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Dicationic hydroxylic surfactants: Aggregation behavior, guest-host interaction and catalytic effect

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ABSTRACT

Herein, supramolecular systems with improved aggregation, solubilization and catalytic activity have been constructed by self-assembly of gemini surfactants with two cationic centers separated by the spacer chain of 10 atoms long and hydroxyl functionality in their head group or in the spacer. It was found that hydroxylic dicationic surfactants capable of forming hydrogen bonds exhibit the ability to micelle formation at a concentration substantially lower than that of their monocationic and non-functionalized dicationic counterparts. They are capable of initiating additional solubilization mechanisms, which are responsible for the enhanced solubilization capacity of the surfactants. The use of the dicationic hydroxylic surfactants in hydrolytic decomposition of esters gives rise to the high catalytic effect and substrate selectivity: the highest, 430-fold, acceleration was observed for *p*-nitrophenyl caprate.

1. Introduction

Cationic surfactants find expanding use as micellar catalysts, corrosion inhibitors, solubilizing agents, drug and diagnostic agent mediators, and antimicrobial agents [1–3]. Innovative applications in these fields require surfactants, which are operable under mild conditions (acidity of media, temperature and concentration range) and possess high solubilization capacity, considerable catalytic efficiency and selectivity. Importantly, primary (chemical) structure of amphiphiles is mainly responsible for the secondary (supramolecular) architecture of aggregates and their practical application. Therefore the majority of recent publications in the field of organized solutions have focused on the evaluation of the correlation between the structure of amphiphilic compounds, their solution behavior and functional activity. In this connection, design of novel surfactants and exploration of their fundamental and practical properties is of current importance. To modify the aggregation and functional activity of cationic surfactants different approaches have been used including covalent and non-covalent ways. Non-covalent way (supramolecular design) assumes the development of polycomponent systems, with surfactants admixed with hydrotropic agents, co-surfactants, polymers, macrocycles, and metal ions [4,5]. Alternative way (chemical design) focuses on the variation of molecular platform of amphiphiles and introduction of functional groups responding to internal stimuli, capable of multicentered interactions, cleavable or biodegradable [6–8]. The latter approach is very promising, since provides the wide possibility for the development of nanocontainers and nanoreactors with high efficacy and controlled characteristics. Analysis of recent literature demonstrates steady interest to dicationic Gemini surfactants (GS), whose structure involves two hydrophobic moieties and two head groups covalently bound by the spacer chain [9–15]. Characteristics of such surfactants are extremely low critical micelle concentration (cmc), large hydrophobic domain, high positive surface charge, and conformation mobility as a contributory factor for the spatial "adjustment" during self-association. There are these properties, which are of interest in design of GS. In this case the possibilities for use of GS as nanocontainers and nanoreactors, nonviral vectors for gene delivery to the living cells, and in analytical chemistry are considerably increased [4,16–20]. Noteworthy, in the case of GS the length and chemical nature of spacer fragment is an additional tool of controlling the aggregation behavior, toxicity and functional activity of the systems [21–23].

Analysis of recent publications covering both monocationic and dimeric surfactants revealed high research activity directed toward the design of amphiphilic molecules bearing polar groups, including those with H-bonding ability. This can significantly improve practically important properties, such as aggregation and solubilization behavior, morphological lability, guest-host interactions, cleavability, etc. This can be exemplified by the so-called esterquat surfactants with improved biodegradability [24,25], geminis with oligooxyethyl spacer, capable of lyotropic phase formation [26,

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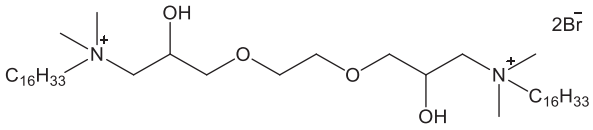
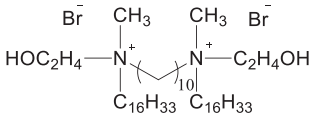
27], surfactants with OH groups in spacer, head groups or alkyl chains [28–35], strongly influencing cmc values, packing density and morphological behavior of systems. Therefore, design of new GS functionalized with polar moieties is a promising way to initiate additional solubilization mechanisms by hydrogen bonding and thereby affect the cmc value and the properties of the reaction medium [36–41]. It is likely that the number of hydroxyl groups and their position in the head group or in the spacer may be the factors responsible for the functional properties of the micellar solutions.

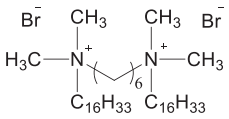
This paper reports detailed physico-chemical studies of the aggregation behavior, solubilization capacity and catalytic action of the surfactants with two cationic centers separated by the spacer chain 10 atoms long and hydroxyl functionality in their head group or in the spacer. The surfactants used are shown below:



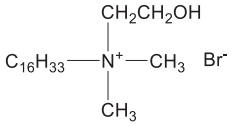
16-10(OH)-16



16-10-16(MEA)



16-6-16



CHAB

The properties of the surfactants were compared with those of their monomeric counterparts - cetylhydroxyethylammonium bromide (CHAB) and hydroxyl-free dicationic surfactant, 1,10-decalyden-bis-(dimethylammonium) dibromide, 16-10-16 and widely used in research 1,6-hexalyden-bis-(dimethylammonium) dibromide, 16-6-16.

2. Methods and materials

2.1. Materials

The surfactant 16-10(OH)-16 was synthesized by the procedure reported earlier [37] by heating of 2,13-diaza-6,9-dioxa-2,13-dimethyl-4,11-dihydroxytetradecane with cetyl bromide in acetonitrile followed by recrystallization of the reaction mixture. The surfactant 16–10-16(MEA) was obtained via quaternization of hydroxyethylmethylcetyl amine with hexamethylendibromide by analogy with the procedure reported elsewhere [36]. The structure of the compounds was confirmed by elemental analysis, IR- and NMR-spectroscopies data. Commercially available esters of carboxylic acids, *p*-nitrophenol, Orange OT and pyrene (Sigma, Aldrich) were 99% pure. All solutions were prepared with double-distilled water purified by a Direct-Q 5 UV apparatus; the water resistivity was 18.2 MΩ·cm at 25 °C. Experimental temperatures were maintained at 25 ± 0.1 °C, unless otherwise indicated. All experiments were accurate within 4%.

