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Aqueous Solutions of Geminal Alkylammonium Surfactants as a Medium for Reactions of Long-Chain Amines

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Abstract—The formation of surfactant–hydrophobic amine mixed aggregates reduces the pK_a of long-chain amines by 1–1.5 units compared with those in molecular solutions and is an important factor responsible for the high catalytic effect of the system in ester bond cleavage. In aqueous solution of geminal surfactants, the rate of azomethine formation in the reaction of long-chain amines with benzaldehydes is an order-of-magnitude higher than in ethanol.

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An important feature of aqueous micellar solutions of surfactants is their ability to solubilize chemically active compounds with various hydrophilic–lipophilic properties, which considerably extends the possibility of using such solutions as a reaction medium [1–4]. The solubilization of reagents in surfactant solutions affects the microenvironment (medium effect) and thus reactivity of the reagents and their acid–base and spectral properties, as well as other physicochemical parameters. Another consequence of solubilization is concentration of the reagents in a micelle, which enhances the probability of their reaction contact (cage effect). These two factors exert a decisive effect of the kinetics of chemical reactions in the micellar medium, and they are primarily controlled by the structure of the surfactant, component ratio in the system, and response of the latter on reagents and modifying additives.

Over the past decade there has been an outburst of interest in germinal (dimeric) surfactants and highly organized systems on their basis. Geminal surfactants contain two hydrophobic radicals and two head (most frequently, charged) groups linked by rigid or flexible spacers. These compounds differ from their amphiphilic analogs in that they have an order-of-magnitude lower critical micelle concentrations (CCM), high surfactant activity, viscoelastic and wetting properties, and exhibit an unusual morphologic behavior [5–8]. A series of papers concerning the aggregation behavior and structural properties of germinal surfactants have been published [9–11]. The catalytic effect of micellar surfactant solutions in nucleophilic substitution reactions have been reported [12–16].

To gain insight into the feasibility of aqueous solutions of водных растворов geminal cationic surfactants as a medium for tractions involving hydrophobic alkylamines, we suggested to determined the solubility of these compounds in micellar solutions of hexamethylenebis(cetyldimethylammonium) bromide (Gem-16) and hexamethylenebis(dimethyldodecylammonium) bromide (Gem-12) and also to assess their effect on the basicity and nucleophilicity of amines. Two processes involving long-chain aliphatic amines were studied: cleavage of *p*-nitrophenyl esters of carboxylic acids and formation of azomethines in reactions with benzaldehyde. The properties of geminal surfactants are discussed in comparison with the behavior of analogous monomeric cationic surfactants: dodecyltrimethylammonium and cetyltrimethylammonium bromides.

Water is an inappropriate medium for reactions involving long-chain aliphatic amines because of the restricted solubility of the latter. This problem is solved in part by using cationic surfactants. The solubilities of octyl-, decyl-, dodecyl-, and cetylamines in water and aqueous solutions of geminal surfactants

Gem-12 and Gem-16 and their analogs dodecyltrimethylammonium and cetyltrimethylammonium bromides were determined by potentiometric titration. The resulting data (see Fig. 1) show that the surfactants studied all favor enhanced solubility of long-chain amines, and, therewith, Gem-16 solutions exhibit the highest solubilizing ability. Thus, for instance, the solubility of decylamine in these solutions is 25 times higher than in water and an order of magnitude higher than in solutions of a monomeric surfactant (cetyltrimethylammonium bromide). Amines dissolved in micellar solutions of the cationic surfactants in study have much lower pK_a values than in water (Table 1). The main reason for this effect consists in preferential solubilization of the neutral form of amines with the positively charged micelle surface. The strongest effect on pK_a (1–1.5 units) is characteristic of Gem-16, in agreement with the higher solubilizing ability of this surfactant.

Importantly, it is unprotonated amines that exhibit nucleophilic properties in chemical reactions. Thus, the use of cationic surfactants (first of all, Gem-16) extends the synthetic potential of amines, allowing reactions to be performed in aqueous solutions in mild conditions (in weakly alkaline media). This statement can be illustrated by the nucleophilic substitution reaction in *p*-nitrophenyl esters of carboxylic acids.

