Influence of the strong electrolyte on the aggregation behavior and catalytic properties of dicationic surfactants

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The introduction of potassium chloride into an aqueous solution of dicationic (gemini) surfactants results in the partial neutralization of the surface charge of micelles, which is accompanied by an increase in their size, a decrease in the critical concentration of micelle formation, a decrease in the surface potential of the system, and a change in the micellar influence on the hydrolytic stability of solubilized carboxylic esters.

Key words: dicationic surfactants, electrolyte, aggregation behavior, surface potential, micellar catalytic effect.

Dicationic (gemini) surfactants contain two hydrophobic radicals and two head groups bound by spacers with different degrees of rigidity. These compounds differ from amphiphilic analogs containing one head group and one hydrocarbon chain by lower (by an order of magnitude) values of critical micelle concentration (CMC) and high surface activity and wetting effect. They are characterized by the unusual morphological behavior, high solubilizing effect, and a possibility to considerably decrease the range of used concentrations.[1—7] The promising use of gemini surfactants as a medium for chemical reactions was shown.[6—11] There are data on high bactericidal activity of gemini surfactants[12,13] and their ability to form complexes with DNA and play a role of vector in genetic engineering.[14,15] Many publications devoted to the structural properties of systems based on gemini surfactants have appeared in the recent years; however, the number of works on studying their influence on the rate of chemical processes and establishing the factors determining their catalytic effect is substantially smaller.

It was shown for classical monocationic surfactants that the modification of their micellar solutions by additives of the background electrolyte substantially affects their aggregation behavior. This is related to the fact that an increase in the concentration of counterions of the surfactant attained by the introduction of an electrolyte results in the partial neutralization of the surface charge of micelles. The latter, in turn, decreases the destabilizing repulsion of likely charged head groups.[16,17] This decreases the absolute value of surface potential of the system and the CMC and increases the aggregation numbers. At certain concentrations, the electrolyte can induce micellar transitions "sphere"—"cylinder." [8,18] All these factors induce a change in the micellar influence on the physicochemical properties and reactivity of solubilized substances.[17,19]

In the present work, the properties of hexamethylene-1,6-bis(dimethylcetylammonium) bromide (Gem 6-16) in the presence of additive of the strong electrolyte (potassium chloride) were studied in order to reveal the possibility of directed control of the rate of chemical processes in solutions of dicationic surfactants. The influence of KCl on the aggregation behavior of this surfactant was considered. The micellar catalytic effect of solutions of Gem 6-16 was estimated for the alkaline hydrolysis of carboxylic esters: *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl caprinate (PNPC).

Experimental

Samples of gemini surfactant Gem 6-16 were synthesized by the reaction of *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexamethylenediamine with cetyl bromide in acetone followed by double recrystallization from EtOH using a known procedure.[20] The structures of the synthesized compounds were confirmed by elemental analysis and IR and NMR spectroscopy data. Commercially available Triton-X-100 (Sigma) and carboxylic esters (Fluka) containing 99% of the major substance were used.

The surface properties were studied by the ring detachment method on a Du Nouy tensiometer (Kruss). The data on the aggregate sizes were obtained by dynamic light scattering on a Malvern Instruments′ Zetasizer Nano spectrometer (He-Ne laser, 633 nm). Prior to measurements, the studied solutions were filtered using the Millipore filters with the pore diameter

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0.4 μm. The measurements were carried out at least three times for each sample.

The acid—base properties of *p*-nitrophenol were studied by measuring the absorbance of its ionized form at different pH values. The spectra were recorded on a Specord UV-VIS spectrophotometer in quartz cells with an absorbing layer thickness (L) of 1 cm in the range from 250 to 600 nm. The molar absorption coefficient (ε) of the phenoxide form was determined from the absorbance (D) measured at the wavelength corresponding to the absorption maximum at pH > 10. The concentration of the *p*-nitrophenoxide ion ($C_{\mathrm{PhO^-}}$) at a specified pH was determined from the equation $C_{\mathrm{PhO^-}} = D/\varepsilon L$, and p$K_\mathrm{a}$ of *p*-nitrophenol (p$K_\mathrm{a,app}$) was calculated by the Henderson—Hasselbach equation[21]

$$\mathrm{p}K_\mathrm{a,app} = \mathrm{pH} + \log\frac{C_\mathrm{PhOH}}{C_{\mathrm{PhO^-}}}, \qquad (1)$$

where C_PhOH is the concentration of *p*-nitrophenol.

