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The catalytic effect of the sodium dodecyl sulfate–hexanol–water reverse micellar system

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The kinetics of the basic hydrolysis of ethyl *p*-nitrophenyl ethylphosphonate in the sodium dodecyl sulfate–hexanol–water reverse micellar system has shown that at high pH and low water content the reaction occurs in the surface layer and is adequately described by a pseudophase model.

Reverse micellar systems are formed by surfactant molecules in hydrocarbon solvents with the polar headgroups pointing inward. Reverse micelles and water-in-oil (w/o) microemulsions are considered as biomimetic systems, because the mechanism of their catalytic action has much in common with the basic principles of a function of biomembranes.[1] Although micellar catalysis of nucleophilic substitution reactions was repeatedly reviewed,[2–4] there are only isolated quantitative studies of the reactivity in reverse micelles in contrast with the kinetics in direct micelles. Prediction and interpretation of the kinetic influence of reverse micelles and microemulsions is relatively easy in the case when both reactants are hydrophilic and incorporated in aqueous microdroplets, which act as molecular-scale reactors, concentrating the reagents. For the reactions in which reagents are distributed in the aqueous and oil phases and at the interface, a quantitative model was constructed by extending the pseudophase model to include three pseudophases. For the reaction occurring at the interface, a first-order rate constant is given by equation (1)[5]

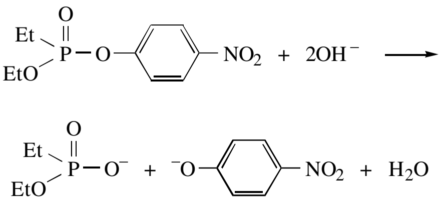
$$k_{\mathrm{obs}} = \frac{k_{\mathrm{i}}K_{\mathrm{s}}K_{\mathrm{OH}}[\mathrm{OH}]_{\mathrm{t}}}{(K_{\mathrm{s}}+Z)(K_{\mathrm{OH}}+w)[\mathrm{SDS}]} \tag{1}$$

where k_{i}, the pseudo-first-order constant in the sodium dodecyl sulfate (SDS) phase, can be expressed in terms of a rate constant k'_{i} and the molar ratio between the nucleophile at the interface and SDS:

$$k_{\mathrm{i}} = k'_{\mathrm{i}}\frac{[\mathrm{OH}]}{[\mathrm{SDS}]},$$

K_{s} and K_{OH} are the partition coefficients of the substrate and the nucleophile. Problems and approximations involved in these definitions have been discussed earlier.[6] The test of this kinetic model[5] using the new experimental results seems to be an important task. It provides an opportunity to determine the factors responsible for the catalysis in reverse systems and to compare them with those in direct micelles. Unlike the AOT–alkane–water reverse system,[5,7,8] the catalytic effect of the SDS–hexanol–water ternary reverse micelles and microemulsions was almost not studied.

The purpose of this work is to study the major tendencies and the mechanism of the catalytic action of the SDS–hexanol–water reverse micelles and microemulsions in the basic hydrolysis of ethyl *p*-nitrophenyl ethylphosphonate **1** (Scheme 1). The composition of the micellar systems was varied over a wide range in accordance with the data.[9,10] This variation changed the sizes and the structural behaviour of droplets used as molecular-scale reactors.



Scheme 1

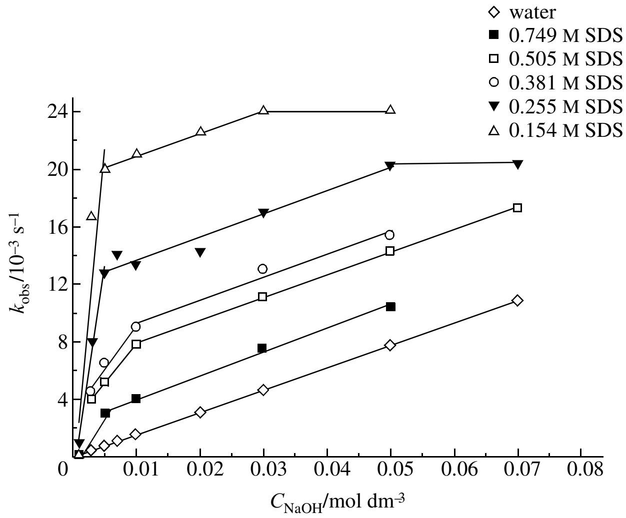


Figure 1 Observed rate constant of the basic hydrolysis of **1** *vs.* NaOH concentration at various SDS concentrations, 25 °C, $w = 15.1$.