Scheme 1 shows two main directions of ester cleavage in the presence of primary amines in molecular aqueous solutions: aminolysis (main reaction) and alkaline hydrolysis (side reaction).

Scheme 1.

$$RC(O)OC_6H_4NO_2\text{-}p \xrightarrow{R'NH_2} RC(O)NHR' + HOC_6H_4NO_2\text{-}p$$

$$RC(O)OC_6H_4NO_2\text{-}p \xrightarrow{^2OH^-} RC(O)O^- + {}^-OC_6H_4NO_2\text{-}p$$

R, R' = C_nH_{2n+1}.

In micellar solutions of cationic surfactants, both reactions can be accelerated. Studying the kinetics of ester cleavage in the presence and in the absence of amines (at the same pH) allows separation of the contributions of aminolysis and hydrolysis in the overall reaction rate. The plots of the observed rate constant (k_{obs}) of cleavage of *p*-nitrophenyl acetate (R = CH_3) versus surfactant concentration are shown in Figs. 2 and 3. As seen, alkaline hydrolysis contributes very little in the overall reaction rate; however, it will be remembered that this contribution can increase with increasing pH of the solution and decreasing fraction of the unprotonated form of the amine. Comparison of the $k_{obs} = f(c_{surf})$ dependences for octylamine in

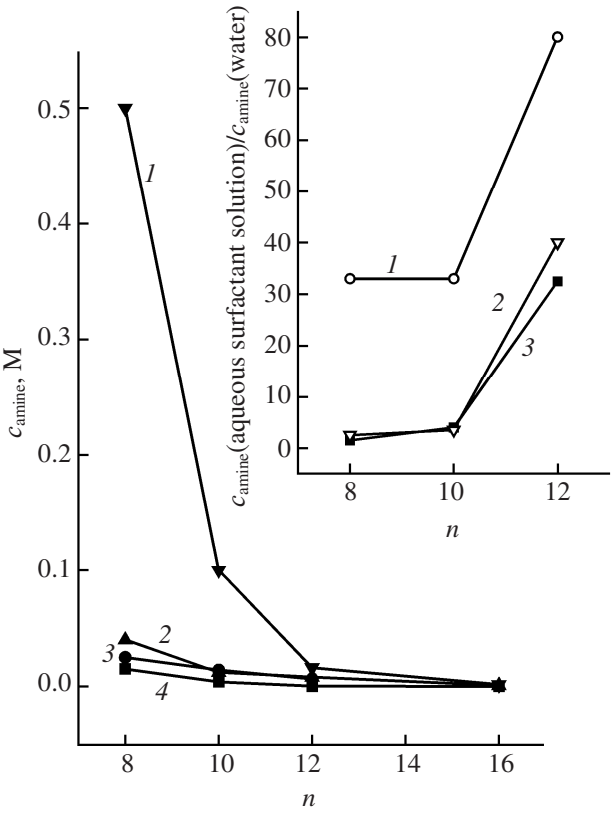


Fig. 1. Effect of the radical chain length in normal primary aliphatic amines on their solubility in water and aqueous solutions of cationic surfactants (c_{surf} 0.005 M, 25°C): (*1*) Gem-16, (*2*) Gem-12, (*3*) cetyltrimethylammonium bromide, and (*4*) no surfactant. Insert: Data on the solubility of amines in micellar solutions, normalized with respect to water (*n* is the number of carbon atoms in the radical).

Table 1. pK_a of amines in aqueous micellar solutions (c_{surf} 0.01, c_{amine} 0.005 M, 20°C)

Surfactant	Octylamine	Decylamine	Dodecylamine[a]
–	10.6	10.1	–
Dodecyltrimethylammonumbromide	10.6	9.8	–
Cetyltrimethylammonium bromide	9.9	9.4	8.00
Gem-12	10.0	9.3	8.05
Gem-16	9.9	9.2	8.00

[a] The pK_a values of dodecylamine in water and aqueous dodecyltrimethylammonium bromide could be determined because of its poor solubility in these media.

