub>2</sub>O in the alkaline hydrolysis of ethyl *p*-nitrophenyl ethylphosphonate (1) (Scheme 1).

#### Scheme 1



The composition of the solution was varied within wide limits during experiments to change, according to

the data in Ref. 5, the sizes, structure, and properties of micellar particles involved in the chemical reaction.

### Experimental

SDS (Sigma) was used in the work. Reverse micellar systems were prepared by mixing of three components<sup>6</sup> followed by shaking until a transparent solution was formed. The ratios of components of the micellar system  $W = [H_2O]/[SDS]$  and Z =[hexanol]/[SDS] were varied within the intervals W = 9.8 -37.0 and Z = 5-22, which corresponded, according to the phase diagram,<sup>6</sup> to the region of reverse micelles and microemulsions. The reaction kinetics was studied by spectrophotometry with a Specord UV-Vis instrument by measuring the optical density of the band at 400 nm corresponding to the concentration of the p-nitrophenolate anion. The initial concentration of the substrate was  $5 \cdot 10^{-5}$  mol L<sup>-1</sup>. Observed rate constants ( $k_{obs}$ ) were derived from the equation  $\ln(D_x - D) =$  $-k_{obs}t$  + const, where D and  $D_x$  are the optical densities of the solution at the moment t and at the end of the reaction. respectively. The  $k_{obs}$  values were calculated by the weighted least-squares method.

## **Results and Discussion**

According to the pseudo-phase model,<sup>7.8</sup> three microareas can be discerned in the reverse micelles: an aqueous phase formed by solubilized water, a surface layer consisting of surfactant (Surf) molecules with head groups directed toward aqueous phase, and a bulk oil pseudo-phase. It can be assumed that the alkaline hydrolysis of 1 occurs at the surface layer where the

<sup>\*</sup> AOT is Aerosol OT or sodium bis(2-ethylhexyl) sulfosuccinate.

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hydrophilic and lipophilic properties are so balanced that a hydrophobic substrate can contact a highly hydrophilic nucleophile. The observed rate constants for the distribution of the substrate between the oil phase and surface layer and for the distribution of the nucleophile between the aqueous phase and surface layer are given  $by^2$ 

$$k_{\rm obs} = \frac{k_{\rm c} K_{\rm S} K_{\rm OH} [\rm OH]_{\rm t}}{(K_{\rm S} + Z)(K_{\rm OH} + W)[\rm Surf]} , \qquad (1)$$

where  $k_i/s^{-1}$  is the rate constant for the reaction at the surface layer\* expressed as the [OH]/[Surf] molar ratio. It is related to the pseudo-first-order rate constant  $k_i'/s^{-1}$  and second-order rate constant  $k_{2,i}/L \mod^{-1} s^{-1}$  by the following equations:

$$k_{i}' = k_{i} \frac{[OH]}{[Surf]}, \qquad k_{2,i} = k_{i} V,$$
 (2)

where V is the molar volume of the surfactant,  $[OH]_{l}/mol L^{-1}$  is the total concentration of OH<sup>-</sup>,  $K_S$  is the constant of distribution of the substrate between the oil phase and surfactant:

$$K_{\rm S} = \frac{[\rm S]_i[hexanol]}{[\rm S]_o[Surf]} \,,$$

 $K_{OH}$  is the constant of distribution of the hydroxide ion between the aqueous phase and surfactant:

$$K_{\rm OH} = \frac{[\rm OH]_i[\rm H_2O]}{[\rm OH]_w[\rm Surf]} \, .$$

Molar concentrations of the substrate (S), hexanol, and surfactant are indicated in brackets; and the indices i, o, and w concern the surface layer and oil and aqueous pseudo-phases, respectively.