SDS from 'Sigma' was used without further purification. Substrate **1**, sodium hydroxide and hexanol were obtained commercially; hexanol was distilled prior to use. Solutions were made in twice-distilled water. Microemulsions were prepared by mixing hexanol, water and SDS in appropriate proportions and by shaking vigorously until a transparent solution was obtained. The micellar parameters $w = [\mathrm{H_2O}]/[\mathrm{SDS}]$ and $Z = [\mathrm{hexanol}]/[\mathrm{SDS}]$ ranged within the limits 9.8–37 and 5–22, respectively. The reaction was followed by monitoring the absorbance of *p*-nitrophenolate at 400 nm. A 'Specord UV VIS' spectrophotometer equipped with thermostatted cell holders was employed. Kinetic measurements were performed at 25 °C. The substrate concentration was usually much lower than the nucleophile concentration.

Figures 1 and 2 represent the kinetic data of the reaction studied at various molar ratios w and Z. Catalysis of the reaction, as compared to the reaction in water, was observed in all the systems independent of their composition. The rate enhancement expressed as $k_{\mathrm{obs}}/k_{\mathrm{w}}$ varied in the range 1.5–35.7 depending on the experimental conditions. This result is in sharp contrast with the retardation of ion–molecule reactions by normal ionic micelles bearing the same sign of charge as an ionic reagent.[3]

As can be seen in Figure 1, the observed rate constant increases with NaOH concentration. Linear k_{obs}–$C_{\mathrm{nucleophile}}$ relationships were usually observed in reverse micellar systems, including AOT-based systems,[5,7,8] so we expected a similar behaviour in the case of SDS reverse micelles and microemulsions. The absence of such a linear dependence over the whole range of NaOH concentrations is probably due to a change in reactivity with NaOH concentration resulting in slope variations. In Figure 1, several linear portions can be seen for each SDS concentration. The slopes of the linear portions can be related cautiously to the apparent second-order rate constants

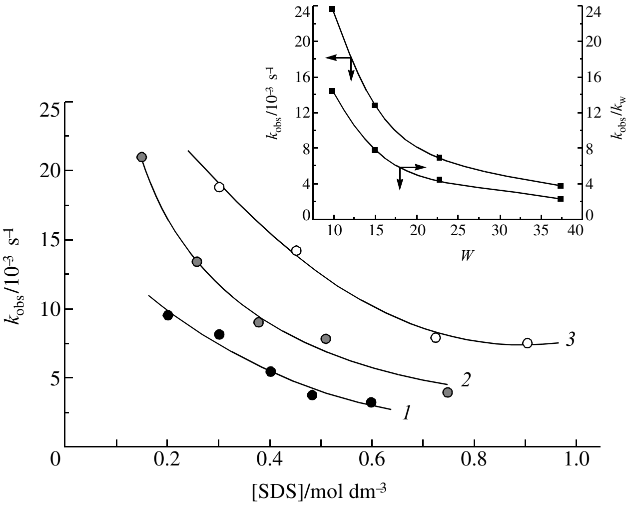


Figure 2 Observed rate constants of the basic hydrolysis of **1** *vs.* SDS concentrations, 0.01 M NaOH: (*1*) $w = 22.8$, (*2*) $w = 15.1$, (*3*) $w = 9.8$. Solid lines are related to the calculated k_{obs}. The insert shows the dependence of the observed rate constant and the rate enhancement of the basic hydrolysis of **1** on the water content.

of the basic hydrolysis of **1** over the given range of NaOH concentrations. From this point of view, a change in the slope of the linear portions with NaOH concentration can be considered as a change in the reactivity. We assume that it can be caused by a transfer of the reaction zone due to a salting-in or salting-out effect as well as a change in the surface potential when the NaOH concentration is increased which favours the OH$^-$ distribution between water and the interface.

