Alkaline hydrolysis of ethyl *p*-nitrophenyl chloromethylphosphonate in the reverse micellar AOT—decane—water system

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The influence of cluster formation of micelles on the rate of alkaline hydrolysis of ethyl *p*-nitrophenyl chloromethylphosphonate in the reverse micellar sodium bis(2-ethylhexyl) sulfosuccinate (AOT)—decane—water system was found. The applicability of the pseudophase model of micellar catalysis below and above the percolation threshold was shown.

Key words: reverse micelles, microemulsion, surface layer, cluster formation, percolation, kinetics, alkaline hydrolysis.

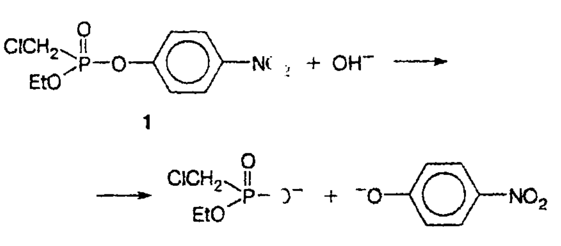
Reverse micellar systems and "water-in-oil" (W/O) microemulsions attract great attention as models for the mechanism of biocatalysts.[1,2] Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) is the most typical anionic surfactant capable of forming reverse micellar aggregates without additives of co-surfactants. The structure and physicochemical properties of reverse micellar systems depend on the temperature, water content, and ionic strength.[3] Although the pseudo-phase model of micellar catalysis[4] does not take into account the geometry of particles, we can assume that a change in these parameters and the corresponding modification of aggregates affect the chemical reactions in micelles. We have previously shown[5,6] that the structural sphere—cylinder transition of normal micelles under the action of electrolytes results in a change in the reactivity.

In this work, we studied the kinetics of alkaline hydrolysis of ethyl *p*-nitrophenyl chloromethylphosphonate (**1**) in the reverse micellar AOT—decane—water system at different parameters Z = [Decane]/[AOT] (mol.) and W = [H_2O]/[AOT] (mol.) (Scheme 1). Quantitative studies of the catalytic effect of water-containing reverse micelles are scarce,[4,7,8] and the interrelation of the reactivity and structural parameters of reverse aggregates were not studied.

Experimental

Compound **1** was obtained by a known procedure.[9] AOT (Sigma) was used without purification. Reverse micellar systems were prepared by the previously described procedure.[10] The reaction kinetics was studied by spectrophotometry on a Specord UV—VIS instrument, following any changes in the optical density of solutions at 400 nm (the formation of *p*-nitrophenolate anion). The initial concentration of the substrate was 5 · 10^{-5} mol L^{-1}. The observed rate constants were calculated using the weighted least-squares method. The electroconductivity was measured on an OK-102/1 conductometer (Radelkis, Hungary) at frequencies of 80 Hz and 3 kHz. The accuracy of temperature maintenance was ±0.2 °C. The temperature of the percolation transition (T_p) was determined as the point of alternation of the sign of the first derivative of the electroconductivity with respect to temperature.

Scheme 1



Results and Discussion

Based on the kinetic data obtained, we checked the adequacy of the pseudo-phase model of micellar catalysis under the experimental conditions. The physicochemical properties of the aggregates, which are nanoreactors, were studied by conductometry in parallel experiments under the same conditions.

Since the electroconductivity of the oil phase of W/O microemulsions is several orders of magnitude lower than that of the dispersed phase, the ions dissolved in the water core of the micelles and the charged groups

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of molecules of ionogenic surfactants can be sources of free charges in the dispersed phase. As a whole, the statistical ensemble of all micelles is electroneutral; however, individual micelles can acquire a charge due to thermal fluctuations. The electroconductivity of these systems is determined by the mobility of micelles that carry a non-compensated electric charge. Diffusion of micelles in a viscous medium obeys the Stokes law, and the conductivity (σ) is determined by the equation[11]

$$\sigma = \frac{\varepsilon_0 \varepsilon k_B T}{2\pi\eta} \frac{\phi_m}{r^3}, \qquad (1)$$

where $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F m^{-1} is the dielectric constant, ε is the dielectric constant of the organic medium, k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the organic medium, ϕ_m is the volume fraction of micelles in the system, and r is the radius of micellar particles.