The kinetic data for the hydrolysis under study obtained at different molar ratios W and Z are presented in Figs. 1 and 2. It can be seen that the addition of SDS results in a catalytic effect for almost all systems, regardless of the composition. The  $k_{obs}/k_w$  ratio varies within the 0.5-35.7 interval, depending on the experimental conditions. This result sharply differs from the inhibition of ion-molecular reactions in normal ionic micelles, which have the same charge as the ionic reactant.<sup>9</sup> In these systems, catalysis is induced by the effect of concentrating the reagents by the influence of the micellar microenvironment. In the case of reverse systems, a combination of micellar and interphase catalysis is the most probable reason for the catalytic effect.<sup>2</sup> The amphiphilic character of the surfactant makes it possible to simultaneously solubilize compounds with different natures in the surface layer, *i.e.*, to perform a transfer between the phases.

It follows from Fig. 1 that  $k_{obs}$  increases with an increase in [NaOH]. A linear dependence of  $k_{obs}$  on the nucleophile concentration is often observed in the re-

 $k_{\rm obs} \cdot 10^3 / {\rm s}^{-1}$ 24 20 16 12 8 4 0 0.06 0.01 0.02 0.03 0.04 0.05 0.07 [NaOH]/mol L<sup>-1</sup>

Fig. 1. Observed rate constant ( $k_{obs}$ ) of alkaline hydrolysis of the substrate as a function of [NaOH] (I, H<sub>2</sub>O) at different [SDS]/mol L<sup>-1</sup> = 0.749 (2), 0.505 (3), 0.381 (4), 0.255 (5), and 0.154 (6); 25 °C, W = 15.1.

verse systems. As shown in Fig. 1, several linear regions whose slope decreases with an increase in [NaOH] can be distinguished for each concentration of SDS. The values of the slope of the linear region, in the first approximation, are comparable with the second-order observed rate constant of alkaline hydrolysis of 1 in this range of [NaOH]. Correspondingly, the decrease in the slope can be explained by a decrease in the reactivity of



**Fig. 2.** Observed rate constant  $(k_{obs})$  of alkaline hydrolysis of the substrate as a function of {SDS}. W = 9.8 (1), 15.1 (2), and 22.8 (3); 25 °C, 0.01 *M* NaOH. The dependences of the observed rate constant and acceleration of this reaction on the water content in the system are shown in the inset.

<sup>\*</sup> Corresponding to the nucleophile concentration.

the system as [NaOH] increases. This decrease can be due to the migration of the reaction zone because of a decrease in the potential of the head groups of the surfactant and effects of salting-salting out that appear on varying [NaOH]. Analysis of the kinetic data performed by us in terms of the pseudo-phase model of micellar catalysis confirmed these assumptions.

Acceleration of the reaction defined as  $k_{obs}/k_w$  depends on the concentrations of the alkali, surfactant, and water in the system. The highest increase in the reaction rate was observed at 0.003 *M* and 0.005 *M* NaOH followed by weakening of the catalytic effects in the region of high pH. An increase in the water content also results in a decrease in  $k_{obs}$  (see Fig. 2, inset).

The plot of  $k_{obs}$  against [SDS] presented in Fig. 2 can indicate that the Coulomb interaction of hydroxide ions with the negatively charged micellar surface makes a specific contribution to the micellar effect, inhibiting the process at higher surfactant concentrations. However, we cannot rule out that, in this case, the weakening of the catalytic effect is not related to the surface charge. When W is decreased from 22 to 9.8,<sup>5</sup> the surface potential of the particles increases from -60 to -90 mV, although the catalytic effect is enhanced (see Fig. 2). In our opinion, the dilution of the reactants with an increase in the surfactant concentration (as in the case of standard micelles<sup>9</sup>) can be an alternative explanation.

By plotting  $1/k_{obs}[SDS]$  against Z values, Eq. (1) can be linearized.<sup>2</sup> Analysis of the  $k_{obs}$  values as a function of  $\{SDS\}$  (Fig. 3) shows that the kinetic data are well described by the linear regression equation at high alkali concentrations ( $\{NaOH\} \ge 0.01 \text{ mol } L^{-1}$ ) and low contents of water. At lower pH and a higher water content, the dependence deviates from linearity.

