



Solubilization and catalytic behavior of micellar system based on gemini surfactant with hydroxyalkylated head group

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ABSTRACT

The correlation between aggregation, solubilization and catalytic properties has been found for series of cationic surfactants with hexadecyl radical of both monomeric and dimeric structures. The highest catalytic effect in the series, reaching three orders of magnitude is observed for a gemini surfactant with oxyethylated head group in the case of hydrolysis of *p*-nitrophenyl caprate.

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1. Introduction

At the present time gemini (dimeric) surfactants have attracted an increased attention. These surfactants are made up of two hydrophobic chains and two polar headgroups covalently linked through a spacer group. These kinds of surfactants have a number of unique aggregation properties in comparison with conventional single-chain surfactants, such as much lower critical micelle concentration (cmc), strong dependence on spacer structure, high surface and wetting activity, special aggregate morphology, and so on. Gemini surfactants are very attractive for catalysis and adsorption application, analytical separation, solubilizing processes, nanoscale technology, biotechnology, enhanced oil recovery and as synthetic vectors for gene transfection. A numbers of papers concerning the aggregation behavior and structural properties of gemini surfactants have been published [1–8]. The catalytic effect of micellar surfactant solution in nucleophilic substitution reactions has been reported [9–16].

In the case of cationic gemini surfactants the majority of studies focuses on compounds with methyl substitutes in ammonium head groups. It is however obvious that introducing other functional groups can result in novel properties, therefore gemini surfactants with alkylammonium head groups bearing polar fragments including hydroxyethyl ones have been designed [17–19]. Correlations

between chemical structure, aggregation behavior and solution properties of gemini surfactants being revealed make it possible to synthesize purposely these compounds and to develop organized systems showing target properties.

In this paper aggregation behavior, solubilization capacity and catalytic activity of gemini surfactant with hydroxyethylated head group, i.e. hexanediyl- α,ω -bis[[(2-hydroxyethyl)methylhexadecylammonium]] bromide (Gem 6-16(OH)) toward the cleavage of ester bonds have been investigated. Surfactants bearing hydroxyalkyl fragments in their heads demonstrate strong ability to form specific interactions in their solutions, i.e. hydrogen bonds along with electrostatic interactions and hydrophobic effect. This is assumed to be reflected in their behavior. The results obtained are compared with data for non-functional gemini surfactant hexanediyl- α,ω -bis(hexadecyldimethylammonium) bromide (Gem 6-16), as well as with single head analogous, i.e. cetyltrimethyl ammonium bromide (CTAB) and *N*-cetyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium bromide (CHAB). *p*-Nitrophenyl esters of carboxylic acids were used as a probe for estimation of solubilization capacity and catalytic activity of micellar systems (See Scheme 1).

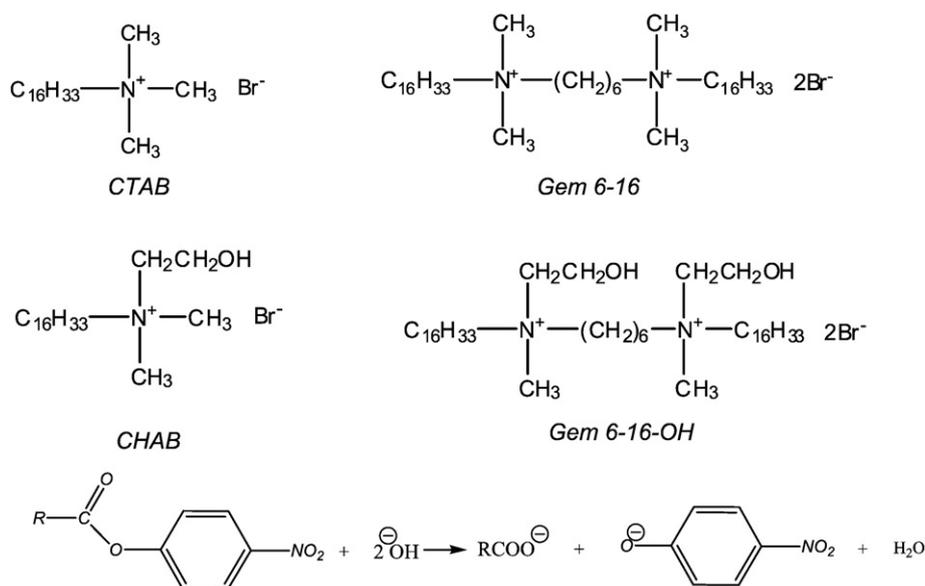
2. Experimental

2.1. Chemicals

CTAB and the esters (acetate, caprilate, caprate, laurate) were from Sigma-Aldrich (basic substance contents of higher than 99%). CHAB and Gem 6-16 were synthesized through reaction of cetyl bromide