2.2. Instruments and methods

Surface tension measurements were performed by the anchor-ring method using KRUSS 6 tensiometer. Specific conductivities were measured with Inolab Cond 720 conductometer. Krafft points were determined in the solutions at a surfactant concentration substantially higher than cmc. The solution was cooled to precipitation of the surfactant and then, as the solution was exposed to heating at a rate of 0.5 °C/min, conductivities of the supernatant fluid were measured.

Solubilization effects toward the Orange OT in the micellar systems were determined as described elsewhere [40,42] by following the change in the absorbance of their saturated solutions with concentration of the surfactant added. The spectra were recorded in the range from 250 to 600 nm with Specord-250 Plus spectrophotometer using the thermostated quartz cells of a 0.5–1.0 cm path length.

Fluorescent spectra of pyrene at a concentration of $1 \cdot 10^{-6}$ mol·l^{-1} in the solutions of the surfactants were recorded using Varian Cary Eclipse spectrophotometer. Emission spectra were recorded within the interval of 350–500 nm at a scanning rate of 120 nm/min using in a 1.0 cm path length cuvette; the excitation of the sample was occurred at a wavelength of 335 nm.

Surface potential of the aggregates was estimated from spectrophotometry data by following the changes in acid-base properties of the indicator (*p*-nitrophenol) with surfactant concentration as described elsewhere [40]. The extinction coefficient (ε) of the phenolate form was determined from optical density (*D*) at wavelength corresponding to the absorption maximum at pH > 10. Concentration of *p*-nitrophenolate (C_{PhO^-}) at a certain pH was obtained from equation $C_{PhO^-} = D / \varepsilon L$ (L is the path length).

The pK_a value of *p*-nitrophenol at a given surfactant concentration was calculated from Henderson-Hasselbalch equation:

The average values of three to five measurements were used, with the reproducibility being of ±0.05.

The kinetics of alkaline hydrolysis of carboxylic acid esters was studied spectrophotometrically (Specord-250 Plus) by following the changes of absorbance at 400 nm corresponding to absorption maximum of *p*-nitrophenolate anion at the initial substrate concentration of (2–5) 10^{-5} mol·l^{-1} up to the conversion degree of >90%. The observed rate constants (k_{obs}) were calculated from equation $\ln(D_\infty - D) = -k_{obs}t + const$, where D and D_∞ are the absorbances at a time t and on completion of the reaction, respectively. The values of k_{obs} were calculated by the least-square method.

3. Results and discussion

3.1. Aggregation behavior of dicationic surfactants 16-10-16(MEA) and 16-10(OH)-16

At the initial stage of the studies, the temperature and concentration ranges of micelle formation of GS 16-10-16(MEA) and 16-10(OH)-16 were determined by tensiometry and conductometry techniques. Interception point of the straight line portions of the concentration plots of conductivity and surface tension isotherms corresponds to the critical

micelle concentration. The plots thus obtained are shown in Figs. 1 and S1.

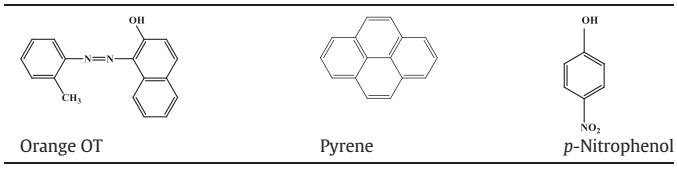
It should be noted that tensiometric procedure failed to obtain reliable cmc for the surfactant 16-10-16(MEA). Presumably, the micelle concentration is too much low and escape detection by tensiometry technique. This restricts the use of anchor-ring method in such systems. Conductometry technique, which takes account of the processes in the bulk solution, is more informative for the 16-10-16(MEA).

The results in Table 1 revealed that micellization of GS 16-10-16(MEA) and 16-10(OH)-16 starts at substantially lower concentrations than in the case of their monocationic counterpart, CHAB, and structurally related non-functionalized surfactant, 16-10-16. Most likely the additional hydration of the micellar surface by hydrogen bonding of hydroxyl groups with water molecules gives rise to decreased electrostatic repulsion of head groups and, hence, to decreased cmc.

Critical temperature of micellization (Krafft temperature) calculated from the temperature plots of conductivity (inset in Fig. 1 and Fig. S2) is of 16 °C and 22 °C for 16-10-16(MEA) and 16-10(OH)-16, respectively. A comparison of aggregation behavior of the above surfactants shows that the concentration and temperature thresholds of micellization for the surfactant with hydroxyethyl functionality in the head group are lower than those for the surfactant with hydroxyl in the spacer. It should be expected that the functional properties (solubilization effects and micellar catalysis) of dicationic surfactants can be exhibited at their micromolecular amount in solution.

3.2. Solubilization effect in micellar solutions of GS 16-10-16(MEA) and 16-10(OH)-16

One of the key features of surfactant-based systems is their capability for solubilizing the low-polarity organic compounds and, hence, increasing their solubility in aqueous media. In order to describe and compare solubilization capacity of various surfactant-based systems, spectral probe methods are widely used. Variations in nature and properties of the probe make it possible to draw conclusions about solubilization effects in the micellar systems and determine such important micellar characteristics as micropolarity, surface potential, cmc and aggregation numbers. Structure of probes studied is given below:



Orange OT Pyrene *p*-Nitrophenol

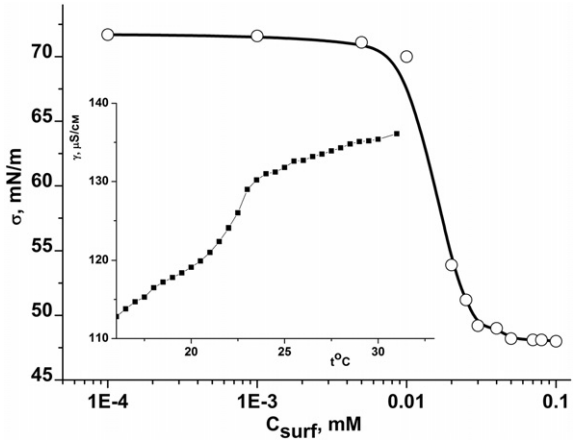


Fig. 1. Concentration plots of surface tension in solutions of 16-10(OH)-16 at 25 °C; inset: conductivity of solution 16-10(OH)-16 (1.5 mM) versus temperature.