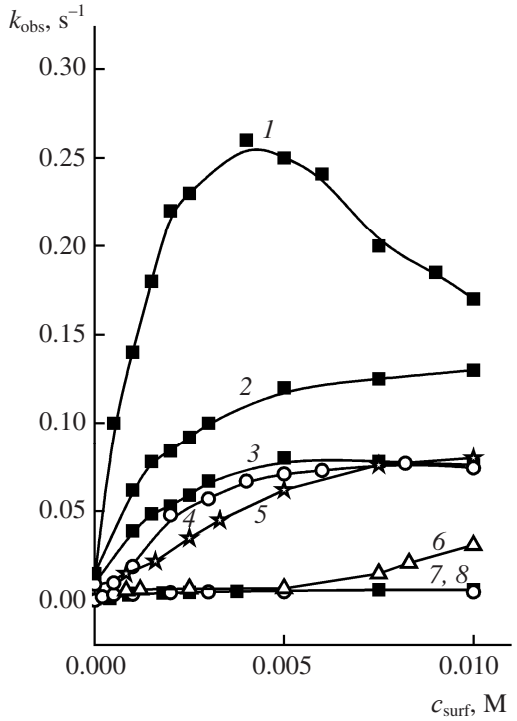


Fig. 2. Plot of the observed rate constants of *p*-nitrophenyl acetate cleavage in the presence of amines and in their absence vs. concentration of cationic surfactants (pH 10.0, 25°C). At c_{amine} 0.0025 M: (*1*) decylamine, Gem-16; (*3*) octylamine, Gem-16; (*4*) octylamine, Gem-12; (*5*) octylamine, cetyltrimethylammonium bromide; and (*6*) octylamine, dodecyltrimethylammonium bromide. At c_{amine} 0.004 M: (*2*) octylamine, Gem-16. In the absence of amine: (*7*) Gem-12 and (*8*) Gem-16.

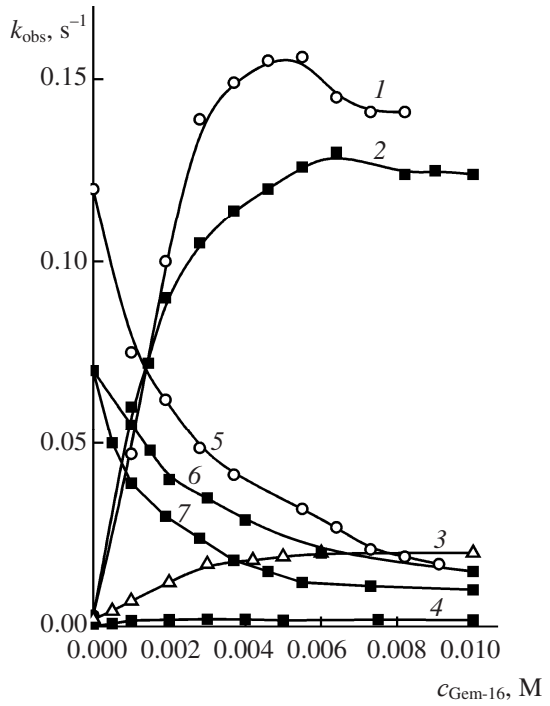


Fig. 3. Plot of the observed rate constants of the reaction of carboxylic esters with amines vs. surfactant concentration (c_{amine} 0.0025 M, pH 9.2, 25°C). *p*-Nitrophenyl acetate, Gem-16: (*1*) dodecylamine, (*2*) decylamine, (*3*) octylamine, (*4*) no amine. *p*-Nitrophenyl laurate, Gem-16: (*5*) dodecylamine, (*6*) decylamine, (*7*) *p*-nitrophenyl laurate, cetyltrimethylammonium bromide, decylamine.

