Table 1. Physicochemical characteristics of compounds **1—4**

Substrate	B.p./°C (p/Torr) [m.p./°C]	n_D^{20}	Found/Calculated (%) C	H	N	P	Molecular formula
1	165 (0.02)	1.5430	38.50	4.01	5.06	11.13	$C_9H_{11}NO_5PCl$
			38.64	3.94	5.01	11.09	
2	160 (0.01)	1.5340	42.85	4.92	4.51	10.11	$C_{11}H_{15}NO_5PCl$
			42.93	4.88	4.55	10.08	
3	180 (0.02)	1.5280	46.46	5.70	4.13	9.29	$C_{13}H_{19}NO_5PCl$
			46.50	5.66	4.17	9.24	
4	[39—40]	—	49.48	6.38	3.90	8.47	$C_{15}H_{23}NO_5PCl$
			49.52	6.33	3.85	8.52	

alkoxy group becomes longer (Table 2), which is apparently due to steric hindrance to the attack by the hydroxide ion.[7] In addition, in micellar solutions, the hydrophobicity of the substituent might influence the binding, localization, and orientation of a substrate in micelles.[8]

The alkaline hydrolysis of all of the substrates studied is accelerated in CPB micelles; the $(k_{obs}/k_w)_{max}$ ratio reaches two orders of magnitude (see Table 2). The dependence of the observed rate constant on the surfactant concentration passes through a maximum, which is the most clearly defined for substrates **3** and **4** (Fig. 1). As the hydrophobicity of the substrate increases, the maximum shifts to lower surfactant concentrations: from ~0.05 (**1**) to ~0.001 mol L^{-1} (**4**) (see Fig. 1). The existence of the maximum can be explained by two reasons. First, highly hydrophobic compounds pass entirely to the micellar phase even at low micelle concentrations. The subsequent increase in the surfactant concentration in these systems can result in lower observed rate constants owing to dilution of reactants.[9] Second, the micellar effect in ion-molecular reactions is mostly due to the accumulation of the ionic reagent on the micellar surface caused by the electrostatic interactions with the head groups. An increase in the surfactant concentration in the solution leads to a higher concentration of the counterions, thus decreasing the potential of the micellar surface and displacing the reactive hydroxide ions from the Stern layer. This is the so-called salt effect, which accounts for the inhibition of micellar catalysts at higher surfactant concentrations.[10]

Several models for the analysis of kinetic dependences in aqueous micellar solutions are known; most of them are based on the pseudophase approach. Equation (1) formally coincides with the Michaelis—Menten equation, describing the kinetics of enzymatic reactions:

$$k_{obs} = \frac{k_w + k_m K'_s C_{surf}}{1 + K'_s C_{surf}}, \qquad (1)$$

where k_{obs}/s^{-1} is the observed pseudo-first-order rate constant; k_w and k_m/(s^{-1}) are the pseudo-first-order rate constants in the aqueous and micellar pseudophases, respectively; K'_s/mol^{-1} L is the constant of substrate binding in the coordinates of Eq. (1); C_{surf} is the surfactant concentration corrected for the critical micelle concentration (CMC).

This model is traditionally used for unimolecular reactions and pseudo-first-order reactions occurring in micellar surfactant solutions. It is applied to S-shaped kinetic curves; previously[11] it has been used for dependences with the maximum. We tested the applicability of Eq. (1) to kinetic profiles having a maximum and compared the results of calculations in terms of Eq. (1) with the results of analysis in terms of Eq. (2).[8] It was found that Eq. (2) allows one to conduct a more

Table 2. Observed rate constant of the alkaline hydrolysis of compounds **1—4** as a function of the concentration of CPB

Substrate	$k_{2,w}$[a] /mol^{-1} L s^{-1}	$(k_{obs}{}^b/k_w{}^c)_{max}$	K'_s /mol^{-1} L	k_m /s^{-1}	K_s mol^{-1} L	K_{OH} mol^{-1} L	$k_{2,m}$ /mol^{-1} L s^{-1}	F_c	F_m	$F_c \cdot F_m$
1	3.97	35	1260	0.080	2020	80	0.78	187	0.19	36
2	3.56	75	1950	0.150	3000	115	1.07	265	0.30	80
3	3.26	105	5750	0.171	4720	307	0.62	650	0.19	125
4	2.68	95	7020	0.155	7600	337	0.38	766	0.14	109

[a] $k_{2,w}$ is the second-order rate constant for the reaction in water without a surfactant.

[b] k_{obs} is the maximum observed pseudo-first-order rate constant in micellar solutions of surfactants.

[c] k_w is the pseudo-first-order rate constant in water without a surfactant under the experimental conditions.

detailed analysis of the kinetic data and to estimate various factors that determine the catalytic effect:

$$k_{obs} = \frac{(k_{2,w} + k_{2,m}) / VK_sK_{OH}C_{surf}}{(1 + K_sC_{surf})(1 + K_{OH}C_{surf})}, \qquad (2)$$

where $k_{2,w}$ and $k_{2,m}$ (mol^{-1} L s^{-1}) are the second-order rate constants for the reaction in the aqueous and micellar pseudophases, respectively; K_s/mol^{-1} L is the constant of substrate binding in the coordinates of Eq. (2); K_{OH}/mol^{-1} L is the constant of the binding of the hydroxide ion; and V is the molar volume of the surfactant, equal to 0.3 L mol^{-1}. The results of mathematical processing in terms of both equations are presented in Table 2 and demonstrate good agreement between the calculated parameters.