Table 1
Krafft temperatures, cmc and solubilization capacity of mono- and dicationic surfactants.

Surfactant	T_{Kr}, °C	cmc, M·10^5			S (Orange OT)
		Tensiometry	Conductometry	Fluorescence	
16-10-16(MEA)	16		1.3	1.5	0.045
16-10(OH)-16	22	3.0	4.8; 5.5 [40]	5.1	0.034
16-10-16		2.6 [43]	2.8 [43], 4.1 [44]	3.2 [43]	
16-6-16		4.0 [38]	5.19 [45]	2.0 [45]	0.027
CHAB	27 [46]	80 [38]	21 [46]		0.022

3.2.1. Solubilization of hydrophobic dye, Orange OT

Orange OT, almost water-insoluble compound (concentration can reach ~$2 \cdot 10^{-9}$ M at most [42]), is frequently used in characterization of solubilization capacity (S) of the micellar solutions. This made it possible to compare the surfactants different in their nature and structure. An increase of solubility of this dye in the surfactants solution is observed at a concentration higher than cmc and is reflected in a sharp increase of absorbance in the visible region (Fig. S3). The absorption band at 495 nm is the most convenient for operation with Orange OT in the solutions of cationic surfactants (molar extinction coefficient ε 18,200 l/mol cm). Spectrophotometry data on absorbance of the Orange OT under conditions of its limiting solubility depending on the surfactant concentration allow one to measure solubilization capacity of the system: $S = b / \varepsilon$, where b is the slope of the plot $D/L = f(C)$, D is the absorbance at 495 nm, L is the width of the absorption layer, C is the surfactant concentration. Figs. 2, S4 give an indication of the D_{495} variations in the solutions of the Orange OT depending on the nature of the surfactants and their structurally related compounds.

The values of S for 16-10-16(MEA) and 16-10(OH)-16 (Table 1) show that their solubilization capacities exceed those for CHAB and non-functionalized dicationic surfactant. This suggests that the high solubilization properties of hydroxyl-containing surfactants can provide efficient binding of hydrophobic reactants and the resulting increase in the reaction rate.

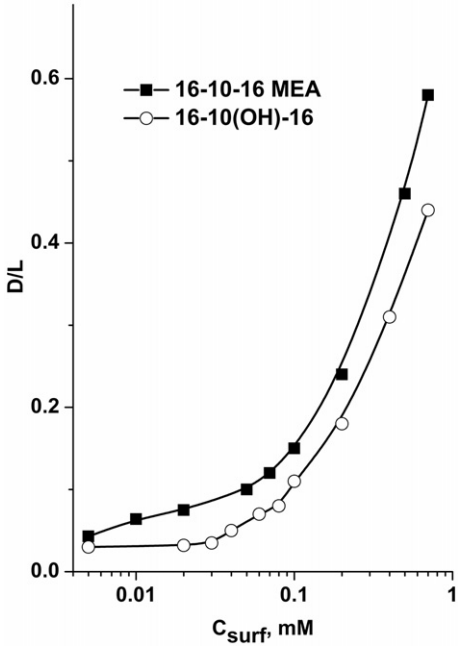


Fig. 2. Absorbance of saturated solutions of Orange OT at 495 nm versus surfactant concentration.

3.2.2. Solubilization of pyrene fluorescent probe

Micropolarity of the area of the reactant localization is another important factor affecting the rate of chemical interactions. Hydrophobic fluorescent probes, pyrene in particular [47,48], are frequently used in estimation of micropolarity of micelles. Fluorescent spectra of pyrene incorporated into micelle have 3 peaks of its monomeric species in the range of 370–390 nm, and another peak in the range of 460–470 nm attributed to its excimer, i.e. dimer involving one excited and one unexcited molecule. The position of absorption maxima depends only slightly on the solvent, whereas their intensity responds markedly to the changes in the reaction medium, mainly to the microenvironmental polarity. The ratio of the intensity of the first peak (I_I) at 373 nm to the intensity of the third (I_{III}) at 384 nm can be served as a parameter for assessment of the medium effects [48,49]. For aqueous pyrene solution, the value of I_I/I_{III} amounts to 1.51. If $I_I/I_{III} < 0.6$, this corresponds to the probe localized in the hydrocarbon core of the micelle. The pyrene location at the surface layer is characterized by the ratio in the range of 1.0–1.4. Variations of (I_I/I_{III}) with surfactant concentration are given in Fig. 3; the typical spectra of pyrene in the solutions of 16-10(OH)-16 are instanced in the inset.

The values of I_I/I_{III} for GS studied are close to one another and fall in the range of 1.02–1.04, thus indicating that the fluorescent probe is localized at the surface layer of the micelle. It should be noted that these values are less than that of their monocationic counterpart, CHAB (I_I/I_{III} 1.14) [50]. It is likely that the covalent bonding between the head groups of the dicationic surfactant provides more tight packing of the surfactant molecules and hinders the penetration of water into the micelle. The plots presented have two portions of different slopes, their intersection point is usually taken as the cmc (Table 1). The cmc values of the fluorometric method agree closely with those determined by other techniques.

The pyrene spectra in the surfactants studied exhibit excimer fluorescence as a broad band with a maximum near 475 nm (inset in Fig. 3). Such behavior takes place at a high concentration of pyrene in the micellar phase (usually at a possibility of the tight stacked arrangement of pyrene molecules), and is an evidence for the high solubilization effect of the surfactants.