different micellar solutions shows that the geminal surfactants studied exhibit a strong catalytic effect in ester cleavage reactions, and this effect reveals itself at lower concentrations than in the case of monomeric analogs. The fraction of the neutral form (α) depends on the pK_a of the amine and the pH of the medium and can be calculated from the equation $\alpha = K_a/(K_a + [H^+])$. At pH 10.0 in aqueous Gem-16, the fractions of octylamine and decylamine are about 0.56 and 0.86, respectively. The higher content of the neutral form is one of the reasons for the higher activity of decylamine compared to octylamine (Fig. 2). Correct reactivity comparisons are possible only at equal concentrations of the neutral forms. This is the case when the concentration of decylamine is 0.0025 M and that of octylamine is 0.004 M: The concentrations of the unprotonated forms of these amines in an aqueous solution of Gem-16 at pH 10.0 with be the same (0.002 M). However, in such conditions, too, decyalmine is more reactive toward *p*-nitrophenyl acetate (Fig. 2, plots *1* and *2*). Previously we showed by self-diffusion NMR and spin-probe ESR [17, 18] that decylamine and its higher homologs prone to self-association form with monomeric cationic surfactants mixed aggregates in which the amine exhibits enhanced nucleophilicity , for example, in cleavage of *p*-nitrophenyl acetate [19, 20]. Probably, alkylammonium geminal surfactants, too, tend to form such associates, which is responsible for the enhanced catalytic effect of Gem-16 in *p*-nitrophenyl acetate aminolysis in going from octylamine to decylamine and further to dodecylamine (Fig. 3).

The data presented in Fig. 2 were analyzed in terms of the pseudophase model of micellar catalysis. To this end, we made use of Eq. (1) that relates k_{obs} to reaction parameters in the micellar phase [2].

$$k_{obs} = \frac{k_m K_s c_{surf} + k_0}{1 + K_{bind} c_{surf}}. \quad (1)$$

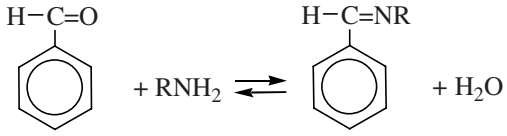
Here c_{surf} is the surfactant concentration corrected for the critical micelle concentration (CCM); k_0 and k_m, rate constants in the aqueous and micellar phases, respectively; and K_{bind}, binding constant of the substrate.

It follows from the resulting data (Table 2) that addition of a long-chain amine to a cationic surfactant adversely affects substrate– micelle binding. In the absence of amines, the binding constants of *p*-nitrophenyl acetate with cetyltrimethylammonium and Gem-16 are 450 and 2000 l mol^{-1}, respectively [15] and in the presence of amines these values decrease about two times. Nevertheless, the rate of ester cleavage increases by an order of magnitude and more (Table 2). The reason for the observed acceleration is a shift of the pK_a of the amine (i.e. increase of the fraction of the neural form) and the ability of the amine to form mixed functionalized aggregates with cationic surfactants.

Unlike what is observed with aminolysis of *p*-nitrophenyl acetate in the system Gem-16–decylamine (or dodecylamine), the reaction with *p*-nitrophenyl laurate (R = $C_{11}H_{23}$) under the same conditions is inhibited (Fig. 3, descending curves). We already faced the same effect with hydrophobic esters in the case of monomeric cationic surfactants [18]. As seen from the kinetic data in Fig. 3, the rate constant of *p*-nitrophenyl laurate in the Gem-16–decylamine system is lower about 7 times compared with aqueous solutions, whereas with *p*-nitrophenyl acetate accelera-tion of about 50 times is observed. In the cetyltrimethylammonium bromide–decylamine under the same conditions, aminolysis of the acetate accelerates 40 times and aminolysis of the laurate decelerates 5 times (Table 2). The inhibition of the reaction with *p*-nitrophenyl laurate with decylamine with micelles of cationic surfactants, including geminal, is in conflict with the observation that these systems are characterized by increased contents of the neutral forms of amines. A probable reason for the inhibition consists in the formation of mixed aggregates between *p*-nitrophenyl laurate and long-chain amines in the absence of surfactants [20]; the rate of aminolysis in such aggregates is very high. Addition of a surfactant in such system results in a rearrangement of micelles and formation of new mixed aggregates. The neutral decylamine and substrate molecules comprised in these aggregates can be separated or unfavorably oriented; as a result, their reaction can be hindered. Thus, cationic surfactants exhibit substrate specificity in aminolysis of carboxylic esters, and this specificity is more pronounced in the case of geminal surfactants compared to their monomeric analogs.