The Brownian motion of micelles and their collisions result in the transfer of charge carriers in the microemulsion bulk, which can be detected by conductometry. A temperature increase results in an increase in the mobility of the micelles in the oil medium; they approach each other and form clusters. At a specific temperature, the micelles are randomly arranged in long chains, which creates channels for the transfer of charges between the electrodes and results in a sharp increase in the conductivity. The phenomenon of the existence of conducting regions in an insulating material is named electric percolation.[12] The structure of the micellar system remains unchanged and represents individual microdrops of water surrounded by a surfactant monolayer. The formation of clusters from micelles has a dynamic character: they are formed and decomposed under the action of thermal motion but exist permanently above the percolation threshold. The clusterization of reverse micelles results, first, in an increase in the rate of exchange of their contents[13,14] and, second, in decrease of the surface area and the contact time of the micellar surface with the oil phase.

The experimental data on the electroconductivity of the reverse micellar AOT—decane—water system at different concentrations of the dispersed phase and alkali are presented in Figs. 1—3. The system under study is characterized by the fulfillment of correlation (1) at a

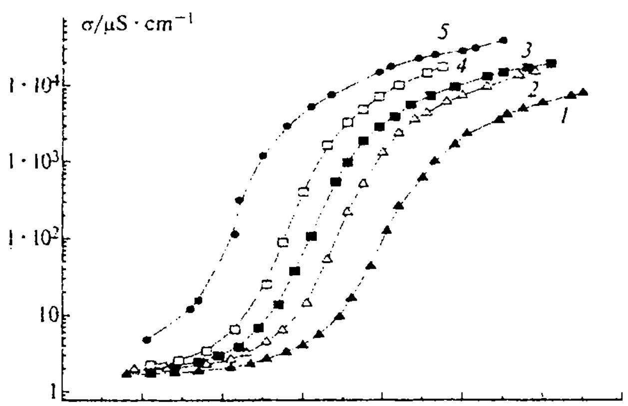

Fig. 1. Temperature dependence of the electroconductivity at different AOT concentrations: 0.26 (*1*), 0.3 (*2*), 0.353 (*3*), 0.42 (*4*), and 0.49 mol L^{-1} (*5*); W = 15.1, [NaOH] = 0.01 mol L^{-1}.

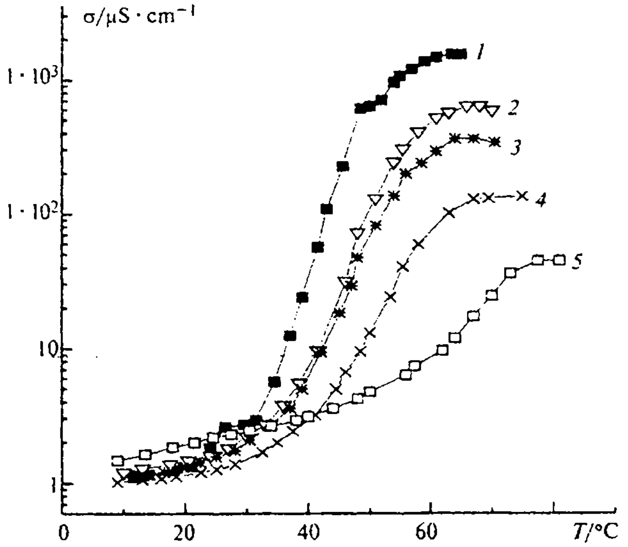

Fig. 2. Temperature dependence of the electroconductivity of the reverse micellar AOT—decane—water system in the absence of alkali (*1*) and at different concentrations of NaOH: 0.025 (*2*), 0.03 (*3*), 0.04 (*4*), and 0.05 mol L^{-1} (*5*).