3.2.3. Solubilization of hydrophilic probe (p-nitrophenol), pK_a shift

Determination of such important characteristic of the micelles as their surface potential requires the studies of spectral properties of hydrophilic probe molecules capable of participating in acid-base equilibria [51,52]. The essence of the method is that the charged surface of the micelle binds the neutral and ionic species of such probes in different ways thus resulting in shift of their pK_a. This study uses *p*-nitrophenol as a spectral probe whose pK_a was measured at a maximum absorption band of its anionic species (λ 400 nm, ε ~ 18,000 mol/l·cm). The observed p$K_{a,obs}$ were calculated by Henderson-Hasselbalch equation from the absorption spectra of *p*-nitrophenol at various pH [53]. Changes in p$K_{a,obs}$ of *p*-nitrophenol with the concentration of the surfactants 16-6-16(MEA) and 16-10(OH)-16 are given in Fig. 4; the inset illustrates the effect of pH on the spectra of the latter.

Solubilization of organic compounds in the micellar solution of the ionic surfactant and the resulting change in pK_a occurs mainly due to hydrophobic and electrostatic interactions. Non-electrostatic component of solubilization by surfactants is usually modeled using non-ionic surfactants, such as Triton-X-100, whereas the electrostatic component is controlled by the surface potential, Ψ.

As the surfactant concentration is increased, p$K_{a,obs}$ tends to the value of its pK in the micellar phase (p$K_{a,m}$), the latter is related with the surface potential by equation:

$$pK_{a,m} = pK_{a,0} - F\Psi/2.303\ RT,$$

where p$K_{a,0}$ is the pK_a in the micellar solutions of non-ionic surfactants (Triton-X-100, pK_a of *p*-nitrophenol is of 7.6), F is the Faraday number (96,486 C·mol^{-1}), R is the gas constant (8.314 J·K^{-1} mol^{-1}). At T = 298 K the equation can be presented in the form:

$$\Psi = 0.0591\ (pK_{a,0} - pK_{a,m}).$$

With the data in Fig. 4, p$K_{a,m}$ of *p*-nitrophenol in the solutions of 16-10(OH)-16 and 16-6-16(MEA) were calculated to be 6.25 and 5.80, respectively. This corresponds to the surface potentials of 80 and 109 mV, whereas those for trialkylammonium surfactants are significantly higher (120–130 mV for CHAB and 140 mV for 16-6-16 [38]). It may be assumed that the approach proposed takes no account of hydrogen bonding in such systems. It is the possibility of the efficient hydrogen bonding of the neutral *p*-nitrophenol with the micelles of the hydroxyl surfactants that can be responsible for not too significant influence on pK_a of this probe as opposed to the non-functionalized surfactants.

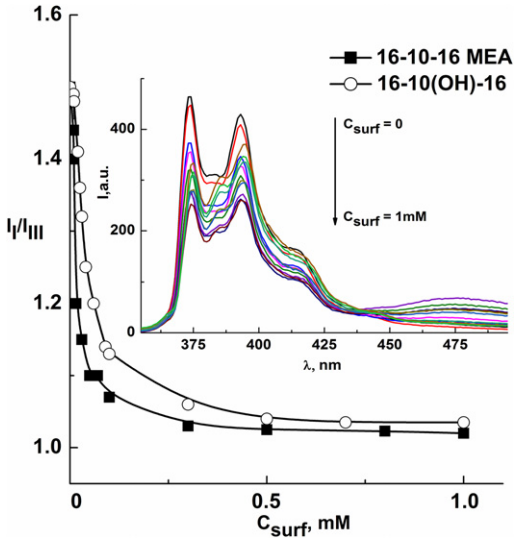


Fig. 3. Changes of I_I/I_{III} with surfactant concentration; inset: fluorescence absorption spectra of pyrene in solutions of 16-10(OH)-16.

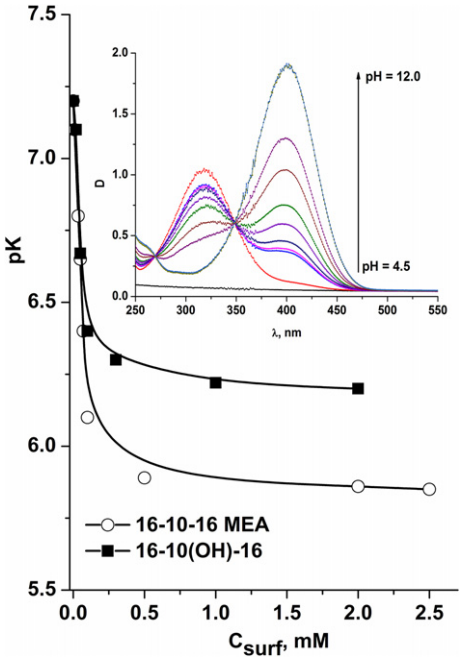
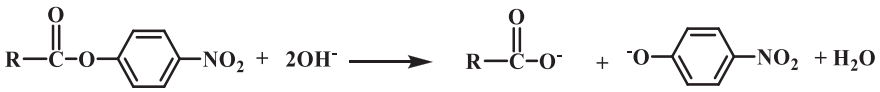


Fig. 4. Change in p$K_{a,obs}$ of *p*-nitrophenol with surfactant concentration; inset: spectra of *p*-nitrophenol (C 0.1 mM) in solution of 16-10(OH)-16 (C 0.15 mM) at various pH.



R = CH_3 (PNPA), *n*-C_9H_{19} (PNPC), *n*-$C_{11}H_{23}$ (PNPL).

Scheme 1. Schematic representation of the hydrolysis of *p*-nitrophenyl esters.

3.3. Micellar catalytic effects of dicationic surfactants 16-10-16(MEA) and 16-10(OH)-16

The solutions of the GS 16-10-16(MEA) and 16-10(OH)-16, were used as a reaction medium in alkaline hydrolysis of carboxylic acid esters. Cationic surfactants are known to accelerate significantly nucleophilic substitutions [2,54–57], especially ion-molecular reactions. In particular, concentrating of hydroxyl ions at a positively charged micellar surface in hydrolysis of ester groups increases the probability of the interaction between hydrophilic nucleophile and solubilized substrate in the micelle thus accelerating the process. Catalytic effect of the hydroxyethyl surfactants can be different from that of their non-functionalized counterparts. For instance, the specific interactions (intermolecular hydrogen bonding), together with hydrophobic and electrostatic forces, may be operative in the interaction of the micelles with reactants. For this reason the influence of the surfactants on the rate of alkaline hydrolysis of *p*-nitrophenyl esters of carboxylic acids, different in their hydrophilic-lipophilic balance, was also studied. The reaction scheme is shown below (Scheme 1).