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Scheme 1. R = CH₃ (acetate), n-C₇H₁₅ (caprilate), n-C₉H₁₉ (caprate), n-C₁₁H₂₃ (laurate).

with 2-dimethylaminoethanol or N,N'-tetramethyl hexamethylenediamine, in analogy with ref. [15,20]. Gem 6-16(OH) was synthesized by quaternization of hydroxyethylmethylcetylamine by hexamethylene dibromide, in analogy with ref. [18].

2.2. Micellization study

Surface tension measurements were performed using the du Nouy ring detachment methods using tensiometer K6 (Kruss). The experimental details are described elsewhere [21].

Dynamic light scattering (DLS) measurements were performed by means of the PhotoCor Complex and Malvern Instruments' Zetasizer Nano. The measured autocorrelation functions were analyzed by Malvern DTS software, the DynaLS program and the second-order cumulant expansion methods. The diffusion coefficient was measured at least three times for each sample. The average error in these experiments was approximately 4%. The solutions were filtered with Millipore filters, to remove dust particles from the scattering volume. The experimental details are described elsewhere [22].

2.3. Solubilization study

Solubilization properties of organized systems toward carboxylic acid esters were determined according known procedure [23], which involved the preparation of saturated solution of the esters followed by their hydrolysis and spectrophotometry monitoring of *p*-nitrophenol released. For this purpose, measured portion of freshly purified ester was agitated by a stirrer for 6 h, whereupon undissolved residue was separated. Then an appointed volume of concentrated (1 M) NaOH solution was added to the aliquot taken from the saturated ester solution, which resulted in the hydrolysis of the substrate and formation of *p*-nitrophenol. Completion of the hydrolysis was controlled by spectrophotometry, by means of reaching the plateau value of the absorbency (*D*) at 400 nm corresponding to *p*-nitrophenolate-anion. Concentration of *p*-nitrophenol coinciding with concentration of the initial ester was calculated as follows: $C_{\text{PhO}^-} = D/(\epsilon \times L)$, here *L* is a cell length, and ϵ is an molar extinction coefficient of 18,000 L mol⁻¹ cm⁻¹.

2.4. Kinetic study

The reaction was controlled by monitoring the *p*-nitrophenolate-anion absorption at 400 nm. A "Specord M-400" spectrophotometer with temperature-controlled cell holders was employed. All runs were performed at the substrate concentration of $5 \cdot 10^{-5}$ mol·L⁻¹. Required pH values were reached applying sodium tetraborate buffer solutions.

The observed rate constants (k_{obs}) were determined from the equation: $\ln(A_{\infty} - A) = -k_{\text{obs}} t + \text{const}$, where *A* and *A*_∞ are the absorbance of the micellar solutions at point *t* during and after completion of the reaction, respectively. The k_{obs} values were calculated using the weighed least-squares computing methods. Each value of k_{obs} is the average of at least three independent determinations differing by no more than 4%.

3. Results and discussion

3.1. Determination of the micellization characteristics

Surface tension study extracted the cmc value of Gem 6-16(OH) equal to $9 \cdot 10^{-6}$ M, which is ca. 80-fold lower than that of the monomer surfactant CHAB ($7 \cdot 10^{-4}$ M) and ca. 5-fold lower than value for non-functional gemini analogue ($4.0 \cdot 10^{-5}$ M) (Fig. 1). On the one hand, the micellization of Gem 6-16(OH) is probably promoted by the covalent fixation of two positively charged centers and on the other, by the formation of hydrogen bonds between head groups.

