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Geminal Alkylammonium Surfactants: Aggregation Properties and Catalytic Activity

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Abstract—Geminal alkylammonium surfactants containing a hexamethylene spacer show a specific behavior, namely, a catalytic effect at low concentrations of the detergent in the system. The critical micellization concentrations of these surfactants are by an order of magnitude lower than those of the related surfactants with one hydrophobic fragment. The effect exerted on the hydrolysis of carboxylic acid esters by micellar structural rearrangements induced by addition of a supporting electrolyte is determined. **DOI:** 10.1134/S1070363206100215

The interest in geminal surfactants and highly organized systems based on them considerably increased in the past decade. Geminal surfactants contain two hydrophobic radicals and two head (as a rule, charged) groups linked by rigid or flexible spacers. These compounds differ from their amphiphilic analogs containing one head group in higher (by an order of magnitude) surface activity and lower critical micellization concentrations (CMC) [1–4]. They are used as gelating substances and biologically active additives, and also in synthesis of new mesoporous materials.

The structural similarity of lipids and geminal

$$[R(CH_3)_2 N(CH_2)_6 N(CH_3)_2 R] 2Br^-,$$

R = C₁₂H₂₅ (Gem-1). C₁₆H₃₃ (Gem-2)



In this study we examined the aggregation behavior and catalytic activity in cleavage of ester bonds of geminal alkylammonium surfactants containing a hexamethylene spacer and differing in the length of the hydrophobic fragment and structure of the head group:



The properties of these compounds are compared to those of the related cationic surfactants containing one hydrophobic fragment.

It is known that geminal surfactants containing a hexamethylene spacer between the charged centers form micelles in aqueous solutions at low concentrations $(10^{-4}-10^{-6} \text{ M})$ [11, 12]. We studied the aggregation behavior of Gem-1–Gem-3 by conductometry. The intersection point of the linear portions of the concentration dependences of the specific electrical conductivity corresponds to the CMC values, and the



Fig. 1. Concentration dependence of the specific electrical conductivity of aqueous solutions of Gem-2. The insert shows the range of low concentrations.

ratio of the slopes above and below CMC corresponds to the degree of ionization of the micelle (α). Table 1 shows that, as compared to "one-tail" analogs (published conductometric data are given), the CMC values of geminal surfactants are lower by an order of magnitude. Also, it can be seen that an increase in the hydrophobicity of the alkyl radical in geminal surfactants facilitates the micelle formation. Replacement

Table 1. CMC values and degrees of binding of counterionsfor the surfactants studied (conductometry, water, 30°C)

Surfactants	CMC ₁ , M	α
Gem-1	0.00125	0.36
Gem-2	0.000045	0.23
	(CMC ₂ 0.0012 M)	
Gem-3	0.0017^{a}	0.29
Cetyltrimethylammonium	0.00092 ^a [13]	0.22 ^a [13]
bromide	0.0092 [14]	0.25 [14]
Tetradecyltrimethyl-	0.0036 ^a [13]	0.23 ^a [13]
ammonium bromide	0.00394 [14]	0.27 [14]
Dodecyltrimethyl-	0.0145 ^a [13]	0.25 ^a [13]
ammonium bromide	0.0153 [14]	

^a At 25°C.

of the dimethyl fragment (Gem-1) by the piperidyl moiety (Gem-3) leads to an increase in CMC, which suggests that CMC is influenced by packing of the surface layer. The curve for Gem-2 shows a second bend at a concentration of 0.0017 M (Fig. 1), which is identified as CMC₂ and may correspond to micellar structural transitions from spherical to ellipsoidal aggregates. For example, a small-angle neutron scattering study of Gem-2 [11] revealed at a concentration of 0.0025 M micelles in the form of elongated ellipsoids with semimajor and semiminor axes of 3.2 and 2.3 nm, respectively. The ratio between the semiaxis lengths increases with the surfactant concentration. The parameter α estimated for Gem-2 by small-angle neutron scattering for limiting concentrations of 0.03 M is 0.25-0.27 [11], which is consistent with our conductometric data (Table 1). It is logical to expect for Gem-2 a transition to cylindrical micelles at a certain high concentration; even at a concentration of 0.05 M, the ratio of the ellipsoid semiaxes increases to 2.5, and α decreases to 0.16 [11]. However, in our conductometric studies we have not reached the Gem-2 concentration at which the formation of cylindrical aggregates could be detected.