We also studied the reaction of long-chain aliphatic amines with benzaldehyde in aqueous solutions of geminal surfactants (Scheme 2).

Scheme 2.



This reaction gives rise to azomethine compounds (Schiff bases) and it forms the basis of the analytical determination of primary amines in mixtures of amines with various substitution degrees, as well as of benzaldehyde. Long-chain amines are used for

Table 2. Parameters of the micelle-catalyzed cleavage of *p*-nitorphenyl acetate in aqueous solutions of various surfactants in the presence of long-chain primary amines (c_{amine} 0.0025 M, 25°C)

Surfactant	Amine	pH	k_0, s^{-1}	k_m, s^{-1}	K_s, l mol^{-1}	CCM, M	k_m/k_0
Gem-12	Octylamine	10.0	0.009	0.09	400	0.0005	9
Cetyltrimethylammonium bromide	Octylamine	10.0	0.009	0.09	200	0.0006	10
Gem-16	Octylamine	9.2	0.002	0.028	430	0.0003	14
Gem-16	Decylamine	10.0	0.013	0.36	650	0.00002	28
Gem-16	Decylamine	9.2	0.003	0.16	700	0.0002	53
Gem-16	Dodecylamine	9.2	0.0035	0.22	660	0.00064	62

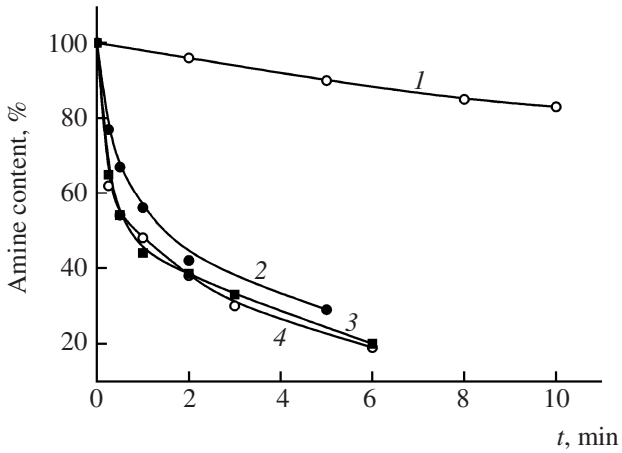


Fig. 4. Variation of the content of free amine on its reaction with benzaldehyde in alcoholic and aqueous micellar media (c_{surf} 0.005 M, 25°C): (*1*) decylamine in ethanol, (*2*) decylamine in aqueous cetyltrimethylammonium bromide, (*3*) decylamine in Gem-16, and (*4*) octylamine in aqueous Gem-16.

manufacturing impregnated resins which, in their turn, are used to clean up waste waters and industrial vapors from benzaldehyde [21].

The formation of azomethine compounds is a reversible reaction, and it is generally performed in nonaqueous solvents (alcohols) [22]. An exception is Schiff bases derived from aniline. These compounds are sufficiently stable in water. Some examples of their preparation in aqueous micellar solutions have been reported [23, 24]. We tried to react long-chain amines with benzaldehyde in aqueous solutions of Gem-16, Gem-12, and cetyltrimethylammonium bromide. It was suggested that the poor solubility of the reagents in water will result in that their reaction will occur in the micellar pseudophase. The resulting azomethine compounds are also hydrophobic and will stay in the micellar phase, thus preventing hydrolysis.

The reaction progress was followed by monitoring the concentration of free amine in the reaction medium by means of potentiometric titration. For the sake of comparison, the reactions were performed not only in aqueous micellar solutions of cationic surfactants, but also in ethanol which is frequently used in azomethine synthesis. As seen from Fig. 4, the conversion rate of amines in alcohol is much lower than in micellar solutions. Geminal surfactants are slightly more efficient than monomeric analogs. For example, the observed rate constants of the reaction of decylamine with benzaldehyde at 25°C in Gem-16 solutions in 0.0069 s^{-1}, in Gem-12 solutions, 0.0041 s^{-1}, and cetyltrimethylammonium bromide solutions, 0.0038 s^{-1} (in ethanol, 0.00031 s^{-1}). The conversion rates of octyl-, decyl, and dodecylamine in the presence of Gem-16 are almost equal to each other and remain practically invariable as the surfactant concentration is varied from 0.0025 to 0.02 M. Such an activity leveling is probably associated with the fact that ionic surfactants exert the greatest impact on ionic and ion-molecular processes, whereas the reaction in focus involves neutral molecules.