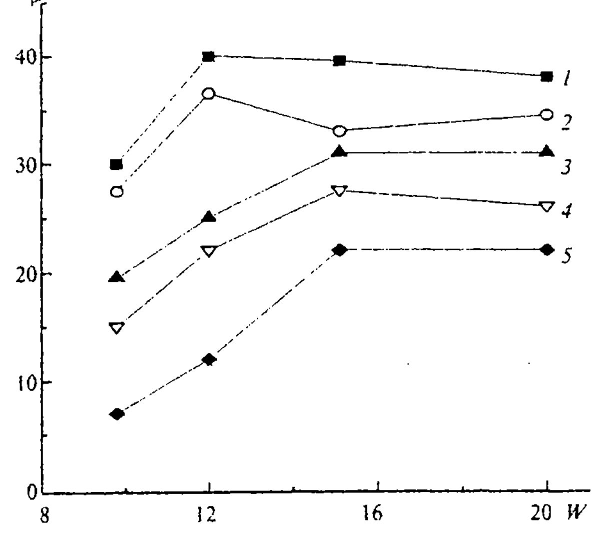

Fig. 3. Temperature percolation threshold of the reverse micellar AOT—decane—water system as a function of W in the presence of 0.01 M NaOH at different concentrations of AOT: 0.259 (*1*), 0.3 (*2*), 0.353 (*3*), 0.42 (*4*), and 0.49 mol L^{-1} (*5*).

temperature lower than the percolation threshold. This proves the fact that the introduction of an alkali into the system does not disturb its micellar structure. At the same time, it is known[15] that the percolation temperature is determined by many factors, such as the size of the reverse micelles, their concentration, the presence of additional ions, and others.

As the concentration of micelles increases (see Fig. 1), T_p decreases. For example, the increase in the AOT concentration from 0.26 to 0.49 mol L^{-1} results in a decrease in T_p by almost 20 °C, which corresponds to the published data[15] and is explained by an increase in the frequency of collisions of the drops. In addition, the charge of the head groups decreases due to screening by counterions, resulting in an increase in the curvature of the water core and impeding the formation of channels for the exchange of the content of adjacent drops.[16] When the alkali concentration increases (see Fig. 2), the temperature of the percolation threshold substantially increases, and the efficiency of the charge transfer decreases, which is manifested as a decrease in the conductivity. When the water content in the system decreases, one could expect a decrease in T_p. However, at $W < 15$ an opposite tendency is observed (see Fig. 3). The anomalous change in the electroconductivity and viscosity of reverse micellar AOT-based systems within the interval $W = 9-12$ has been observed by several authors.[17,18]

Based on the measurements of the electroconductivity, we chose conditions for the kinetic measurements below and above the percolation threshold (Figs. 4—7). The dependence of $\log k_{obs}$ on $1/T$ at different W values ([AOT] = 0.42 mol L^{-1}, [NaOH] = 0.01 mol L^{-1}) is presented in Fig. 4. Unlike aqueous solutions, in reverse micellar systems a change in the slope of the Arrhenius dependence is observed at a specific temperature (T_{cr}). For the systems with $W = 26.6$, a decrease in the slope is observed, *i.e.*, a decrease in the activation energy (E_a), and in the cases of $W = 15.1$ and $W = 20.0$, transition to a region of negative E_a is observed. The T_{cr} and T_p values (see Figs. 1—4 and Table 1) at the same W virtually coincide. The change in the slope of the Arrhenius dependence is related to the cluster formation of reverse micelles. However, the effect of dynamic processes on the kinetics is characteristic of very fast processes, whose rates are controlled by the diffusion of the reagents.[19] It is most likely that for the alkaline hydrolysis of compound **1**, which is not attributed to these reactions, an indirect influence of the percolation phenomenon on the reactivity takes place. It can be assumed that some parameters of the micellar microenvironment of the reagents (micropolarity, surface potential, and others) that affect the reaction kinetics change due to the cluster formation and exchange of the content of the aqueous phase between the micelles.