Fig. 5 gives the concentration plots of the observed hydrolytic rate constants of *p*-nitrophenyl acetate (PNPA), caprate (PNPC) and laurate (PNPL) in the micellar solutions of GS 16-10-16(MEA) and 16-10(OH)-16 in the borate buffer (pH 9.2) at 25 °C. The plots are typical for the reactions catalyzed by micelles: rather sharp increase of the rate constant followed by flattening out of the curve. This suggests that the kinetic experiment can be described by a pseudophase model of micellar catalysis [58] (Eq. (1)):

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

where k_0 and k_m (s^{-1}) are the first-order rate constants in aqueous medium and micellar phase, respectively; K_S ($l \cdot mol^{-1}$), is the constant of substrate binding, C is the overall concentration of the surfactant less cmc.

The characteristics calculated by this equation are given in Table 2 as against those determined earlier for similar surfactants – monocationic CHAB and dicationic 16-6-16 [38]. Catalytic effect of 16-10-16(MEA) and 16-10(OH)-16 defined as k_m/k_0 ratio and binding constants of the substrates in the systems involved are increased in passing from acetate to caprate and somewhat diminished in passing to laurate. A similar regularity is also observed for reference compounds and agrees with the changes in solubility of carboxylic acid esters in passing from water to micellar solutions of cationic surfactants [38]. Catalytic effect of 16-10-16(MEA) and 16-10(OH)-16 is substantially higher than that of 16-6-16 despite the fact that the micelles of non-functionalized surfactants exhibit higher Ψ. Usually this results in efficient concentrating of hydroxide ions at the micellar surface and provides high reaction rates. Thus, hydrolysis of PNPC in the solutions of 16-10-16(MEA) is accelerated by a factor of 432, whereas for 16-6-16 the acceleration is only 115 times. It can be assumed that, on the one hand, the polar head group of hydroxylic surfactants increases the micropolarity in the zone of chemical interaction thus affecting favorably the rate of hydrolysis and, on the other hand, results in stabilization of the transition state at the cost of the hydrogen bonding and thereby facilitates the redistribution of electron density during the reaction. The accelerations observed for 16-10(OH)-16 are slightly less than those for 16-10-16(MEA) in all substrates involved. It is likely that hydroxyl functionalities in the head group, localized in essence at the periphery of the molecule, are more readily available for hydrogen bonding than those in the spacer fragment. Not to be overlooked in this respect that the high micellar

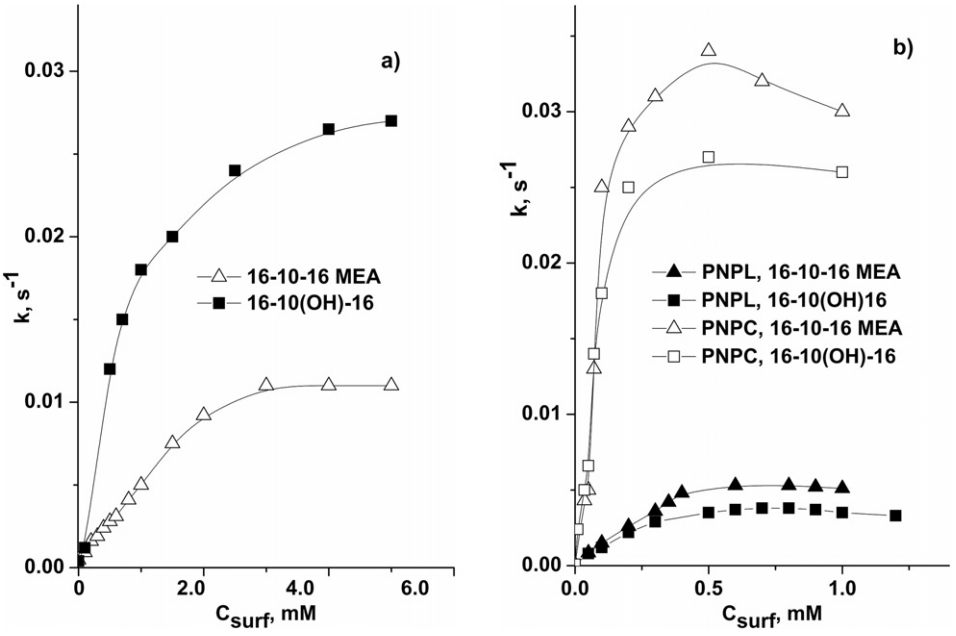


Fig. 5. Observed rate constants of alkaline hydrolysis of PNPA (a), PNPC and PNPL (b) versus concentration of dicationic surfactants (pH 9.2, 25 °C).

Table 2
Hydrolysis of carboxylic acid esters in micellar solutions of dicationic surfactants.

Surfactant	Substrate	k_m, s^{-1}	K_S, M^{-1}	cmc, M	k_m/k_0[a]
16-10(OH)-16	PNPA	0.0280	220	$5.35 \cdot 10^{-5}$	56[b]
	PNPC	0.0291	23,200	$2.71 \cdot 10^{-5}$	363[b]
	PNPL	0.0049	5210	$4.16 \cdot 10^{-5}$	98[b]
	NPDEPN[c]	0.0030	460	$7.50 \cdot 10^{-5}$	200
16-10-16(MEA)	PNPA	0.0307	1450	$8.13 \cdot 10^{-5}$	61
	PNPC	0.0346	38,200	$4.60 \cdot 10^{-5}$	432
	PNPL	0.0076	3580	$2.14 \cdot 10^{-5}$	152

[a] k_m/k_0 is the acceleration relative to substrate hydrolysis in the solution with no surfactant at pH 9.2. The values of k_0 are 0.0005 s^{-1} (PNPA), 0.00008 s^{-1} (PNPC) and 0.00005 s^{-1} (PNPL).