As the hydrophobicity of the alkoxy group increases, the constants of substrate binding (K_s and K'_s) increase. The binding constant for the hydroxide ions is also somewhat higher for hydrophobic substrates **3** and **4**. This difference can be explained by the fact that an increase in the hydrophobicity facilitates association of compounds **3** and **4**. Due to the cooperative character of micelle formation, it can be suggested that hydrophobic substrates favor the formation of larger aggregates with a larger surface charge,[12] which efficiently bind nucleophiles. The K_{OH} values found are in good agreement with those reported previously,[13] although they are somewhat higher than the K_{OH} values found in another study.[14]

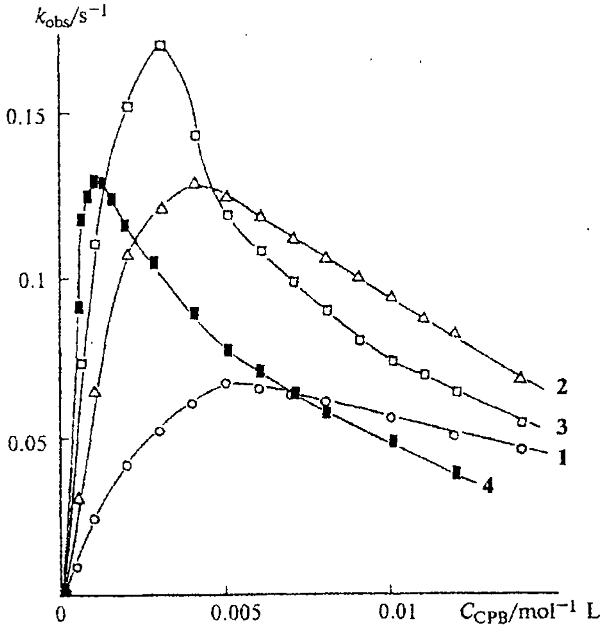

Fig. 1. Observed rate constant (k_{obs}) of the alkaline hydrolysis of substrates **1**—**4** as a function of the surfactant concentration in aqueous micellar solutions of CPB (25 °C, 0.0005 NaOH).

For all the substrates studied, the second-order reaction rate constant in the micellar phase is lower than that in water (see Table 2), which is consistent with published data.[8—10] The interaction of hydrophobic compounds with an anionic nucleophile occurs only in the surface layer of the micelle. The decrease in the reactivity of compounds in the micellar phase is apparently due to the decrease in the entropy of the process, caused by the restricted orientation of the substrate molecules in the micelle surface layer. The increase in $k_{2,m}$ observed on passing from substrate **1** to **2** points to the fact that a slight increase in the length of the substituent chain accelerates the reaction; however, further growth of the alkyl radical decreases the $k_{2,m}$ value. This decrease in the reaction rate may be related to an unfavorable entropy change, associated with the decrease in the mobility of substrates **3** and **4** as a result of dispersion interaction of the alkyl fragments with the hydrocarbon chains of surfactants. The decrease in the reaction rate can also be due to a decrease in the polarity of the microenvironment following the immersion of substrates in the micelle nucleus.

The Berezin model makes it possible to estimate quantitatively the factors determining the micellar catalytic effect and to describe the maximum acceleration by the following expression:[8]

$$(k_{obs}/k_w)_{max} = \frac{k_{2,m}}{k_{2,w}} \cdot \frac{K_sK_{OH}}{V(\sqrt{K_s} + \sqrt{K_{OH}})^2}, \qquad (3)$$

where $k_{2,m}/k_{2,w}$ (F_m) characterizes the influence of the change in the microenvironment of the reactants upon transfer of the reaction from water to the micellar phase, and $K_sK_{OH} / V(\sqrt{K_s} + \sqrt{K_{OH}})^2$ (F_c) takes into account the effect of accumulation of the reagents in the micelles. The data presented in Table 2 indicate that the maximum observed acceleration of the reaction, $(k_{obs}/k_w)_{max}$, is adequately described by the calculated parameter $F_c \cdot F_m$. It also follows from Table 2 that the concentration factor increases as the hydrophobicity of the substrates increases from 187 to 766. Evidently, the increase in the reaction rate due to the closer arrangement of the reactants could be nearly three orders of magnitude in the case of favorable influence of the micellar microenvironment. However, for all the substrates studied, $F_m < 1$, and this decreases the catalytic effect.

Thus, the observed reaction rate constant in the micellar solution of surfactants, unlike that in water, changes more than threefold as a function of hydrophobicity of the substrates. The catalytic effect increases in the series of substrates **1**—**3**. The major contribution to the micellar effect in this series comes from the accumulation of the reactants in the micelles. When the substrate hydrophobicity further increases, the catalytic effect diminishes, as shown by a decrease in the bimolecular reaction rate constant in the micellar phase.

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