# The micellar effect of the sodium bis(2-ethylhexyl)sulfosuccinate—decane—water reverse system on the hydrolysis of phosphonic acid esters

L. Ya. Zakharova,\* F. G. Valeeva, R. A. Shagidullina, and L. A. Kudryavtseva

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation. Fax: +7 (843-2) 75 2253

> The reactivity of alkyl aryl chloromethylphosphonates in alkaline hydrolysis in the sodium bis(2-ethylhexyl)sulfosuccinate—decane—water reverse micellar system is mainly determined by the electronic properties of substituents and depends only slightly on their hydrophobicity.

> Key words: reverse micelles, microemulsions, surface layer, kinetics, alkaline hydrolysis, substrate specificity.

Reverse micelles and microemulsions present interest as close analogs of biocatalysts.<sup>1</sup> Previously, we studied the influence of the surfactant nature on the reactivity of esters of phosphorus-based acids in reverse micellar systems.<sup>2,3</sup> Catalytic alkaline hydrolysis of esters of tetracoordinated phosphorus acids has been observed in systems based on sodium dodecyl sulfate (SDS), while in systems based on sodium bis(2-ethylhexyl)sulfosuccinate (AOT), the reaction is inhibited. The reactivity of a broad range of esters of phosphonic acid in the SDS-hexanol-water system has been studied.<sup>4</sup> In the present work, we investigated the kinetics of alkaline hydrolysis of alkyl aryl chloromethylphosphonates (1-9) in the sodium bis(2-ethylhexyl)sulfosuccinate (AOT)-decane-water reverse micellar system (Scheme 1) in order to elucidate the role of the surfactant nature and study the problem of substrate specificity in reverse micellar systems.

### Scheme 1



$$\begin{split} &X = NO_2; R = Et (1), Bu^n (2), n \cdot C_6 H_{13} (3) \\ &R = Et; X = Br (4), H (5), Et (6), Bu^n (7), n \cdot C_8 H_{17} (8), \\ &\mu \cdot C_{12} H_{25} (9) \end{split}$$

#### Experimental

Compounds 1–9 were synthesized by a procedure reported previously<sup>5</sup>: AOT (Sigma) was used as received. The reverse micellar systems were prepared by mixing the components and shaking the mixture until a transparent solution formed, as proposed in a known procedure.<sup>6</sup> The molar ratios of the system components  $W = [H_2O]/[AOT]$  and Z = [decane]/[AOT] varied from 9.8 to 37.6 and from 5 to 22, respectively. The micellar solutions always remained optically uniform and, according to the phase diagram of AOT,<sup>7</sup> their state corresponded to the region of reverse micellar systems. The kinetics of hydrolysis was studied by spectrophotometry using a Specord M-400 instrument at 25 °C to measure absorption of the leaving-group anion under the conditions of observed pseudo-first-order kinetics. Quantitative analysis of the kinetic data was performed in the same way as in a known study<sup>4</sup> using the equation<sup>6</sup>

$$k_{\text{obs}} = \frac{k_x K_s K_{\text{OH}} [\text{OH}]_t}{(K_s + Z)(K_{\text{OH}} + W)[\text{AOT}]}$$

where  $k_i/s^{-1}$  is a rate constant related to the pseudo-first-order rate constant  $k_i'/s^{-1}$  and to the second-order rate constant  $k_{2,i}/L$  mol<sup>-1</sup> s<sup>-1</sup> by the relations  $k_i' = k_i$ [OH]/[AOT];  $k_{2,i} = k_i V$ . V is the molar volume of the surfactant, taken to be 0.37 L mol<sup>-1</sup>; [OH]<sub>i</sub>/mol L<sup>-1</sup> is the total concentration of OH<sup>-</sup>;  $K_s$  is the distribution constant for the substrate between the oil phase and the surfactant;  $K_{OH}$  is the distribution constant for hydroxide ions between the aqueous phase and the surfactant; the subscripts i. o, and w refer to the surface layer and to the oily and aqueous pseudo-phases, respectively.

## **Results and Discussion**

Three microregions can be distinguished in this type of reverse micelles, namely, the aqueous core (formed by solubilized water), the surface layer (consisting of surfactant molecules oriented with their head groups toward

Published in Izvestiva Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 1712-1715, October, 2000.