Table 1. T_p, T_{cr}, and parameters of the Arrhenius equation (E_a and $\log A$) of alkaline hydrolysis of **1** in the reverse micellar AOT—decane—water system* below the percolation threshold

W	T_p	T_{cr}	E_a/kJ mol^{-1}	$\log A$
	°C			
15.1	27.5	27.5	37.5	4.75
20.0	26	26	39.5	4.86
26.3	25	25.5	44.2**	5.6

* In water in the absence of AOT, E_a = 30.6 kJ mol^{-1}, $\log A$ = 3.95.

** Above the percolation threshold, E_a = 14.9 kJ mol^{-1}, $\log A$ = 0.51.

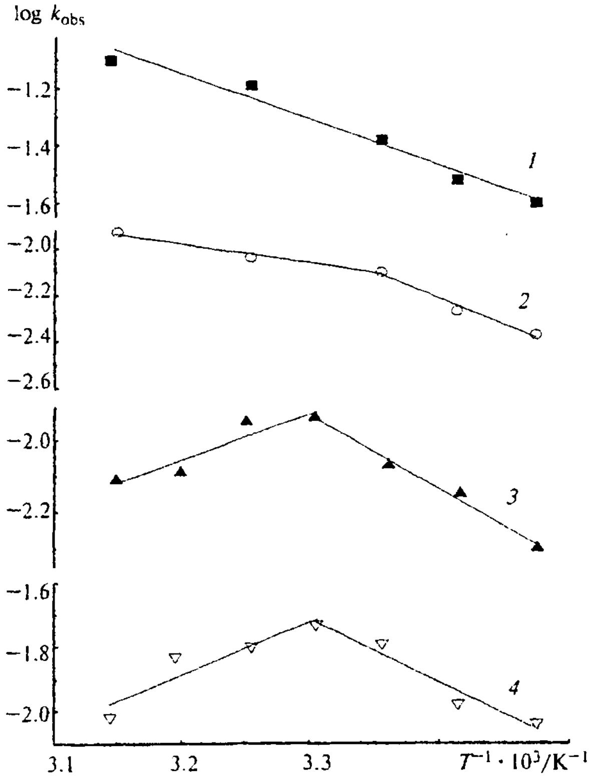

Fig. 4. Arrhenius dependences of the observed rate constant (k_{obs}) of alkaline hydrolysis of **1** in the reverse micellar AOT—decane—water system in water (*1*) and at different W: 26.6 (*2*), 20.0 (*3*), and 15.1 (*4*); [NaOH] = 0.01 mol L^{-1}; [AOT] = 0.42 mol L^{-1}.

Quantitative analysis of the kinetic data was performed in the framework of the pseudo-phase model of micellar catalysis.[4] According to this model, the reagents are distributed between three pseudo-phases according to their partition coefficients: an aqueous core, surface layer, and oil. The reaction involving hydrophobic substrate **1** and a hydrophilic nucleophile occurs probably in the surface layer, whose balanced hydrophilic-lipophilic properties make it possible to solubilize compounds with different natures. For this case, the equation of the pseudo-phase model has the form[4]

$$k_{obs} = \frac{k_i K_S K_{OH}[OH]_t}{(K_S + Z)(K_{OH} + W) / [AOT]}, \quad (2)$$