The averaged values of p$K_\mathrm{a,app}$ determined from three to five independent experiments at different pH were used.

The kinetics of alkaline hydrolysis of *p*-nitrophenyl carboxylates was studied in 1 mM NaOH by spectrophotometry on a Specord UV-VIS instrument in temperature-controlled cells. The occurrence of the process was monitored by a change in the absorbance of the solutions at the wavelength 400 nm (formation of the *p*-nitrophenoxide anion). The initial concentration of the substrate was (2—8) $\cdot$ 10^{-5} mol L^{-1}, and the conversion was higher than 90%. The apparent rate constants of the pseudo-first order (k_app) were determined from the dependence

$$\log(D_\infty - D_\tau) = -0.434k_\mathrm{app}\tau + \mathrm{const},$$

where D_τ and D_∞ are the absorbances of solutions at the moment τ and after the completion of the reaction. The values of k_app were calculated by the least-squares method.

Results and Discussion

The values of CMC in solutions of Gem 6-16 were determined by the tensiometric method. It was shown that an additive of potassium chloride facilitated the process of micelle formation: at the concentrations C_KCl equal to 0, 0.001, and 0.01 mol L^{-1} the CMC value is $4.5 \cdot 10^{-5}$, $2.8 \cdot 10^{-5}$, and $1.7 \cdot 10^{-5}$ mol L^{-1}, respectively. The micelle size increased, as it was detected by the dynamic light scattering method. The increase in the hydrodynamic diameter (d_h) caused by the addition of potassium chloride to a solution of Gem 6-16 with the concentration 0.005 mol L^{-1} is illustrated in Fig. 1. As the electrolyte concentration increases from 0 to 0.1 mol L^{-1}, the value of d_h varies from 2 to 7 nm. The result obtained agrees with the data of the work[22] in which the change in the micellar size in an aqueous solution of Gem 6-16 (C_Surf = = 0.03 mol L^{-1}) under the action of potassium bromide additives was observed by the dynamic light scattering method. The aggregates become larger due to a decrease in the repulsion of the head groups upon the neutralization of the surface charge of the micelles by anions of the added electrolyte, resulting in an increase in the aggregation numbers and, hence, the micelle size.

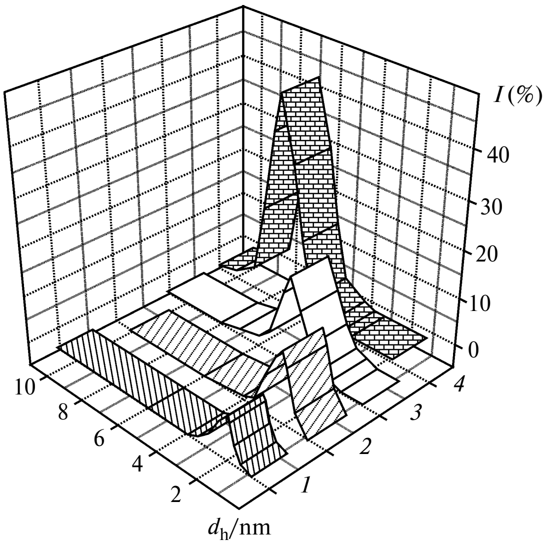

Fig. 1. Size of micelles Gem 6-16 in an aqueous solution in the absence (*1*) and in the presence of potassium chloride in the concentration 0.001 (*2*), 0.01 (*3*), and 0.1 mol L^{-1} (*4*) (C_Surf = = 0.005 mol L^{-1}, 25 °C).