1066-5285/00/4910-1696 \$25.00 © 2000 Kluwer Academic/Plenum Publishers

the water pool), and the bulky oil pseudo-phase.<sup>8</sup> According to published data<sup>6</sup> and our earlier results,<sup>2-4</sup> alkaline hydrolysis of hydrophobic substrates proceeds in the surface layer of the micelles. It was found<sup>9</sup> that the dielectric constant (c) of the surface layer increases with an increase in W from 2.3 (W = 0) to 9.0 (W = 12) and then remains constant.<sup>10</sup> This is attributed to the hydration of the head groups and the surfactant counter-ions. The properties of the aqueous core also vary with an increase in  $W^{10}$  When W is low, water is completely consumed in solvation shells. Due to the high content of ions in the shell, the properties of the "bound" water differ substantially from those of bulk water; in particular, the polarity decreases ( $\varepsilon \le 36$ ). When  $W \ge 9$ , water in the surface layer shows the properties of the aqueous phase, with a network of individual molecules crosslinked by hydrogen bonds. The foregoing implies that the reactivity of compounds is largely determined by the properties of the micellar microenvironment and changes when the reaction is transferred from an aqueous solution to a micellar medium.

The kinetics of hydrolysis of substrates in water in the absence of surfactants have been described previously.<sup>4</sup> The kinetic data for the AOT-decane-water



Fig. 1. Observed rate constants  $(k_{obs})$  of the alkaline hydrolysis of compounds 1-3 in the AOT-decane-water reverse micellar system vs. surfactant concentration, 25 °C, W = 15.1. The inset shows the observed rate constants of the alkaline hydrolysis of compounds 1-3 in the AOT-decane-water reverse micellar system vs. NaOH concentration; the numbers of curves 1-3 coincide with the designations of substrates in Scheme 1.



Fig. 2. Observed rate constants  $(k_{obs})$  of the alkaline hydrolysis of compounds 4-9 in the AOT-decane-water reverse micellar system vs. surfactant concentration, 25 °C, W = 15.1; the numbers of curves 4-9 coincide with the designations of substrates in Scheme 1.

reverse micellar system are presented in Figs. 1-3. In general, the reactivity in the micellar system varies in the following series of substituents: Et > Bu  $\approx$  Hex (for  $X = NO_2$ ) >> Br  $\approx$  H > Et  $\approx$  Bu  $\approx$  n-C<sub>8</sub>H<sub>17</sub>  $\approx$  i-C<sub>12</sub>H<sub>25</sub>



Fig. 3. Observed rate constants  $(k_{obs})$  of the alkaline hydrolysis of compounds 1 (1), 3 (2), 5 (3), and 7 (4) in the AOT-decane-water reverse micellar system vs. content of water, 25 °C, [AOT] = 0.4 mol L<sup>-1</sup>. Other substrates of the series exhibit a similar type of dependence.

(for R = Et). For the first three substrates, the rate of hydrolysis carried out in a micellar system sharply decreases (by a factor of up to five) with respect to that in water. The observed rate constant  $(k_{obs})$  depends linearly on the alkali concentration and decreases with an increase in [AOT] and an increase in the content of water (see Figs. 1 and 3). This is apparently due to the dilution of reactants following an increase in the volume fraction of the disperse phase. This regularity is typical of reactions proceeding in the surface layer of reverse micellar systems.<sup>2-4.6</sup> A pronounced change in the reactivity is observed only on going from compound 1 to compound 2, while a further increase in the hydrophobicity of R does not change the reaction rate.

The effect of the substituent in the leaving group (substrates 1, 4-9) is somewhat different. The replacement of the nitro group by the less electronegative Br decreases  $k_{obs}$  by more than an order of magnitude, while further decrease in the electronegativity of X (the replacement of Br by H) does not influence reactivity. The increase in the hydrophobicity of X has an effect only on passing from compound 5 to 6, while further increase in the length of the alkyl group in the series of compounds 6-9 does not change  $k_{obs}$  (see Fig. 2).