It is known that benzaldehyde in alkaline media tends to disproportionate to form an alcohol and acid, and it is also readily oxidized in air [22]. Benzoic acid that is formed in both cases can bind amines in the reaction in focus and thus decrease the yield of azomethines.

To find out what is the contribution of these side reactions, we performed additional experiments. The contribution of benzaldehyde disproportionation in aqueous surfactants solutions was estimated in a system that contained a tertiary amine instead of primary. We used dimethyloctylamine and benzyldimethylamine, since their pK_a are close to the pK_a of decylamine, and they create a weakly alkaline medium in aqueous micellar solutions (pH ~10). Potentiometric titration showed that the conversion of decylamine after 10-min reaction is more than 90%, whereas those of the above tertiary amines (due to reaction with benzoic acid) are lower than 5%, which allows the disproportionation reaction to be neglected in discussing the results.

To avoid oxidation of benzaldehyde, we prepared micellar solutions with a freshly prepared benzaldehyde. The reactions with amines were performed with a solution of benzaldehyde, that contained no more than 3% of benzoic acid which was preliminarily neutralized with alkali. Thus, under our experimental conditions, the main reaction products of benzaldehyde with long-chain amines are azomethine compounds.

The use of alkylammonium surfactants offers an undeniable advantage of providing the possibility of preparing azomethine compounds in aqueous media. The solubilization of the starting reagents and reaction products in a micelle completely shift the equilibrium reaction (Scheme 2) to the right. Note that complete conversion of hydrophilic amines in this reaction is almost impossible to reach, since the reaction will partially occur in the aqueous phase, and the equilibrium will be shifted to the starting compounds. The high solubilizing activity of Gem-16 with respect

to long-chain amines and benzaldehyde allows one to deal with high reagent concentrations, which opens up possibilities for the reaction in focus to find not only analytical, but also synthetic applications.

EXPERIMENTAL

Commercial dodecyltrimethylammonium and cetyltrimethylammonium bromides (Sigma), long-chain normal aliphatic amines (Acros Organics), and *p*-nitrophenyl acetate and *p*-nitrophenyl laurate (Fluka) with main substance contents of 99% were used. Benzaldehyde (Acros Organics) was distilled immediately before use (bp 178–179°C). The quantity of benzoic acid appearing in solutions on standing was controlled by titration with alkali. Geminal surfactants were synthesized by reactions of *N,N'*-tetrasubstituted hexamethylenediamine with alkyl bromides in acetone followed by double recrystallization from ethanol [16].

The pK_a values of amines were determined by potentiometric titration of their solutions with 0.1 N HCl using a pH-340 device. The surfactant concentration was measured in the range 0–0.02 M. In solubilization studies, amines were added in small portions to vigorously shaken and thermostated micellar surfactant solutions until the system got visually inhomogeneous. Aliquots were then taken and titrated with HCl to determine the concentration of amine in the solution.

Reaction kinetics were studied in freshly prepared micellar solutions under pseudofirst-order reaction conditions. Ester cleavage was studied by spectrophotometry on a Specord UV–Vis instrument at 25°C. Reaction progress was followed by measuring the optical density of solutions at 400 nm (formation of the *p*-nitrophenolate anion). Initial substrate concentration 5×10^{-5} M, conversion > 90%.

Azomethine formation was followed by the concentration of amine in the reaction medium, measured by potentiometric titration. Initial concentration of amine and aldehyde 0.005 and 0.05 M, respecttively. The titrant was 0.02 N aqueous HCl. The observed pseudofirst-order constants (k_{obs}) were determined by the equation $\log (c_\infty - c_t) = -0.434k_{obs}t +$ const, where c_t и c_∞ are the concentrations of the reaction product at time t and after reaction completion. The k_{obs} values were calculated by the least-squares method. Reported are the mean k_{obs} values obtained from two parallel runs and differing from each other by no more than 4%.

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