Mendeleev Commun., 1998, 8(6), 224–226

Kinetics of hydrolysis of *p*-nitrophenyl ethyl chloromethyl phosphonate in a sodium bis(2-ethylhexyl)sulfosuccinate–decane–water reverse micellar system, below and above the percolation threshold

Lucia Ya. Zakharova,*[a] Farida G. Valeeva,[a] Lyudmila A. Kudryavtseva,[a] Nataliya L. Zakhartchenko[b] and Yuri F. Zuev[b]

[a] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 8432 75 2253; e-mail: vos@iopc.kcn.ru*

[b] *Kazan Institute of Biochemistry and Biophysics, Russian Academy of Sciences, 420503 Kazan, Russian Federation*

A kinetic study of the basic hydrolysis of the substrate in a sodium bis(2-ethylhexyl)sulfosuccinate–decane–water reverse micellar system has shown a change in the reactivity of *p*-nitrophenyl ethyl chloromethyl phosphonate above the percolation threshold. The applicability of the pseudophase model of micellar catalysis, below and above the percolation threshold, is shown.

Reverse micelles and water-in-oil microemulsions have drawn wide attention as biomimetic systems.[1,2] The most typical anionic surfactant capable of forming reverse micellar aggregates without any co-surfactant is sodium bis(2-ethylhexyl)sulfosuccinate (AOT).[†] The structural behaviour of reverse systems depends on several parameters, such as temperature, water content, ionic strength, *etc.*[3] Although the pseudophase model of micellar catalysis[4] does not take into account the geometry of the particles, it is reasonable to assume that altering the above parameters, resulting in the modification of aggregates, will affect the reaction rate in micelles.

When either the volume fraction of dispersed phase ϕ or the temperature is varied percolation phenomenon can take place in the AOT-based reverse micellar systems.[5–7] The occurrence of percolation reveals that the process of micellar clustering increases very rapidly. Percolation can be manifested by a rapid increase, by 3-4 orders of magnitude, of the electric conductivity of the system. The structure of the micellar system is assumed[7] to be unaffected by percolation, *i.e.* as before it is formed by isolated water droplets surrounded by an AOT monolayer. It is undoubtedly of interest to study the influence of clustering phenomena on the reaction rate in micelles.

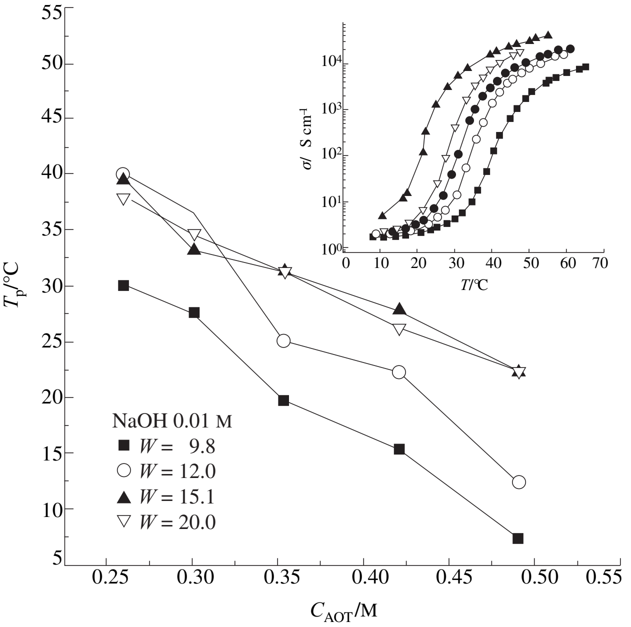
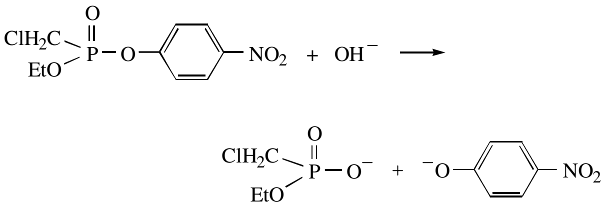


Figure 1 Dependence of the percolation threshold temperature on AOT concentration in the AOT–decane–water reverse micellar system at various W values. The insert gives an example of the electric conductivity change *vs.* temperature for W = 15.1, C_{NaOH} = 0.01 M, the AOT concentrations: ■ 0.26 M, ○ 0.30 M, ● 0.35 M, ▽ 0.42 M, ▲ 0.49 M.