[b] The values of k_m/k_0 in solutions of 16-6-16 are 5, 115 and 10 for PNPA, PNPC and PNPL; respectively; those for solutions of CHAB are 66, 470 and 336, respectively [34].

[c] k_0 $1.5 \cdot 10^{-5}$ s^{-1}, pH 10.0; data on alkaline hydrolysis of NPDEPN were treated by Eq. (1) (cf. [34]).

effect can be caused by a further reaction route – alcoholysis with the participation of the ionized hydroxyl group (pK_a, CHAB ≈ 12.4 [59]).

It should be noted that the high acceleration is also observed in the hydrolysis of the esters in the solutions of monocationic hydroxyethylated surfactant, CHAB. Its micellar catalytic effect is actually somewhat higher than that for dicationic surfactants studied (notes to Table 2). However, such acceleration requires the surfactant concentration by an order of magnitude more.

Earlier we showed that 16-10(OH)-16 is capable to catalyze alkaline hydrolysis not only carboxylic acid esters, but the esters of phosphoric, phosphonic and toluenesulphonic acid as well [37]. Thus, abnormally high catalysis by 16–10(OH)-16 was detected in decomposition of *p*-nitrophenyldiethyl phosphonate (NPDEP) (Table 2), with the acceleration being $>10^2$ times. This significantly exceeds catalytic activity of cetyltrimethylammonium bromide ($k_m/k_0 \sim 36$). The fact that catalytic effect in the reactions involved is reached at a lower surfactant concentrations than that for conventional cationic surfactant, is the significant advantage of the 16-10(OH)-16 surfactant.

4. Conclusions

Thus, hydroxylic dicationic surfactants capable of forming hydrogen bonds exhibit the ability to micelle formation at a concentration substantially lower than that of their monocationic and non-functionalized dicationic counterparts. They are capable of initiating additional solubilization mechanisms which are responsible for the enhanced solubilization capacity of the surfactants. The use of 16-10-16(MEA) and 16-10(OH)-16 in hydrolytic decomposition of esters gives rise to the high catalytic effect and substrate selectivity: the highest, 430-fold, acceleration is observed for *p*-nitrophenyl caprate. Micelle-forming ability, solubilization behavior and catalytic activity of 16-10(OH)-16 is slightly lower than that of 16-10-16(MEA). It is likely that hydroxide functionalities in the head group are more readily available for hydrogen bonding than those in the spacer fragment, which is reflected on the behavior of the surfactants.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2017.11.175.