Micellar solutions of the surfactants were used as reaction media for base hydrolysis of carboxylic acid esters: *p*-nitrophenyl acetate and *p*-nitrophenyl laurate. The general equation of the reaction is as follows:

The catalytic effect expected for this reaction in solutions of cationic surfactants is primarily associated with accumulation of hydroxide ions at the positively charged interphase surface, which increases the probability of the reaction contact of the hydrophilic nucleophile with the substrate solubilized by the micelle. The dependences of the observed rate constant (k_{obs}) of the base hydrolysis on the concentration of the cationic surfactant are shown in Figs. 2 and 3. These data show that the geminal surfactants in hand exert on the cleavage of ester bonds a strong catalytic effect manifested at lower concentrations compared to "one-tail" analogs.

It should be noted that the esters we chose differ in the hydrophilic–lipophilic properties (the distribution ratio between oil and water is 10.8 for *p*-nitrophenyl acetate and 205.4 for *p*-nitrophenyl laurate [15]), which should be reflected in the effect of surfactants on the rate of their hydrolysis. Figures 2 and 3 show that the micellar catalytic effect for these substrates differs essentially. Whereas the rate constant for the



Fig. 2. Observed rate constant of base hydrolysis of *p*-nitrophenyl acetate as a function of surfactant concentration (pH 10.0, 25° C): (1) Gem-1, (2) cetyltrimethylammonium bromide, (3) Gem-2, (4) Gem-3, (5) tetradecyltrimethylammonium bromide, and (6) dodecyltrimethylammonium bromide.

acetate increases by a factor of $\sim 4-8$, for the laurate the reaction is accelerated by two orders of magnitude. The amphiphilic structure of the laurate in aqueous solutions promotes its self-association, which leads to shielding of the active centers of the substrate and, as a consequence, to abnormally low reactivity of the laurate, compared to acetate, in base hydrolysis in aqueous solutions [16]. In micellar solutions, incorporation of the hydrophobic laurate into a surfactant micelle is accompanied by unrolling of its globular associates, which makes the substrate accessible to the attack of a nucleophile and results in considerable acceleration of the hydrolysis (Fig. 3).

Quantitative characteristics reflecting the interaction of a substrate with a micelle can be derived from the experimental kinetic data using a pseudophase model of micellar catalysis [17], Eq. (1):

$$k_{\rm obs} = \frac{k_{\rm m} K_{\rm s} C_{\rm det} + k_0}{1 + K_{\rm s} C_{\rm det}},\tag{1}$$

where C_{det} is the surfactant concentration corrected for the critical micellization concentration (CMC); k_0



Fig. 3. Observed rate constant of base hydrolysis of *p*-nitrophenyl laurate as a function of surfactant concentration (pH 10.0, 25° C): (1) cetyltrimethylammonium bromide, (2) Gem-1, (3) Gem-3, (4) Gem-2, and (5) tetra-decyltrimethylammonium bromide.

and $k_{\rm m}$ are the rate constants in aqueous solution and in the micellar phase, respectively; and $K_{\rm s}$ is the substrate binding constant. The calculation results are given in Table 2.

These data show that, for surfactants with one hydrophobic fragment, the *p*-nitrophenyl acetate binding constants are low, and the catalytic effect strongly depends on the number of carbon atoms in the alkyl radical. The strongest acceleration of the hydrolysis of the ester is observed with cetyltrimethylammonium bromide, whereas the effect of dodecyltrimethylammonium bromide is so weak that, e.g., curve 6 in Fig. 2 is not described by the equation of the pseudophase model. Geminal surfactants, compared to those with one hydrophobic fragment, are characterized by better binding of the substrate (Table 2). For Gem-1 and Gem-3 containing the same dodecyl fragment, the $K_{\rm s}$ values are close, and for the cetyl derivative they are higher. However, the extent of the reaction acceleration is similar for all the three surfactants. This fact suggests that, for geminal surfactants, the contribution of the electrostatic interactions providing accumula-

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Surfactant	Substrate	$k_{\rm m}, \ {\rm s}^{-1}$	$K_{\rm s}$, 1 mol ⁻¹	CMC, M	$k_{\rm obs}({\rm max})/k_0^{a}$
Cetyltrimethylammonium bromide	Acetate	0.0073	450	0.0004	7
5 5	Laurate	0.011	1100	0.00044	275
Tetradecyltrimethylammonium bromide	Acetate	0.0043	360	0.0007	3
	Laurate	0.0038	710	0.0006	95
Gem-1	Acetate	0.0065	820	0.00008	8
	Laurate	0.0045	4000	0.0006	113
Gem-2	Acetate	0.0053	2300	0.00004	6
	Laurate	0.0044	8000	0.00008	110
Gem-3	Acetate	0.0052	850	0.00005	6
	Laurate	0.0053	1100	0.00008	125