In this work the kinetics of the basic hydrolysis of *p*-nitrophenyl ethyl chloromethyl phosphonate **1** in AOT–decane–water reverse micelles at various molar ratios $W = [H_2O]/[AOT]$ and Z = [decane]/[AOT] has been investigated (Scheme 1).



Scheme 1

An analysis of the kinetic data in terms of the pseudophase model and a test of the model under different experimental conditions with high concentrations of the ionic reagent and a variation in temperature and W, Z parameters have been carried out.

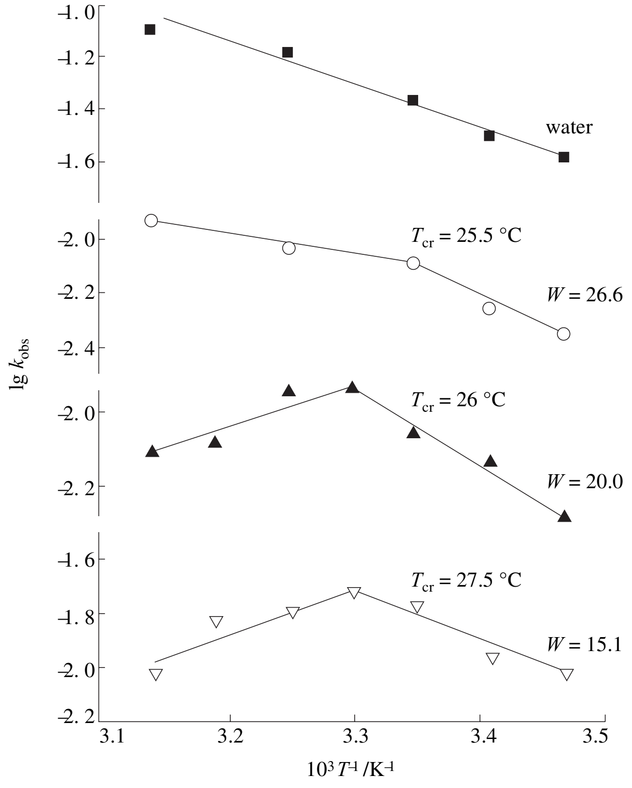


Figure 2 The Arrhenius dependence of the observed rate constant for the basic hydrolysis of **1** in the AOT–decane–water reverse micellar system at various W values (C_{NaOH} = 0.01 M, C_{AOT} = 0.42 M).

[†] AOT or Aerosol OT is a trivial name for bis(2-ethylhexyl)sulfosuccinate.

Substrate **1** was prepared according to the previously reported procedure.[8] The surfactant AOT was from 'Sigma' and used without further purification. Sodium hydroxide and decane were obtained commercially and decane was distilled prior to use. Solutions were made up in twice-distilled water. Microemulsions were prepared by mixing AOT, decane and water, in the appropriate proportions, and shaking vigorously until a transparent solution was obtained. Under experimental conditions the reverse micellar systems always exist in accordance with the AOT phase diagram.[9] The reaction was monitored by observing the *p*-nitrophenolate absorption at 400 nm. A spectrophotometer 'Specord UV VIS' equipped with temperature-controlled cell holders was employed. The substrate concentration (5×10^{-5} M) was much less than the nucleophile concentration, and the kinetic data always fitted the first order equation with correlation $r \geq 0.999$. The electrical conductivity was measured using a OK 102/1 conductivity meter (Radelkis, Hungary), operating at 80 Hz and 3 kHz. The temperature was controlled in a parallel-plane cell with ±0.2 °C accuracy. The temperature of the percolation threshold was determined as the point at which the first derivative of conductivity with respect to temperature changes its sign.