References

[1] Th.F. Tadros, Applied Surfactants: Principles and Application, Wiley-VCH, Weinheim Germany, 2005 (634 pp).
[2] L.Y. Zakharova, A.B. Mirgorodskaya, E.P. Zhiltsova, L.A. Kudryavtseva, A.I. Konovalov, Reactions in supramolecular systems, in: U.H. Brinker, J.-L. Mieusset (Eds.), Molecular Encapsulation: Organic Reactions in Constrained Systems, John Willey and Sons, Chichester, U.K. 2010, pp. 397–420.
[3] L. Sanders, Cationic Surfactants: Properties, Uses and Toxicity, Nova Science Publishers, Incorporated, 2016 (132 pp).
[4] L.Ya. Zakharova, A.I. Konovalov, Supramolecular systems based on cationic surfactants and amphiphilic macrocycles, Colloid J. 74 (2012) 194–206.
[5] R.R. Kashapov, T.N. Pashirova, A.B. Mirgorodskaya, O.G. Sinyashin, Self-assembly strategy for the design of soft nanocontainers with controlled properties, Mendeleev Commun. 26 (2016) 457–468.
[6] P. Brown, C.P. Buttsand, J. Eastoe, Stimuli-responsive surfactants, Soft Matter 9 (2013) 2365–2374.
[7] A. Tehrani-Bagha, K. Holmberg, Cleavable surfactants, Curr. Opin. Colloid Interface Sci. 12 (2007) 81–91.
[8] D. Xu, X. Ni, C. Zhang, J. Mao, Ch. Song, Synthesis and properties of biodegradable cationic gemini surfactants with diester and flexible spacers, J. Mol. Liq. 240 (2017) 542–548.
[9] R. Sharma, A. Kamal, M. Abdinejad, R.K. Mahajan, H.-B. Kraatz, Advances in the synthesis, molecular architectures and potential applications of gemini surfactants, Adv. Colloid Interf. Sci. 248 (2017) 35–68.
[10] M.T. Garcia, O. Kaczerewska, I. Ribosa, B. Brycki, P. Materna, M. Drgas, Hydrophilicity and flexibility of the spacer as critical parameters on the aggregation behavior of long alkyl chain cationic gemini surfactants in aqueous solution, J. Mol. Liq. 230 (2017) 453–460.
[11] F.M. Menger, J.S. Keiper, Gemini surfactants, Angew. Chem. Int. Ed. Eng. 112 (2000) 1906–1920.
[12] R. Zana, Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review, Adv. Colloid Interf. Sci. 97 (2002) 205–253.
[13] M.H. Mondal, S. Malik, A. Roy, R. Saha, B. Saha, Modernization of surfactant chemistry in the age of gemini and bio-surfactants: a review, RSC Adv. 112 (2016) 92707–92718.
[14] O. Nacham, A. Martín-Pérez, D.J. Steyer, M.J. Trujillo-Rodríguez, J.L. Anderson, V. Pino, A.M. Afonso, Interfacial and aggregation behavior of dicationic and tricationic ionic liquid-based surfactants in aqueous solution, Colloids Surf. A Physicochem. Eng. Asp. 469 (2015) 224–234.
[15] Q.Q. Baltazar, J. Chandawalla, K. Sawyer, J.L. Anderson, L.C. Cabana Saavedra, E.M. Pachón Gómez, R.G. Oliveira, M.A. Fernández, Aggregation behaviour and solubilization capability of mixed micellar systems formed by a gemini lipoamino acid and a non-ionic surfactant, Colloids Surf. A Physicochem. Eng. Asp. 533 (2017) 41–47.
[16] A.A. Shahir, S. Javadian, B.B.M. Razavizadeh, H. Gharibi, Comprehensive study of tartrazine/cationic surfactant interaction, J. Phys. Chem. B 115 (2011) 14435–14444.
[17] T.M. Prokop'eva, I.V. Kapitanov, I.A. Belousova, A.E. Shumeiko, M.K. Kostrikin, M.K. Turovskaya, N.G. Razumova, A.F. Popov, Supernucleophilic system based on functionalized surfactants in the decomposition of 4-nitrophenyl esters derived from phosphorus and sulphur acids: III. Reactivity of mixed system based on tetraalkylammonium and imidazolium surfactants, Russ. J. Org. Chem. 51 (2015) 1083–1090.
[18] D. Gabdrakhmanov, D. Samarkina, V. Semenov, V. Syakaev, R. Giniyatullin, N. Gogoleva, V. Reznik, S. Latypov, A. Konovalov, A. Pokrovsky, Y. Zuev, L. Zakharova, Novel dicationic pyrimidinic surfactant: self-assembly and DNA complexation, Colloids Surf. A Physicochem. Eng. Asp. 480 (2015) 113–121.
[19] A.B. Mirgorodskaya, E.I. Yackevich, D.R. Gabdrakhmanov, S.S. Lukashenko, Yu.F. Zuev, L.Ya. Zakharova, Self-organization and lipoplex formation of cationic surfactants with morpholinium head group, J. Mol. Liq. 220 (2016) 992–998.
[20] T. Ahmed, A.O. Kamel, S.D. Wettig, Interactions between DNA and gemini surfactant: impact on gene therapy: part 1, Nanomedicine 11 (2016) 289–306.
[21] P. Zana, Dimeric (Gemini) surfactants: effect of the spacer group on the association behavior in aqueous solution, J. Colloid Interface Sci. 248 (2002) 203–220.
[22] M.T. Garcia, O. Kaczerewska, I. Ribosa, B. Brycki, P. Materna, M. Drgas, Biodegradability and aquatic toxicity of quaternary ammonium-based gemini surfactants: effect of the spacer on their ecological properties, Chemosphere 154 (2016) 155–160.
[23] L.Ya. Zakharova, D.R. Gabdrakhmanov, A.R. Ibragimova, E.A. Vasilieva, I.R. Nizameev, M.K. Kadirov, E.A. Ermakova, N.E. Gogoleva, D.A. Faizullin, A.G. Pokrovsky, V.A. Korobeynikov, S.V. Cheresiz, Yu.F. Zuev, Structural, biocomplexation and gene delivery properties of hydroxyethylated gemini surfactants with varied spacer length, Colloids Surf., B 140 (2016) 269–277.
[24] L.Ma. Bergström, A. Tehrani-Bagha, G. Nagy, Growth behavior, geometrical shape, and second cmc of micelles formed by cationic gemini esterquat surfactants, Langmuir 31 (2015) 4644–4653.
[25] G. Para, J. Łuczyński, J. Palus, E. Jarek, K.A. Wilk, P. Warszyński, Hydrolysis driven surface activity of esterquat surfactants, J. Colloid Interface Sci. 465 (2016) 174–182.
[26] S. De, V.K. Aswal, P.S. Goyal, S. Bhattacharya, Novel gemini micelles from dimeric surfactants with oxyethylene spacer chain. Small angle neutron scattering and fluorescence studies, J. Phys. Chem. B 102 (1998) 6152–6160.
[27] M. Dreja, Cationic amphitropic gemini surfactants with hydrophilic oligo(oxyethylene) spacer chains, Chem. Commun. (1998) 1371–1372.
[28] Q. Li, X. Wang, X. Yue, Xia, Unique phase behaviors in the gemini surfactant/EAN binary system: the role of the hydroxyl group, Langmuir 31 (2015) 13511–13518.
[29] S. Sonu, S. Halder, R. Kumari, V.K. Aggrawal, S.K. Aswal, Saha, Study on interactions of cationic gemini surfactants with folded and unfolded bovine serum albumin: effect of spacer group of surfactants, J. Mol. Liq. 243 (2017) 369–379.
[30] S. Sinha, D. Tikariha, J. Lakra, T. Yadav, S. Kumari, S.K. Saha, K.K. Ghosh, Interaction of bovine serum albumin with cationic monomeric and dimeric surfactants: a comparative study, J. Mol. Liq. 218 (2016) 421–428.
[31] M. Borse, V. Sharma, V.K. Aswal, P.S. Goyal, S. Devi, Effect of head group polarity and spacer chain length on the aggregation properties of gemini surfactants in an aquatic environment, J. Colloid Interface Sci. 284 (2005) 282–289.
[32] I.V. Kapitanov, I.A. Belousova, A.E. Shumeiko, M.K. Kostrikin, T.M. Prokop'eva, A.F. Popov, Supernucleophilic system based on functionalized surfactants in the decomposition of 4-nitrophenyl esters derived from phosphorus and sulphur acids: II. Influence of the length of hydrophobic alkyl substituents on micellar effects of