Table 2. Parameters of micellar-catalyzed base hydrolysis of *p*-nitrophenyl acetate and *p*-nitrophenyl laurate in solutions of various surfactants (pH 10.0, 25° C)

^a The $k_{obs}(max)/k_0$ ratio characterizes the micellar catalytic effect (without surfactant at pH 10.0, for the hydrolysis of the acetate, $k_0 = 0.0008 \text{ s}^{-1}$, and for the laurate, $k_0 = 0.0004 \text{ s}^{-1}$).

tion of hydroxide ions at the micellar surface appreciably exceeds the contribution of hydrophobic interactions.



Fig. 4. Observed rate constant of base hydrolysis of *p*-nitrophenyl acetate as a function of surfactant concentration with addition of KBr and without it (0.005 M NaOH, 25°C): (1) Gem-2, $C_{\text{KBr}} = 0$; (2) cetyltrimethyl-ammonium bromide, $C_{\text{KBr}} = 0$; (3) cetyltrimethylammonium bromide, $C_{\text{KBr}} = 0$; (3) cetyltrimethylammonium bromide, $C_{\text{KBr}} = 0.01$ M: and (4) Gem-2, $C_{\text{KBr}} = 0$.

The low value of CMC of Gem-2, estimated from the kinetic data, is consistent with that determined from the conductometric rata (Tables 1, 2). For geminal surfactants with the dodecyl fragment, however, such agreement is not observed. Apparently, in this case premicellar aggregation is possible, which favorably affects the localization of the reactants in the system but is not manifested in the electrical conductivity. The geminal compounds examined allow preparation of micellar systems containing small amounts of surfactants but exhibiting a strong catalytic effect.

As expected, the hydrolysis of the esters is accelerated in going to more alkaline solutions (Fig. 4). However, an increase in the concentration of hydroxide ions in going from the buffer system with pH 10.0 to 0.005 M NaOH does not cause significant changes in the binding constants of the substrate with the micelle and in the CMC values determined from the kinetic data (Tables 2, 3). This fact suggests the absence of significant changes in the structure of the micelles and accounts for the similar extent of acceleration of the *p*-nitrophenyl acetate hydrolysis.

Additions of supporting electrolytes are frequently used to initiate structural transformations in micellar systems and thus to alter their catalytic effect [18, 19]. An increase in the concentration of surfactant counterions on adding an electrolyte leads to partial neutralization of the surface charge of the micelles, which, in turn, decreases the destabilizing repulsion of the similarly charged head groups. This leads to a decrease in the absolute value of the surface potential of the system, a decrease in CMC, an increase in the aggregation number, and also a change in the micellar effect on the physicochemical properties and reactivity of solubilized substances.

Surfactant	C _{KBr} , M	k_0, s^{-1}	$k_{\rm m}, {\rm s}^{-1}$	$K_{\rm s}$, $1 {\rm mol}^{-1}$	СМС, М	$k_{\rm m}/k_0$	
Cetyltrimethylammonium bromide Gem-2	0 0.01 0 0.01	0.042 0.032 0.042 0.032	0.18 0.06 0.28 0.058	420 230 2500 3100	0.0005 0.0002 0.000047 0.00035	4.3 1.9 6.7 1.8	

Table 3. Parameters of micellar-catalyzed base hydrolysis of *p*-nitrophenyl acetate without supporting electrolyte and in the presence of potassium bromide (0.005 M NaOH, 25° C)

Zakharova et al. [19–21] showed that addition of KBr to a micellar solution of cetyltrimethylammonium bromide decreases the amount of hydroxide ions (species inducing cleavage of ester bond) in the Stern layer and, under certain conditions, can induce sphere–cylinder micellar transitions.

The dependences of the observed rate constant of base hydrolysis (0.005 M NaOH) of *p*-nitrophenyl acetate in micellar solutions of cetyltrimethylammonium bromide and Gem-2 on the cationic surfactant concentration (Fig. 4) show that addition of KBr $(C_{\text{KBr}} = 0.01 \text{ M})$ decreases the catalytic effect. The system based on the geminal surfactant is more sensitive to the addition of the supporting electrolyte. However, analysis of our data using Eq. (1) shows that this concentration of KBr is insufficient to induce structural rearrangements in the system (Tables 2, 3). A decrease in the rate of the base hydrolysis is caused by a decrease in the surface potential of the micelle (by analogy with [21]), leading to a decrease in the capability of the system to concentrate hydroxide ions at the interphase layer. As a result, the catalytic effect decreases.