 $1/k_{obs}[SDS]$ 

Fig. 3. Kinetic data (see Fig. 2) linearized according to Eq. (1). [NaOH]/mol  $L^{-1} = 0.005$  (1), 0.01 (2), 0.03 (3), and 0.05 (4).

This behavior of the system confirms the assumption that the reaction zone migrates with changing [NaOH].

The fact that the pseudo-phase model is valid in the region of high pH indicates that the reaction occurs, under these conditions, in the surface layer, despite the Coulomb repulsion of the hydroxide ions from the negatively charged head groups of the surfactant. Higher concentrations of the alkali provide more favorable conditions for the redistribution of the hydroxide ions between the aqueous phase and surface layer due to a high gradient of concentrations and a partial compensation of the charge of the head groups by the sodium cations. The contributions of reactions in other microregions becomes substantial at low [NaOH], making Eq. (1) invalid.

We performed a conductometric study of the SDS micelles to obtain a more detailed information about the behavior of the micellar system and verify the assumption about changes in location of the reactants under the experimental conditions. We have previously studied the conductometric behavior and micellar effect of the reverse AOT-decane-water system in alkaline hydrolysis of ethers of phosphorus acids.<sup>3</sup> The character of the micellar effect of AOT differs from that of SDS micelles. In particular, in the AOT-based system, the catalytic effect and linearity of the  $k_{obs}$ -[NaOH] plot are observed over the entire [NaOH] interval. It was shown that Eq. (1) was fulfilled even under conditions where the reaction occurred above the percolation threshold. It is of interest to compare the conductometric data for the two micellar systems. The temperature dependences of the electroconductivity of the AOT- and SDS-based micellar solutions at close concentrations of the surfactant and alkali are presented in Fig. 4. Figure 4 indicates marked differences in the electroconductivities

 $\sigma/\mu S \ cm^{-1}$ 



Fig. 4. Temperature dependences of the electroconductivity ( $\sigma$ ) of reverse micellar AOT-based ([NaOH]/mol L<sup>-1</sup> = 0 (1), 0.01 (2), and 0.03 (3)) and SDS-based systems ([NaOH]/mol L<sup>-1</sup> = 0 (1') and 0.03 (2')).

of the systems. The behavior of the AOT-based system is characteristic of the phenomenon of electric percolation in reverse micellar solutions and microemulsions.<sup>10,11</sup> In these systems, most of the electric charges created on dissociation of some anionic head groups of AOT are concentrated in the core of the reverse micelles. The electroconductivity of the organic phase (decane) is negligible, and the total electroconductivity of the microemulsion at low temperatures is determined by the thermal motion of particles in the organic medium and transfer of the charge carriers that takes place when micelles collide and exchange their ion atmospheres. The temperature increase results in the formation of clusters of reverse micelles that form extended channels and surfaces for charge transfer, giving rise to a sharp (4-5)orders of magnitude) increase in the electroconductivity.

The behavior of the SDS—hexanol—water system is basically different (see Fig. 4). Even at low temperatures, the electroconductivity of these solutions is much higher than that of the AOT-based systems. The conductometric data do not confirm cluster formation among the reverse SDS micelles. The main feature of the system under study is the noticeable mutual solubility of water and hexanol. The electroconductivity of hexanol saturated with a concentrated aqueous solution of NaOH can reach  $10^{-3}$  Ohm<sup>-1</sup> cm<sup>-1</sup> at 25 °C, which is several orders of magnitude higher than that of pure hexanol. Evidently, in these systems, a substantial portion of charges (Na<sup>+</sup> ions, hydroxide and hexanolate ions) is concentrated in the organic phase.