functionalized monomeric and dimeric imidazolium surfactants, Russ. J. Org. Chem. 50 (2014) 694–704.
[33] D.R. Gabdrakhamanov, D.A. Samarkina, V.E. Semenov, L.F. Saifina, F.G. Valeeva, V.S. Reznik, L.Ya. Zakharova, Substrate specific nanoreactors based on pyrimidine-containing amphiphiles of various structures for cleavage of phosphonates, Phosphorus Sulfur Silicon 191 (2016) 1673–1675.
[34] A.B. Mirgorodskaya, L. Ya Zakharova, E.I. Khairutdinova, S.S. Lukashenko, O.G. Sinyashin, Supramolecular systems based on gemini surfactants for enhancing solubility of spectral probes and drugs in aqueous solution, Colloids Surf. A Physicochem. Eng. Asp. 510 (2016) 33–42.
[35] H. Fu, Y. Li, Y. Song, J. Li, Zh. Wang, L. Zhao, Synthesis and aggregation behaviors of a new bis-quaternary ammonium surfactant, J. Mol. Liq. 230 (2017) 329–336.
[36] M.S. Borse, S. Devi, Importance of head group polarity in controlling aggregation properties of cationic gemini surfactants, Adv. Colloid Interf. Sci. 123–126 (2006) 387–399.
[37] T.M. Zubareva, A.V. Anikeev, E.A. Karpichev, I.V. Kapitanov, T.M. Prokop'eva, A.F. Popov, Catalysis of the alkaline hydrolysis of 4-nitrophenyl diethyl phosphonate by cationic dimeric surfactant micelles, Theor. Exp. Chem. 47 (2011) 108–114.
[38] A.B. Mirgorodskaya, E.I. Yatzkevich, S.S. Lukashenko, L.Ya. Zakharova, A.I. Konovalov, Solubilization and catalytic behavior of micellar system based on gemini surfactant with hydroxyalkylated head group, J. Mol. Liq. 169 (2012) 106–109.
[39] Y. Karpichev, N. Jahan, N. Paul, Ch.P. Petropolis, T. Mercer, T.B. Grindley, D.G. Marangoni, The micellar and surface properties of a unique type of two-headed surfactant – pentaerythritol based di-cationic surfactants, J. Colloid Interface Sci. 423 (2014) 94–100.
[40] A.B. Mirgorodskaya, E.I. Yackevich, F.G. Valeeva, V.A. Pankratov, L.Ya. Zakharova, Solubilizing and catalytic properties of supramolecular systems based on gemini surfactants, Russ. Chem. Bull., Int. Ed. 63 (2014) 82–87.
[41] Z. Ding, Sh. Fang, Synthesis, surface and antimicrobial activities of novel cationic gemini surfactants, J. Surfactant Deterg. 18 (2015) 1051–1057.
[42] H. Schott, Solubilization of a water-insoluble dye as a method for determining micellar molecular weights, J. Phys. Chem. 70 (1996) 2966–2973.
[43] J. Lakra, D. Tikariha, T. Yadav, S. Das, K.K. Ghosh, Mixed micellization of gemini and cationic surfactants: physicochemical properties and solubilization of polycyclic aromatic hydrocarbons, Colloids Surf. A Physicochem. Eng. Asp. 451 (2014) 56–65.
[44] H. Akbaş, M. Boz, A. Elemenli, Interaction between cationic gemini surfactant and related single-chain surfactant in aqueous solutions, Fluid Phase Equilib. 370 (2014) 95–100.
[45] N. Barbero, P. Quagliotto, C. Barolo, E. Artuso, R. Buscaino, G. Viscardi, Characterization of monomeric and gemini cationic amphiphilic molecules by fluorescence intensity and anisotropy, Dyes Pigments 83 (2009) 396–402.
[46] M.S. Borse, T.J. Patil, S.S. Borse, Oil solubilization and aggregation behavior of cetyltrimethyl ammonium bromide surfactant and its derivatives by SANS, Chem. Sci. Trans. 3 (2014) 1326–1333.
[47] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Springer Science, New York, 2006 (954 pp).
[48] G.E. Dobrezov, Fluorescentnye zondy v issledovanii kletok, membrane i lipoproteinov, Nauka, Moscow, 1989 (277 pp).
[49] R. Zarganian, A.K. Bordbar, R. Amiri, M. Tamannaei, A.R. Khosropour, I. Mohammadpoor-Baltork, Micellization of pentanediyl-1,5-bis(hydroxyethylmethylhexadecylammonium bromide) as a cationic gemini surfactant in aqueous solutions: investigation using conductometry and fluorescence techniques, J. Solut. Chem. 40 (2011) 921–928.
[50] E.I. Yackevich, A.B. Mirgorodskaya, S.S. Lukashenko, L.Ya. Zakharova, Polyfunctional supramolecular systems based on surfactants containing the hydroxyalkyl moiety in the head group, Russ. Chem. Bull. 63 (2014) 1801–1806.
[51] R.A. Mackay, C. Hermansky, Phosphate ester-nucleophile reactions in oil-in-water microemulsions, J. Phys. Chem. 85 (1981) 739–744.
[52] N.O. Mchedlov-Petrossyan, Protolytic equilibrium in lyophilic nanosized dispersions: differentiating influence of the pseudophase and salt effects, Pure Appl. Chem. 80 (2008) 1459–1510.
[53] A. Albert, E.P. Sergeant, The Determination of Ionization Constants: A Laboratory Manual, 3rd ed. Chapman and Hall, London; New York, 1984 (300 pp).
[54] G.A. Gaynanova, G.I. Vagapova, F.G. Valeeva, E.A. Vasilieva, I.V. Galkina, L.Ya. Zakharova, O.G. Sinyashin, A novel supramolecular catalytic system based on amphiphilic triphenylphosphonium bromide for the hydrolysis of phosphorus acid esters, Colloids Surf. A Physicochem. Eng. Asp. 489 (2016) 95–102.
[55] T. Dwars, E. Paetzold, G. Oehme, Reactions in micellar systems, Angew. Chem. Int. Ed. 44 (2005) 7174–7199.
[56] I.V. Kapitanov, A.B. Mirgorodskaya, F.G. Valeeva, N. Gathergood, K. Kuca, L.Ya. Zakharova, Y. Karpichev, Physicochemical properties and esterolytic reactivity of oxime functionalized surfactants in pH-responsive mixed micellar system, Colloids Surf. A Physicochem. Eng. Asp. 524 (2017) 143–159.
[57] Yu. Sadovskii, T.N. Solomoichenko, M.K. Turovskaya, I.V. Kapitanov, Zh.P. Piskunova, M.K. Kostrikin, T.M. Prokop'eva, A.F. Popov, Peroxyhydrolysis of 4-nitrophenyl diethyl phosphate in micellar systems based on imidazolium Gemini surfactants, Theor. Exp. Chem. 48 (2012) 122–128.
[58] I.V. Berezin, K. Martinek, A.K. Yatsimirskii, Physicochemical foundations of micellar catalysis, Russ. Chem. Rev. 42 (1973) 787–802.
[59] S.F. Yunes, H.J. Foroudian, N.D. Gillitt, C.A. Bunton, Effect of micellization on acid dissociation and headgroup conformation of hexadecyl (2-hydroxyethyl) dimethylammoniumbromide, Colloids Surf. A Physicochem. Eng. Asp. 262 (2005) 260–268.