To determine the values of surface potential of Gem 6-16 in the presence of the electrolyte, we used the accepted approach to imply the study of the spectral properties of probing molecules capable of incorporating into the interfacial layer and respond to the changes in its structure.[23] *p*-Nitrophenol, whose pK$_\mathrm{a}$ values were determined by spectrophotometry at the absorption band maximum of its anionic form (λ = 400 nm, $\varepsilon \approx$ 18000 L mol^{-1} cm^{-1}), was chosen as such a probe. The apparent value of pK_a (p$K_\mathrm{a,app}$) was calculated using Eq. (1) by the determination of *p*-nitrophenol absorption at different pH. The changes in p$K_\mathrm{a,app}$ of *p*-nitrophenol at different concentrations of the studied surfactants are shown in Fig. 2.

According to Ref. 23, the surface potential (Ψ) was estimated by Eq. (2)

$$\mathrm{p}K_\mathrm{a,m} = \mathrm{p}K_\mathrm{a,n} - \frac{F\Psi}{2.303RT}, \qquad (2)$$

where p$K_\mathrm{a,m}$ is the negative logarithm of the dissociation constant in the micellar phase ($K_\mathrm{a,app} = K_\mathrm{a,m}$ at $C_\mathrm{Surf} \to \infty$); p$K_\mathrm{a,n}$ is the non-electrostatic component determined as pK_a in micellar solutions based on non-ionic surfactants (in a solution of Triton-X-100 pK_a of *p*-nitrophenol is 7.6); F = 96486 C mol^{-1} is Faraday´s constant, and R = 8.314 J K^{-1} mol^{-1} is the gas constant.

It follows from the data in Table 1 that the influence of *p*-nitrophenol on p$K_\mathrm{a,m}$ decreases with an increase in the concentration of potassium chloride, which is explained by a decrease in the surface potential. A similar decrease in Ψ upon the introduction of the strong electrolyte has

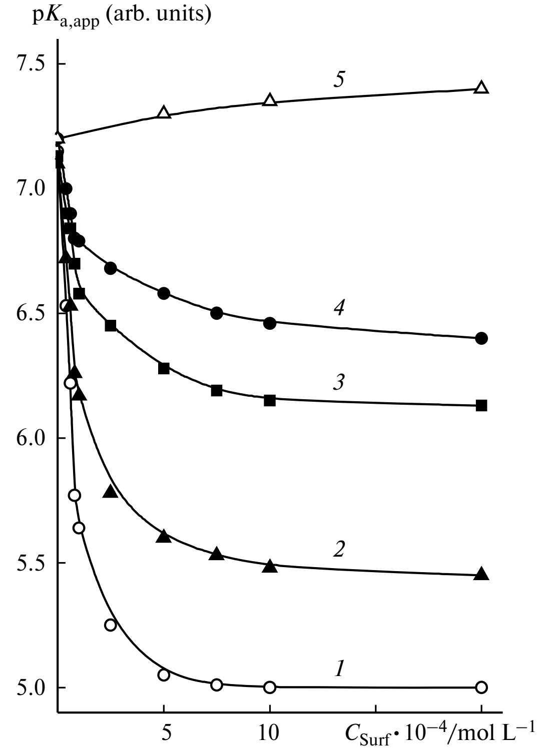

Fig. 2. Dependence of p$K_{a,app}$ of *p*-nitrophenol on the concentration of the surfactants Gem 6-16 (*1—4*) and Triton-X-100 (*5*) in the absence (*1* and *5*) and in the presence of KCl in the concentration 0.001 (*2*), 0.01 (*3*), and 0.1 mol L^{-1} (*4*).

been observed previously[24] for cetyltrimethylammonium bromide (CTAB); however, the changes in the case of this monomeric surfactant are substantially lower than that of the dimeric analog (for CTAB, the values of Ψ are 133 and 120 mV at the KCl concentration 0 and 0.01 mol L^{-1}, respectively).

Micellar solutions of Gem 6-16 were used as a reaction medium for the alkaline hydrolysis of carboxylic esters, *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl caprinate (PNPC) (Scheme 1).