Figure 1 plots the dependence of the percolation threshold temperature (T_p) on the AOT concentration at various W values. The occurrence of the percolation threshold reveals that cluster size, attractive interactions and the rate of exchange of material between micelles through collisions all increase. The appearance of a percolation threshold corresponds to the formation of the first 'infinite' cluster.

Based on the electric conductivity measurements the conditions for the kinetic study below and above the percolation threshold were chosen. The kinetic data are shown in Figures 2–4. In Figure 2 the lg k_{obs} *vs.* $1/T$ plot at various W values is represented ($C_{AOT} = 0.42$ M, $C_{NaOH} = 0.01$ M). The Arrhenius dependence changes its slope at definite critical temperatures (T_{cr}). At $W = 26.6$ a decrease in the slope occurs, which is in line with a reduction in activation energy (E_a), whereas at $W = 20.0$ and 15.1 a transition to negative E_a values is observed. It is evident that the values T_{cr} (Figure 2) and T_p (Figure 1) for the same W value are nearly identical, which makes it possible to assume that the change of the slope in the Arrhenius dependence is connected with the clustering phenomenon. At the same time, it should be assumed that a decrease in E_a above the percolation threshold is not directly due to the acceleration of the dynamic processes resulting from clustering. Such a direct effect would be expected in the case of fast reactions, in which the rate is controlled by diffusion of reagents.[10] The reaction in this study does not belong to these fast processes, so the basic assumption of the pseudophase model should be observed, suggesting that the exchange of materials between droplets is much faster than the reaction in this study, and therefore has no effect on the kinetics. We can assume that clustering and acceleration of the dynamic processes result in the alteration of some characteristics of the micellar microenvironment of the reagents (*i.e.* micropolarity, surface potential, *etc.*), thus influencing their reactivity.

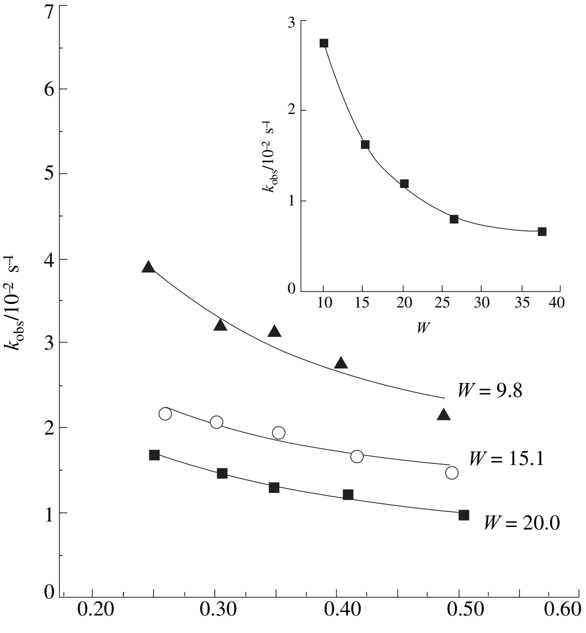


Figure 3 The AOT concentration dependence of the observed rate constant for the basic hydrolysis of **1** at various W values ($C_{NaOH} = 0.01$ M, 25 °C). The insert shows the observed rate constant *vs.* W. The solid lines are related to the calculated k_{obs} values.

The kinetic data were treated in terms of the pseudophase model[4] with the assumption that there is competition between reactions in different microphases of the reverse micelles. The problems and approximations involved in these definitions have been discussed previously.[11] For the reaction occurring at the interface the first order rate constant is given by equation (1):

$$k_{obs} = \frac{k_i K_S K_{OH}[\mathrm{OH}]_t}{(K_S + Z)(K_{OH} + W)[\mathrm{AOT}]} \tag{1}$$

where k_i/s^{-1} is a bimolecular interfacial rate constant, expressed in terms of the molar ratio [OH]/[AOT]; it is connected to the conventional pseudo first order constant k_i'/s^{-1} and the second order constant $k_{2,i}$/M^{-1} s^{-1} as follows:

$$k_i = k_i'\frac{[\mathrm{OH}]}{[\mathrm{AOT}]};\; k_{2,i} = k_i V \tag{2}$$

V is the molar volume of AOT, $[\mathrm{OH}]_t$ is the total OH concentration and K_S and K_{OH} are partition coefficients, which are defined as

$$K_S = \frac{[\mathrm{S}]_i[\mathrm{decane}]}{[\mathrm{S}]_0[\mathrm{AOT}]};\; K_{OH} = \frac{[\mathrm{OH}]_i[\mathrm{H_2O}]}{[\mathrm{OH}]_w[\mathrm{AOT}]} \tag{3}$$

where the molar concentrations of substrate (S), decane and AOT are given in square brackets; subscripts i, o, w are related to the interface, oil and water, respectively.

Figure 3 plots the k_{obs} *vs.* C_{AOT} dependence for the various W values at 25 °C. As one can see from Figure 1 the experimental conditions for the kinetic study are as follows. The micellar system is below the percolation threshold for $W = 15.1$ and 20.0 whereas for $W = 9.8$ the clustering process is very active. The kinetic data in Figure 4 suggest that in the system studied a 2–2.5-fold retardation of the hydrolysis of **1** takes place by comparison with the reaction in water but the observed rate constant still depends linearly on the NaOH concentration. An increase in the AOT concentration results in some inhibition of the reaction (Figure 3) evidently due to dilution of the reagents with increasing volume fraction of the dispersed phase. The observed rate constant is reduced with the increase in W (Figure 3, insert).

Equation (1) can be linearized in the $1/k_{obs}C_{AOT}$ *vs.* Z coordinates, which makes it possible to determine the values K_{OH}, K_S and k_i. In this work our task was to test the pseudophase model during the clustering process of reverse micelles. A comparison of the experimental and calculated kinetic data shown in Figure 3 demonstrates a rather good agreement between them both below and above the percolation threshold. The calculated parameters are $K_{OH} = 2.6$ and $k_i = 5.8$ s^{-1}. Assuming $V = 0.37$ l mol^{-1},[12] we can calculate $k_{2,i} = 2.15$ M^{-1} s^{-1} (for the sake of comparison $k_{2,w} = 4.0$ M^{-1} s^{-1}).

From the analysis of the calculated parameters some conclusions can be drawn with respect to the factors responsible for the micellar rate effects in the system studied. The observed effect $k_{obs}/k_w \approx 0.4$–0.5 is mainly determined by two factors. The first results from a change in the microenvironment of the reagents and the second results from concentrating the reagents in the microdroplets and has some resemblance to interfacial catalysis. The first effect can be expressed *via* the $k_{2,i}/k_{2,w}$ ratio. It is evident that this value is comparable with the observed ratio k_{obs}/k_w, *i.e.* it is a fundamental contribution to the total

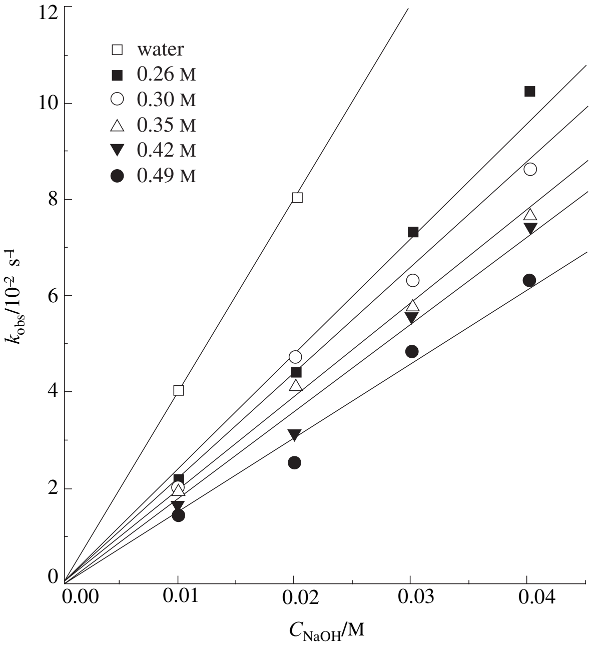


Figure 4 Dependence of the observed rate constant for the basic hydrolysis of **1** on the NaOH concentration in the system at various AOT concentrations. *W* = 15.1, 25 °C.