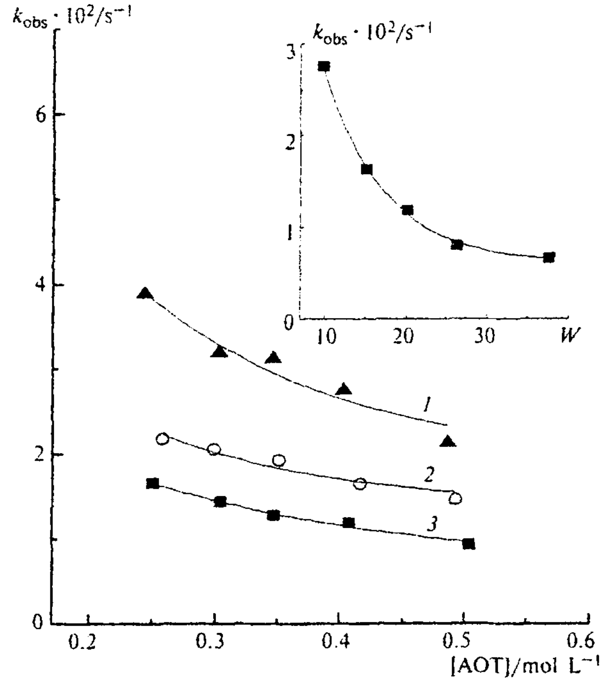

Fig. 5. Observed rate constant (k_{obs}) of alkaline hydrolysis of **1** as a function of the AOT concentration at different *W*: 9.8 (*1*), 15.1 (*2*), and 20.0 (*3*); 25 °C; 0.01 *M* NaOH. In insertion: the observed rate constant (k_{obs}) as a function of *W*. Solid lines correspond to the theoretical k_{obs} values.

where k_i (s^{-1}) is the rate constant in the surface layer, corresponding to the concentration of the nucleophile expressed as the [OH]/[SURF] molar ratio; k_i (s^{-1}) is related to the pseudo-first-order rate constant k'_i (s^{-1}) and the second-order rate constant $k_{2,i}$ (L mol^{-1} s^{-1}) by the following correlations:

$k_i = k'_i[OH]/[AOT]$, $k_{2,i} = k_i V$,

where *V* is the molar volume of the surfactant; $[OH]_t$ is the total concentration of OH^- (mol L^{-1}); K_S is the partition constant of the substrate between the oil phase and the surfactant: $K_S = ([S]_i[Decane])/([S]_o[AOT])$; and K_{OH} is the partition constant of the hydroxide ions between the water phase and the surfactant: $K_{OH} = ([OH]_i[H_2O])/([OH]_w[AOT])$. The molar concentrations of substrate (S), decane, and the surfactant are given in brackets; the indices i, o, and w represent the surface layer, oil phase, and water phase, respectively. The main assumptions and approximations used in the pseudophase model have been considered previously.[20]

We also measured the kinetic dependences of k_{obs} on [AOT] at 25 °C for different *W* (see Fig. 5). As shown by the measurements of the electroconductivity, no percolation is observed under the experimental conditions at *W* = 15.1 and *W* = 20.0, whereas at *W* = 9.8 for all [AOT] values, the micellar system exists above the percolation threshold. According to the data obtained (see

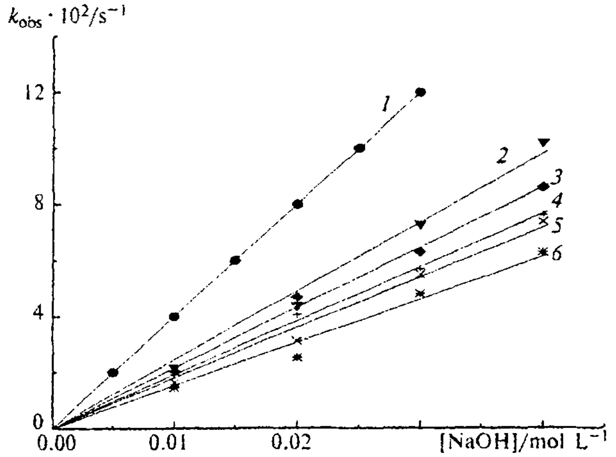

Fig. 6. Dependences of the observed rate constant (k_{obs}) of alkaline hydrolysis of **1** on the concentration of NaOH in water (*1*) and at different concentrations of AOT: 0.259 (*2*), 0.3 (*3*), 0.353 (*4*), 0.417 (*5*), and 0.494 mol L^{-1} (*6*); *W* = 15.1; 25 °C.