By method of dynamic light scattering the size of the micelles was estimated. Hydrodynamic radius (R_h) of gemini surfactants are shown to equal 3.4 и 3.2 nm for Gem 6-16 and Gem 6-16(OH) respectively at concentration of 0.01 M under neutral solution pH. The higher values of hydrodynamic radius for the gemini surfactants as compared to monomeric analogous at the same concentration (2.2–2.5 nm for CTAB) are probably due to the asymmetry of aggregates based on dimeric surfactants. It is noteworthy that under neutral pH Gem 6-16 and Gem 6-16(OH) form micelles similar in size, while in alkali solutions, hydrodynamic radii of their aggregates considerably differ. Value of R_h for Gem 6-16(OH) in 0.01 M alkali solution reaches 4.9 nm, while R_h for Gem 6-16 remains unchanged. This may be due to the fact that hydroxyalkylated surfactants show

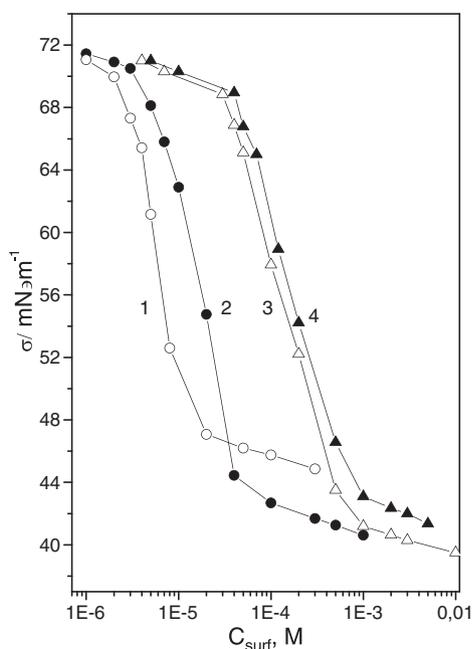


Fig. 1. Surface tension isotherms of cationic surfactants; 1 – Gem 6–16 OH; 2 – Gem 6–16; 3 – CHAB; 4 – CTAB, 25 °C.

properties of weak acids and under solution $\text{pH} > 12$ may exist in a betaine form [24]. In this case repulsion between head groups becomes lower, which allows to form micelles with higher numbers of aggregation and larger size. Our further investigation were carried out in neutral or slightly alkaline environments ($\text{pH} 9.2$), when hydroxyalkylated surfactants demonstrate behavior typical for cationic surfactants.

3.2. Solubilization and catalytic behavior

Micellar solutions of the above cationic surfactants are used as reaction media for the alkaline hydrolysis of *p*-nitrophenyl esters of carboxylic acids with different lengths of hydrocarbon radical. The first task was to compare solubilization capacity of the micelles towards the substrates. The maximum concentration of *p*-nitrophenyl esters in the surfactant solutions was determined by using the methodology including the preparation of a saturated solution of this compound, followed by its alkaline hydrolysis and spectroscopic monitoring of *p*-nitrophenol liberation [23]. Data obtained reflect a change in the substrate solubility, when transit from water to surfactant solution (Fig. 2).

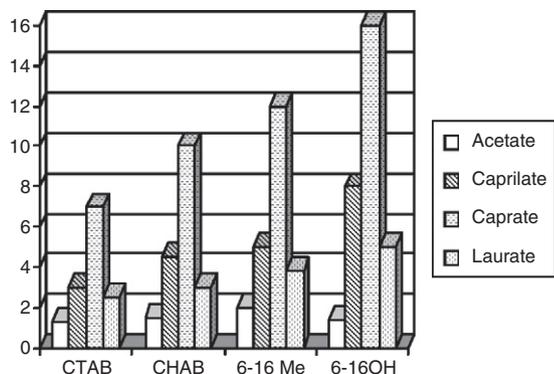


Fig. 2. Relative solubility of *p*-nitrophenyl esters of carboxylic acid when transit from water to micellar solution of cationic surfactants.

As can be seen, an increase in the solubilization capacity occurs in the series $\text{CTAB} < \text{CHAB} < \text{Gem 6-16} < \text{Gem 6-16(OH)}$. Probably the latter member of the series combines high micellization and solubilization properties of gemini surfactants [25,26] with the contribution of hydrogen bonds between the substrate and head groups of surfactant. In all the systems studied an increase in solubility of esters correlates with their hydrophobicity, reaching a maximum in the case of *p*-nitrophenylcaprate. The structure of this substrate is probably most suitable for the embedding into the micelles. The change in the substrate solubility and in their microenvironment in surfactant solutions can result in changes in ester reactivity, in particular in hydrolytic stability.