Although the replacement of the aqueous medium by the micellar system inhibits the reaction for substrates 1-3 ( $k_{\rm obs}/k_{\rm w} \le 1$ ), the inhibition effect gradually decreases in the series 1, 4-9. In the case of substrates 8 and 9, the rates of hydrolysis in water and in the micellar system are equal  $(k_{obs}/k_w \approx 1)$ . In addition, whereas for substrates 1, 4, and 5 (X = NO<sub>2</sub>, Br, H), the  $k_{obs}$  value tends to decrease with an increase in the surfactant concentration and water content, in the case of 6-9 $(X = Et, Bu, n-C_8H_{17}, i-C_{12}H_{25}), k_{obs}$  does not depend on [AOT] as long as W remains constant, although it does decrease as W increases (see Figs. 2 and 3). This apparently points to a change in the localization of reactants in the case of reactions involving highly hydrophobic substrates, caused by changes in the distribution constants. These substrates might be involved in the formation of mixed micelles; this could also result in the transfer of the reaction from the micelle surface layer to another pseudo-phase. The fact that  $k_{obs}$  does not depend on the surfactant concentration implies that the reaction proceeds in the aqueous core of the micelles, as has been observed previously.<sup>11</sup>

The results of quantitative analysis of kinetic data for substrates 1-5 are summarized in Table 1. Since  $k_{obs}$ does not depend on [AOT] and the reaction of substrates 6-9 is supposed to proceed in the aqueous core, the kinetic data for these substrates cannot be analyzed in terms of the pseudo-phase model. It follows from Table 1 that the structure of the substrate virtually does not influence the distribution constants for the reactants between the phases: an exception is compound 1 for which  $K_s$  is twice as great as those for other phosphonates. Evidently, the change in  $k_{obs}$  in the series 1-5 is mainly due to the difference between the substrate reactivities in 
 Table 1. Results of quantitative analysis of the kinetic data in terms of the pseudo-phase model

Substrate	K <sub>s</sub>	К <sub>ОН</sub>	k <sub>i</sub> /s <sup>-1</sup>	k <sub>2.i</sub>	k <sub>2.w</sub> *
				/L mol <sup>++</sup> s <sup>++</sup>	
1	90	1.3	9.0	2.43	4.0
2	45	1.3	6.0	2.22	3.6
3	45	1.5	5.0	1.85	3.0
4	40	6.0	0.2	0.074	0.55
5	30 .	1.5	0.65	0.24	0.24

\* For compound **6**,  $k_{2,w}/L \mod^{-1} s^{-1} = 0.2$ ; **7**, 0.16; **8**, 0.12; **9**, 0.08.

the surface layer, which is characterized by the  $k_{2,i}$  value. This value is lower than the similar second-order rate constant in water  $(k_{2,w})$  for all substrates, which accounts for the retardation of the reaction in the reverse micellar system with respect to that in water.

Thus, the rate of alkaline hydrolysis of the series of reactants in question performed in the AOT-decane-water reverse micellar system decreases with respect to the reaction rate in water. This is due to the unfavorable influence of the microenvironment of the compounds in the micellar phase. The reactivity in the series of compounds 1-9 is mainly determined by the electronic effects of substituents and depends slightly on their hydrophobicity.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-32372, 99-03-32037a).

#### References

- 1. J. H. Fendler, Chem. Rev., 1987, 87, 877.
- L. Ya, Zakharova, F. G. Valeeva, L. A. Kudryavtseva, N. L. Zakhartchenko, and Y. F. Zuev, *Mendeleev Commun.*, 1998. 8, 224.
- L. Ya. Zakharova, F. G. Valeeva, L. A. Kudryavtseva, and E. P. Zhiltsova, Mendeleev Commun., 1999, 9, 125.
- L. Ya, Zakharova, F. G. Valeeva, R. A. Shagidullina, and L. A. Kudryavtseva, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1366 [*Russ. Chem. Bull.*, 2000, 49, 1360 (Engl. Transl.)].
- D. F. Toy and K. H. Rattenbury, US Pat. No 2922810, 1960, Chem. Abstr., 1960, 54, 9848.
- L. Garsia-Rio, J. R. Leis, M. E. Pena, and E. Iglesias, J. Phys. Chem., 1993, 97, 3437.
- S. Peres-Casas, R. Castillo, and M. Costas, J. Phys. Chem., 1997, B, 101, 7043.
- E. B. Leodidis and T. A. Hatton, J. Phys. Chem., 1990, 94, 6400; 6411.
- 9. M. Belletete, M. Lachapelle, and G. Durocher, J. Phys. Chem., 1990, 94, 5337.
- 10. E. B. Leodidis and T. A. Hatton, Langmuir, 1989, 5, 741.
- 11. M. L. Moya, C. Izquierdo, and J. Casado, J. Phys. Chem., 1991, 95, 6001.

Received February 2, 2000; in revised form April 21, 2000