Scheme 1

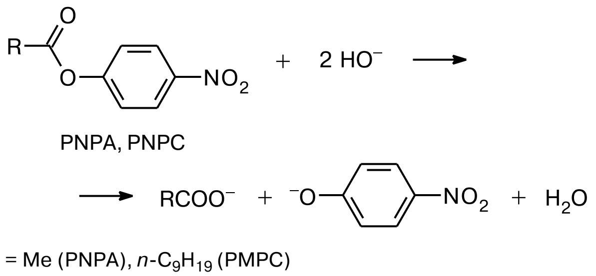

Table 1. Influence of the electrolyte (KCl) on p$K_{a,m}$ of *p*-nitrophenol and on the surface potential (Ψ) micelles Gem 6-16

C_{KCl}/mol L^{-1}	p$K_{a,m}$	Ψ/mV
0	5.00	154
0.001	5.45	127
0.01	6.15	91
0.1	6.40	71

The catalytic effect expected for this process in solutions of cationic surfactants is explained, first of all, by concentrating of hydroxide ions at the positively charged interface, which increases the probability of the reaction contact of the hydrophilic nucleophile with the substrate solubilized by the micelle. A decrease in the surface potential caused by the introduction of additives of the strong electrolyte should decrease the concentrating effect and, hence, the catalytic action of micelles. Another factor affecting the catalytic effect in the system is binding of the substrate by the micelle, which determines the distribution of the substrate between the voluminous medium and dispersion phase. The results of kinetic experiments illustrating the changes in the apparent rate constant of alkaline hydrolysis of PNPA and PNPC at different concentrations of Gem 6-16 are shown in Fig. 3. The data obtained indicate a decrease in the catalytic effect of the system upon the introduction of potassium chloride, and PNPC is more sensitive to the electrolyte additive than PNPA.

The obtained kinetic data were analyzed in terms of the pseudo-phase model of micellar catalysis[25] using Eq. (3)

$$k_{app} = \frac{k_m K_S C_{Surf} + k_0}{1 + K_S C_{Surf}}, \qquad (3)$$

where k_0 and k_m (s^{-1}) are the first-order rate constants in an aqueous medium and in the micellar phase, respectively; K_S (L mol^{-1}) is the binding constant of the substrate; and C_{Surf} is the total concentration of the surfactant minus the CMC.

The quantitative characteristics determined by this equation are given in Table 2. The obtained results revealed the decrease in the substrate binding by micelles of Gem 6-16 upon the addition of potassium chloride to the solution. The calculated values of the alkaline hydrolysis rate constants in the micellar phase make it possible to estimate the catalytic effect characterized by the ratio k_m/k_0, which reaches one order of magnitude for PNPA and 530 for PNPC in the absence of electrolyte additives. In the case of PNPA, the electrolyte additive insignificantly decreases the catalytic effect. In the case of PNPC, the electrolyte additive results in a sharp (by an order of magnitude and more) decrease in the value of hydrolysis acceleration. This distinction can be explained by different hydrophobicities of the substrates and, hence, their