A kinetic study of the base hydrolysis of p-nitrophenyl esters in relation to the KBr concentration at a constant content of Gem-2 in solution shows that, with increasing KBr content, the observed rate constant decreases nonuniformly. The dependences of $k_{\rm obs}$ on log $C_{\rm KBr}$ (Fig. 5) are broken lines with a bend in a point $C_{\rm cr}$. At the same surfactant concentration, the $C_{\rm cr}$ values virtually coincide for both substrates. The fact that the value obtained is independent of the structure of the ester means that it characterizes the properties of the micellar system itself. With an increase in the surfactant content in the system, smaller amounts of the electrolyte are required to induce the rearrangement: The transition is observed at a total concentration of bromide ions of about 0.023 M. Similar dependences were obtained with micellar solutions of cetyltrimethylammonium bromide as media for the hydrolysis of carboxylic acid esters (Fig. 5, insert). The $C_{\rm cr}$ value for this surfactant is higher than for Gem-2; the total concentration of bromide ions at which the transition is observed is 0.03 M.

Presumably, in solutions of geminal surfactants, addition of an electrolyte induces micellar rearrangements similar to those occurring with an increase in the surfactant concentration. Passing to cylindrical systems leads to an increase in the density of packing



Fig. 5. Observed rate constant of base hydrolysis of carboxylic acid esters (25°C) in micellar solutions of Gem-2 as a function of the logarithm of the KBr concentration: (1, 2) $C_{\text{surfactant}} = 0.0025$ M, (1) p-nitrophenyl acetate and (2) p-nitrophenyl laurate; (3) $C_{\text{surfactant}} = 0.005$ M, p-nitrophenyl acetate. Insert: similar dependence for cetyltrimethylammonium bromide: (1) p-nitrophenyl acetate, $C_{\text{surfactant}} = 0.005$ M; (2) p-nitrophenyl laurate; C_{surfactant} = 0.005 M;

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Surfactant	T _m , °C	C, %		Н, %		N, %		Br, %	
		found	calculated	found	calculated	found	calculated	found	calculated
Gem-1 Gem-2 Gem-3	232–234 203–204 209–210	60.8 64.3 64.2	60.92 64.42 64.00	11.91 12.13 11.15	11.13 11.58 10.93	4.24 3.56 3.80	4.18 3.57 3.73	24.2 21.0 21.65	23.84 20.41 21.33

Table 4. Characteristics of the synthesized samples of geminal surfactants

of surfactant molecules in the aggregate, enhancement of hydrophobic interactions, changes in the degree of hydration, amd decrease in the degree of ionization of the head groups. As a result, in the range of existence of cylindrical micelles, the catalytic effect of solutions of geminal alkylammonium surfactants on the base hydrolysis of carboxylic acid esters is weak, like that of cylindrical micelles of cetyltrimethylammonium bromide. The strongest acceleration of the process is observed at low concentrations of the detergent in solution, in the range of existence of spheroidal aggregates, which makes systems based on geminal surfactants attractive for efficient cleavage of ester bonds.

EXPERIMENTAL

For the studies we used commercial samples of cetyl-, tetradecyl-, and dodecylammonium bromides (Sigma), and also *p*-nitrophenyl esters of carboxylic acids (Fluka) with the main substance content of 99%. Samples of geminal surfactants were prepared by reactions of *N*,*N*-tetrasubstituted hexamethylenediamine with alkyl bromides in acetone, followed by double recrystallization of the products from ethanol, as described in [5]. The structures of the compounds were confirmed by elemental analysis (Table 4) and ¹H NMR spectroscopy.

The kinetics of decomposition of esters in alkaline solutions was monitored spectrophotometrically on a Specord UV-Vis device at 25°C. The reaction progress was monitored by variation of the optical density of solutions at $\lambda = 400$ nm (formation of *p*-nitrophenolate anion). The initial concentration of the substrate was 5×10^{-5} M, and the conversion, >90%.

The observed pseudo-first-order rate constants k_{obs} were determined from the dependence $\log (D_{\infty} - D_t) =$ $-0.434k_{obs}t$ + const, where D_t and D_{∞} are the optical densities of solutions at time t and after the reaction completion, respectively. The k_{obs} values were calculated by the least-squares method.

The specific electrical conductivity of surfactant solutions prepared in double-distilled water (conduc-

tivity $\leq 1.8 \ \mu S \ cm^{-1}$) was determined with a CDM-2d device (Denmark).

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