micellar rate effect. It can be connected with changes in the reactivity of the substrate due to changes in the micropolarity, solvation or orientation of the reagents. According to Ingold's theory,[13] lowering the polarity of the microenvironment should favour the ion–molecular reaction, in particular, the reaction of phosphorus acid esters with OH^-.[14] One can therefore assume that inhibition of the reaction probably results from the loss in entropy due to the lowered mobility of the substrate rather than to a change in the micropolarity.

The effect of concentrating the reagents in microdroplets plays a minor role in the catalytic mechanism due to the low value of the partition coefficient of the nucleophile (K_{OH} = 2.6) connected with its high hydrophilicity and electrostatic repulsion from the negatively charged micellar surface.

In conclusion, in this work the kinetics of **1** in AOT-based reverse micelles and the influence of droplet clustering have been studied. A change in the reactivity of **1** above the percolation threshold was observed, which is reflected in the alteration of the slope in the Arrhenius plot. This anomalous behaviour can be caused by a reduction in the area of micellar contact with the oil and the alteration of some properties of the surface layer due to micelle clustering, both of which influence the reactivity. It has been found that the pseudophase model is adequate both below and above the percolation threshold.

This work was supported by the Russian Foundation for Basic Research (grant no. 97-03-32372).

References

1 Yu. L. Khmel'nitsky, A. V. Levashov, N. L. Klyachko and K. Martinek, *Usp. Khim.*, 1984, **53**, 545 (*Russ. Chem. Rev.*, 1984, **53**, 319).
2 *Microemulsions: Structure and Dynamics*, eds. S. E. Friberg and P. Bothorel, CRC Press, Inc. Boca Raton, Florida, USA, 1987.
3 E. B. Leodidis and T. A. Hatton, *Langmuir*, 1989, **5**, 741.
4 L. Garsia-Rio, J. R. Leis, M. E. Pena and E. Iglesias, *J. Phys. Chem.*, 1993, **97**, 3437.
5 A. Jada, J. Lang and R. Zana, *J. Phys. Chem.*, 1989, **93**, 10.
6 C. Cametti, P. Codastefano, P. Tartaglia, R. Rouch and S. H. Chen., *Phys. Rev. Lett.*, 1990, **64**, 1461.
7 Y. Feldman, N. Kozlovich, I. Nir, N. Garti, V. Archipov, Z. Idiyatullin, Yu. Zuev and V. Fedotov, *J. Phys. Chem.*, 1996, **100**, 3745.
8 V. E. Bel'skii, L. A. Kudryavtseva, O. M. Il'ina and B. E. Ivanov, *Zh. Obshch. Khim.*, 1970, **49**, 2470 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1970, **49**, 2180].
9 S. Perez-Casas, R. Castillo and M. Costas, *J. Phys. Chem.*, 1997, B, **101**, 7043.
10 M. Almgren and R. Johannsson, *J. Phys. Chem.*, 1992, **96**, 9512.
11 P. Stilbs, *J. Colloid Interface Sci.*, 1982, **87**, 385.
12 K. Martinek, A. K. Yatsimirsky, A. V. Levashov and I. V. Beresin, *Micellization, Solubilization, and Microemulsions*, ed. K. L. Mittal, Plenum Press, New York–London, 1977, p. 489.
13 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca–London, 1969.
14 N. A. Loshadkin, in *Toksichnye efiry kislot fosfora* (*Toxic Ethers of Phosphorus Acids*), ed. P. O'Brain, Mir, Moscow, 1964, p. 460 (in Russian).

Received: Moscow, 7th July 1998
Cambridge, 9th September 1998; Com. 8/05577G