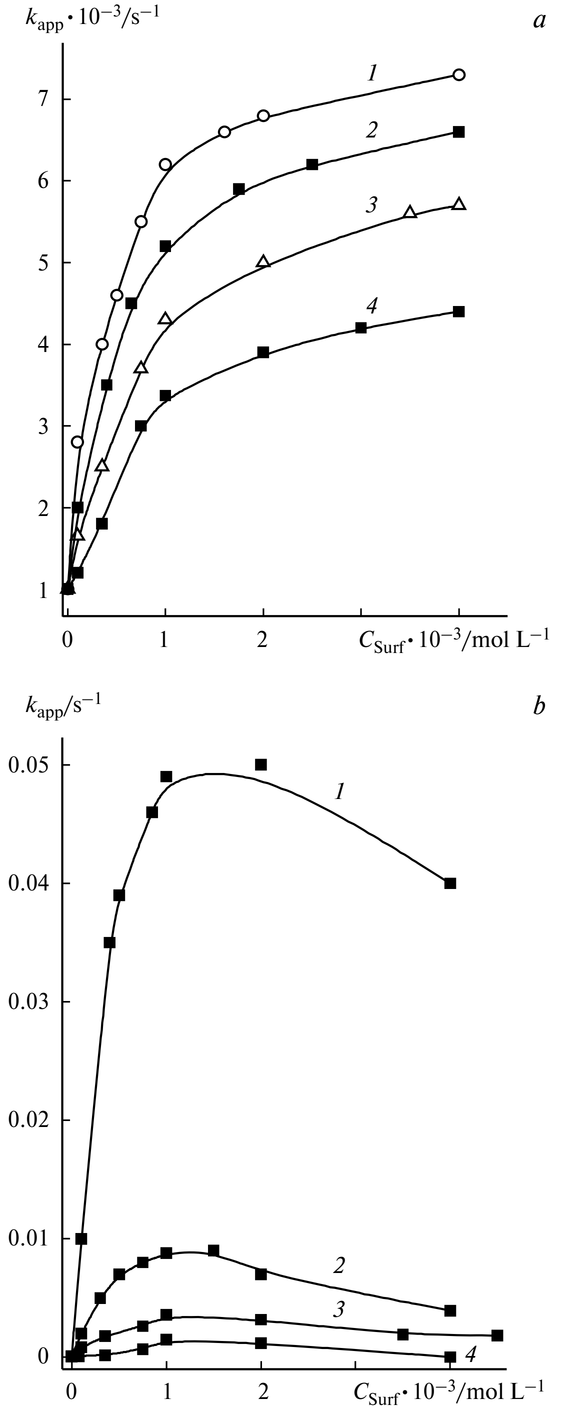

Fig. 3. Apparent rate constant of alkaline hydrolysis (k_{app}) of PNPA (*a*) and PNPC (*b*) *vs* concentration of Gem 6-16 in the absence (*1*) and in the presence of KCl in the concentration 0.001 (*2*), 0.01 (*3*), and 0.1 mol L^{-1} (*4*) (NaOH, 25 °C).

Table 2. Influence of KCl on the parameters of the alkaline hydrolysis[a] of PNPA and PNPC in micellar solutions of Gem 6-16

C_{KCl}/mol L^{-1}	k_m /s^{-1}	K_S /L mol^{-1}	CMC /mol L^{-1}	k_m/k_0[b]
		PNPA		
0	0.0079	3010	0.00010	9
0.001	0.0072	2430	0.00011	8
0.01	0.0064	1650	0.00012	7
0.1	0.0050	1420	0.00068	5.5
		PNPC		
0	0.0530	7290	0.000069	530
0.001	0.0110	3490	0.000042	110
0.01	0.0044	2510	0.000019	44

[a] Hydrolysis conditions: 1 m*M* NaOH, 25 °C.

[b] The values of k_0 for PNPA and PNPC are $0.9 \cdot 10^{-3}$ and $0.1 \cdot 10^{-3}$ s^{-1}, respectively.

different localization in a micellar solution. More hydrophilic PNPA is characterized by a lower binding constant, which results in its distribution between the voluminous phase and micelle, whereas the value of K_S for PNPC indicates that this substrate is localized in the micelle. According to the pseudo-phase model of micellar catalysis, the apparent rate constant is an additive value and describes the occurrence of the process in the both phases. A decrease in the surface potential upon the introduction of the electrolyte diminishes the ability of the micelle to concentrate the nucleophile, which decreases the rate constant in the micellar phase. Therefore, the introduction of the electrolyte should strongly affect the hydrolysis rate of the hydrophobic substrate. For PNPA, whose portion reacts in the voluminous aqueous phase, the decrease in the surface potential upon the introduction of KCl is not so substantial and the micellar catalytic effect decreases insignificantly.

Thus, the influence of the strong electrolyte on the aggregation behavior and catalytic properties of the dicationic surfactants was examined using Gem 6-16 as an example. The data obtained show that Gem 6-16 exerts a high catalytic effect on the cleavage of carboxylic esters, which is displayed at lower concentrations than that for monomeric analogs. The introduction of a strong electrolyte into a solution of Gem 6-16 substantially decreases the surface potential and decreases the micellar catalytic effect. On the one hand, understanding of the role of the electrolyte will allow one to control the rate of chemical processes in solutions of the dicationic surfactants. On the other hand, the possibility of the micellar catalytic effect in media with a certain amount of salt additives containing the high concentration of buffer components or background electrolytes can really be estimated.

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