Thus, the conductometric studies that showed the presence of charge carriers in the microemulsion bulk suggest the oil phase as the reaction medium. We have previously<sup>12</sup> studied reactivity of substrate 1 toward alcoholate ions, including hexanolate ions, in alcohol media. Study of the alkaline hydrolysis of 1 in alcohol media (Fig. 5) showed that the bimolecular rate constants of the reaction of substrate 1 with the hydroxide ion in water and alcohol media were by an order of magnitude higher than the corresponding rate constants of the alcoholate ions. However, at low [NaOH], the reaction of the substrate with the hexanolate ions in the oil phase can be competitive. This can be favored by both a low concentration of OH<sup>--</sup> and by charge of the head groups that when uncompensated by Na<sup>+</sup> cations prevent the penetration of the hydroxide ions into the surface layer.

The values the of the distribution constants ( $K_S = 104$ ,  $K_{OH} = 0.88$ ) and the magnitude of reaction constants in the surface layer ( $k_i = 8.1 \text{ s}^{-1}$ ) confirm the assumption about the mechanism of the catalytic effect. Although the high hydrophilicity of the hydroxide ions and Coulomb repulsion of these ions from the core surface result in low  $K_{OH}$  values, the concentrating factor makes a certain contribution to the micellar effect due to the high  $K_S$  value and small volume of the micellar phase as compared to that of the oil phase. The high value of  $k_i$  indicates that the micellar microenvi-



**Fig. 5.** Observed rate constant  $(k_{obs})$  of alkaline hydrolysis of the substrate as a function of [NaOH] in alkaline media: *I*, water; *2*, *n*-butanol; and *3*. *n*-propanol.

ronment increases the reactivity of the reactants. Accepting V = 0.37 L mol<sup>-1</sup> in Eq. (2).<sup>2.13</sup> we obtain  $k_{2,i} = 2.9$  L mol<sup>-1</sup>s<sup>-1</sup>, which is 19-fold higher than the corresponding rate constant in water. This effect is opposite to the inhibition effect of the micellar medium on the reactivity in nucleophilic substitution in normal micelles<sup>9</sup> and can be due to either a favorable orientation of the reactants in the surface layer or a change in the polarity and solvation properties of the microenvironment.

Polarity of the surface layer is much lower than that of water and decreases with removal from the water core.<sup>7</sup> Lower alcohols (propan-1-ol, butan-1-ol), which are capable of specific solvation of a nucleophile, but are less polar than water, were chosen as model media to study the effect of the medium polarity on the rate of alkaline hydrolysis. The data indicating the increase in  $k_{obs}$  as the solvent polarity decreases are presented in Fig. 5. As the dielectric constant decreases in the series H<sub>2</sub>O, propan-1-ol, and butan-1-ol ( $\varepsilon = 78.3$ , 20.45, and 17.5, respectively),14 the second-order rate constant increases  $(k_{2,OH} = 0.155, 0.46, \text{ and } 0.8 \text{ L mol}^{-1} \text{ s}^{-1},$ respectively). These data are consistent with the Hughes-Ingold concept, which postulates that if in the transition state the charge is delocalized to a higher extent than in the initial state, a decrease in the solvent polarity favors the reaction.<sup>15</sup> As [NaOH] increases (see Fig. 5), the curve of the  $k_{obs}$ -[NaOH] function exhibits a break, which can be explained by a decrease in the activity of hydroxide ions related to an increase in the ion strength of the solution and an insufficiently high dissociating power of the medium.

Thus, on going from water to the reverse micellar SDS—hexanol— $H_2O$  system,  $k_{obs}$  of the alkaline hydrolysis of ethyl *p*-nitrophenyl ethylphosphonate increases by almost 40 times. The catalytic effect decreases with increase in the concentrations of the surfactant, alkali and water in the system. The reaction occurs in the surface layer, and a change in [NaOH] and water content changes the location of the reactants. The main contribution to the micellar effect in the system under study comes from the variation in the microenvironment of the reactants when the reaction is transferred to the surface layer. The factor of concentrating the reactants is not related to the micellar charge and plays a secondary role.

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