Figs. 3 and 4 show dependence of observed rate constants (k_{obs}) of alkaline hydrolysis of *p*-nitrophenyl esters of different structures on the surfactant concentration. The reaction was studied at $\text{pH} 9.2$ under pseudo first order conditions, by monitoring the absorbance of solutions at a wavelength of 400 nm (formation of *p*-nitrophenoxide-anion). Catalytic action of cationic surfactants on hydrolysis of esters is mainly connected with the concentration of hydroxide ion near the positively charged micelles, where the substrate is solubilized. From the kinetic data evident, that the maximum effect of gemini surfactants is achieved at the concentrations lower than 0.001 M, i.e. substantially lower as compared to their monomer analogues. Surfactants with hydroxyalkylated head groups demonstrate higher (by order of magnitude) catalytic effect than their non-functional analogues; k_{obs} values for Gem 6-16(OH) is by 2–5 times higher than those for CHAB. The kinetic curves obtained were analyzed in terms of the pseudophase approach using the Eq. (1) [27]

$$k_{\text{obs}} = \frac{k_0 + k_m K_S C}{1 + K_S C}, \quad (1)$$

where k_0 и k_m (s^{-1}) are the first order rate constants in aqueous and micellar phase respectively, K_S (M^{-1}) is the binding constant of substrate; C is the total concentration of surfactant minus cmc. Calculated parameters are summarized in Table 1.

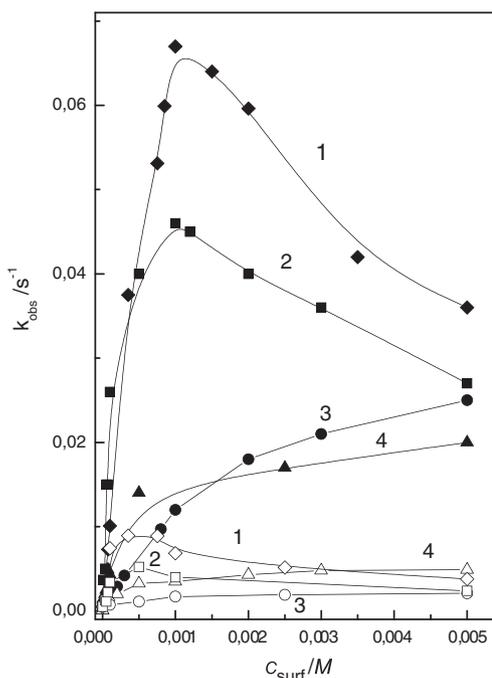


Fig. 3. The dependence of observed rate constant of hydrolysis of *p*-nitrophenyl esters of carboxylic acids in micellar solution of gemini surfactants on their concentration (1 – caprate, 2 – caprilate, 3 – acetate, 4 – laurate); full symbol for Gem 6–16 OH; empty symbols for Gem 6–16; $\text{pH} 9.2$, 25 °C.

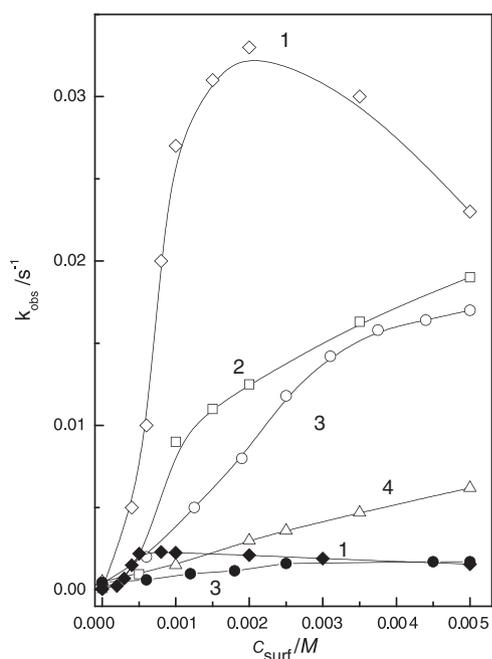


Fig. 4. The dependence of observed rate constant of hydrolysis of p-nitrophenyl esters of carboxylic acids in micellar solution of cationic surfactants on their concentration (1 – caprate, 2 – caprylate, 3 – acetate, 4 – laurate); full symbol for CTAB; empty symbols for CHAB; pH 9.2, 25 °C.