The observed rate constant and the micellar rate effect depend on the NaOH and surfactant concentrations and the water content (Figure 2). The maximum micellar effect was observed in 0.003 and 0.005 M NaOH, followed by a decrease of the catalysis at high pH. An increase in the water content of the system at fixed NaOH and surfactant concentrations results in a decrease in the micellar rate effect (Figure 2, insert).

Equation (1) can be linearised on the $1/k_{obs}$[SDS]–Z coordinates. The analysis of the kinetic curves on these coordinates is demonstrated in Figure 3 which indicates that the kinetic data fit well the linear regression at high NaOH concentrations, while at low pH the $1/k_{obs}$[SDS]–Z plot is not linear, as seen from the large discrepancy of the values. This behaviour confirms the above assumption on the transfer of the reaction zone with NaOH concentration. The agreement of the model at high pH gives evidence that under these conditions the reaction occurs at the interface in spite of the electrostatic repulsion of OH$^-$ by negatively charged head groups. In addition, the surface potential decreases as the Na$^+$ concentration increases. Thus, at higher NaOH concentrations, the distribution of OH$^-$ between the water core and the interface results from concentration and charge gradients. At lower NaOH concentrations, contributions from reactions in the oil and water pseudo-phases probably result in the inadequacy of equation (1).

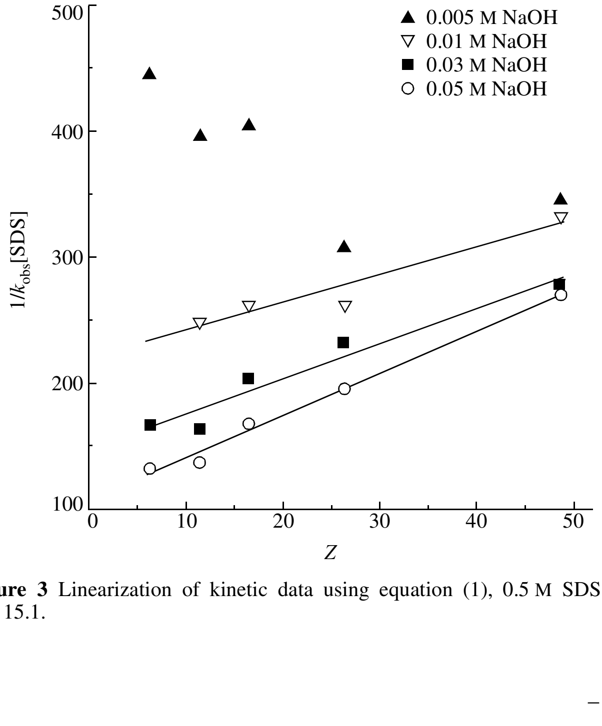


Figure 3 Linearization of kinetic data using equation (1), 0.5 M SDS, $w = 15.1$.

The partition coefficients ($K_s = 104$, $K_{OH} = 0.88$) and the intrinsic rate constant ($k_i = 8.1$ s^{-1}) substantiate the above assumption dealing with the mechanism of the micellar effect in the systems studied. In spite of the low value of K_{OH} resulting from the hydrophilic nature of OH$^-$ and the repulsion by micellar head groups, the concentration factor is responsible for some contributions to the micellar rate effect due to (i) the high value of K_s and (ii) the small molar volume of the micellar phase as compared to the oil phase. The high value of k_i yields evidence that the micellar microenvironment favours the reaction. The conventional bimolecular constant $k_{2,i} = k_iV$.[5] If $V = 0.37$ dm^3 mol^{-1} ,[4,5] then $k_{2,i} = 2.9$ dm^3 mol^{-1} s^{-1}, which is higher than the corresponding constant in water by a factor of 19. This effect is opposite to the decrease in bimolecular rate constants in the micellar pseudo-phase by normal micelles[3] and can be caused either by a favourable orientation of the reactants in the surface layer or a change in the polarity and solvation.

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