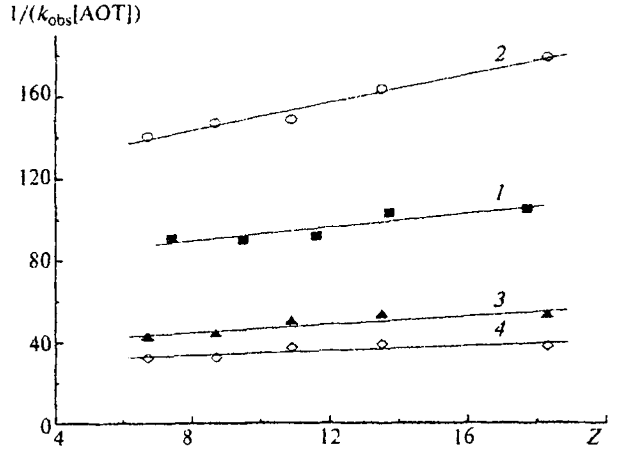

Fig. 7. Linearization of the data (see Fig. 5) in the coordinates of Eq. (2): *W* = 9.8 (*1*), 15.1 (*2*—*4*); [NaOH] = 0.01 (*1*, *2*), 0.03 (*3*), and 0.04 mol L^{-1} (*4*).

Figs. 5 and 6), the reaction is 2—2.5-fold slower in the reverse system under study as compared to that in water. Under the experimental conditions, the observed rate constant linearly depends on the concentration of NaOH (see Fig. 6). An increase in the AOT concentration results in some retardation of the reaction (see Fig. 5) due to either dilution of the reagents with an increase in the volume fraction of the dispersed phase or the electrostatic repulsion of the OH^- ion from the anionic head groups of AOT. A decrease in k_{obs} is observed as *W* increases (see Fig. 5, insertion).

Equation (2) is linearized in the coordinates $1/(k_{obs}[AOT])$ against *Z*. The graphical solution of this equation (see Fig. 7) makes it possible to determine K_{OH}, K_S, and k_i. Analysis showed a very good correspondence between the experimental and calculated kinetic data both below and above the percolation threshold (see Fig. 5). The following parameters were calculated from Eq. (1): K_{OH} = 2.6 and k_i = 5.8 s^{-1}. The K_S value changes within 38—45, *i.e.*, it is almost independent of the content of water and alkali. This indicates the adequacy of the pseudo-phase model under the experimental conditions. Taking V being equal to 0.37 L mol^{-1},[21] we can determine $k_{2,i}$ = 2.15 L mol^{-1} s^{-1} (for comparison, $k_{2,w}$ = 4.0 L mol^{-1} s^{-1}).

Some conclusions about factors that determine the micellar effect in the system under study can be drawn analyzing the obtained values of the constants. According to the published data,[21] the reaction rates in micelles change due to two main effects: by change in the microenvironment of the reagents upon transferral of the reaction from the aqueous pseudo-phase to the micellar pseudo-phase and concentrating of the reagents in micelles. The observed change in the rate (k_{obs}/k_w) amounts to 0.4—0.5. The influence of the micellar microenvironment can be characterized[21] by $k_{2,i}/k_{2,w}$ = 0.54. This component of the micellar effect reflects a change in the reactivity due to a change in the local polarity, solvation, and orientation of the reagents and is comparable in value to the observed k_{obs}/k_w effect, *i.e.*, makes the main contribution to the inhibition of the reaction in micelles. According to the Ingold—Hughes theory,[22,23] the transfer of the ion-molecular reaction to a lower-polarity environment has a favorable effect on the reactivity. Therefore, it can be assumed that the inhibition of the process is related to an increase in the entropy of reaction due to a change in the orientation and a decrease in the mobility of the reagents rather than to a change in the polarity. The concentrating of the reagents in the surface layer does not noticeably contribute to the micellar effect because of a low distribution constant of the nucleophile (K_{OH} = 2.6), which is due to high hydrophilicity and electrostatic repulsion of the OH^- ions from the negatively charged surface of the micelles.

Thus, the cluster formation of micelles substantially affects the kinetics of alkaline hydrolysis of **1** in the reverse AOT—decane—water system. A decrease in the activation energy above the percolation threshold was found. Analysis of the kinetic data by the pseudo-phase model showed that Eq. (2) is valid both below and above the percolation threshold.

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