Calculated values of rate constants in micellar phase make it possible to estimate the catalytic effect as a k_m/k_0 ratio. The effect for the systems studied increases when transiting from acetate to caprylate and then to caprate. However, further increase in hydrophobicity of substrates results in a decrease in the acceleration effect. The similar trend occurs for the substrate binding constants and the substrate solubilization in micellar solutions (Table 1, Fig. 2). Comparison of data in pairs CTAB-Gem 6–16 and CHAB-Gem 6-16(OH) reveals that values of K_S and catalytic effect for gemini surfactants is higher as compared to monomeric analogues. Unlike the data in Fig. 2, calculated values of K_S for hydroxyalkylated surfactants, both for monomeric and gemini are lower than those for non-functional analogues, although the opposite trend occurs for catalytic effect. One can assumed, that more polar head group increases micropolarity in the reaction site

Table 1

Calculated parameters resulted from quantitative treatment of k_{obs} vs. surfactant concentration plot for hydrolysis of p-nitrophenyl esters of carboxylic acid in micellar solutions of surfactants (pH 9.2, 25 °C)^a.

Surfactant	substrate	k_m/s^{-1}	$K_S/mol^{-1} L$	cmc/mol L ^{-1b}	k_m/k_0^c
CTAB	Acetate	0.0019	880	$5.30 \cdot 10^{-4}$	4
	Caprate	0.00235	4440	$1.86 \cdot 10^{-4}$	29
CHAB	Acetate	0.033	230	$2.40 \cdot 10^{-4}$	66
	Caprylate	0.0225	786	$1.98 \cdot 10^{-4}$	112
	Caprate	0.0376	1750	$3.25 \cdot 10^{-4}$	470
	Laurate	0.0168	1200	$1.97 \cdot 10^{-4}$	336
Gem 6-16	Acetate	0.0023	1460	$2.05 \cdot 10^{-5}$	5
	Caprylate	0.0053	2000	$2.43 \cdot 10^{-5}$	27
	Caprate	0.0091	30900	$2.17 \cdot 10^{-5}$	115
	Laurate	0.00051	3320	$2.63 \cdot 10^{-5}$	10
Gem 6-16(OH)	Acetate	0.0279	780	$2.36 \cdot 10^{-5}$	56
	Caprylate	0.049	11000	$2.48 \cdot 10^{-5}$	245
	Caprate	0.074	6800	$5.61 \cdot 10^{-5}$	925
	Laurate	0.021	4300	$1.03 \cdot 10^{-5}$	420

^a Calculated from the quantitative treatment of kinetic data (Figs. 3 and 4) in terms of Eq. (1) within the concentration interval before maximum in the dependence.

^b Extracted from the fitting procedure.

^c k_0 values are equal to $0.0005 s^{-1}$ (acetate), $0.0002 s^{-1}$ (caprylate), $0.00008 s^{-1}$ (caprate), $0.00005 s^{-1}$ (laurate).

thus favors the reaction, and stabilizes the transition state due to delocalization of electron density through hydrogen bonds. It is noteworthy that for all the systems studied substrate specificity is observed, i.e. the correlation between the rate of hydrolysis of substrates and their solubility occurs. The highest k_{obs} values are observed for p-nitrophenyl caprate in the Gem 6-16(OH), for which the acceleration reaches three orders of magnitude. It can be assumed that the localization of this substrate is suitable for the nucleophilic attack.

4. Conclusion

Thus, in micellar solution of gemini surfactant with hydroxyethylated head group specific interactions are probable contributors along with electrostatic interactions and hydrophobic effect. The hydrogen bonds favor micellization in the system and the solubilization of reagents. This in turn results in the activation of the substrates and enhancement of the catalytic effect, occurring within extremely low concentration range, which provides perspectives for the use of these micellar systems for reaction media.

Acknowledgements

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