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Micellization and Catalytic Properties of Cationic Surfactants with Head Groups Functionalized with a Hydroxyalkyl Fragment

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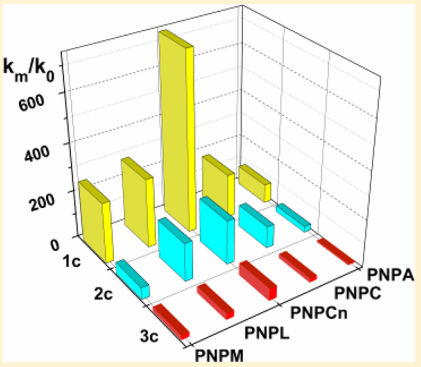
Supporting Information

ABSTRACT: The catalytic activity of two homological series of cationic surfactants bearing a hydroxyalkyl fragment in the head groups $R(CH_3)_2N^+(CH_2CH_2OH)Br^-$ and $R(CH_3)_2N^+(CH_2CH_2CH_2OH)Br^-$ toward the cleavage of the *p*-nitrophenyl esters of carbonic acids of different hydrophobicity (acetate, caprilate, caprinate, laurate, myristate) is shown to exceed that of typical cationic surfactants with the trimethylammonium (TMA) headgroup. The catalytic effect increases with the alkyl chain length of surfactants and nonmonotonous changes in the series: acetate < caprilate < myristate < laurate < caprinate, reaching 750 times. NMR and IR spectroscopy studies and the surface potential calculations revealed that the higher catalytic effect of hydroxyalkylated surfactants is not due to their higher surface potential and binding capacity toward substrates. This is in line with finding that binding constants for TMA series are higher than for their hydroxyalkylated analogues, which was demonstrated by the fitting of kinetic data in terms of the pseudophase model. The microenvironment factor rather than concentrating effect is responsible for the advanced catalytic properties of hydroxyalkylated surfactants in the micellar phase.



INTRODUCTION

The molecular structure of surfactants, namely, the nature of the head groups, the length and structure of hydrophobic tails, as well as solution pH, and the presence of electrolytes or organic solutes, strongly control their aggregation behavior. In its turn, the morphology of the surfactant assemblies determines the thermodynamic stability and physicochemical properties of the organized systems.[1−5] Cationic surfactants are widely involved in various nanotechnological strategies,[6−12] and therefore much attention is devoted to the correlation of their chemical structure with their aggregation and functional activity. The nature of head groups markedly affects the aggregation, solubilization, and catalytic properties of cationic surfactants,[13−27] with the role of substituents in head groups capable of H-bonding being of particular interest. These investigations are stimulated by the wide application of cationic surfactants as drug and gene carriers, micellar catalysts, emulsifiers, inhibitors of corrosion, and so forth. The role of hydroxyalkyl substituents in the DNA condensation mediated by cationic agents, in the regulation of lipase activity toward the hydrolysis of ester bonds, and in the formation of polymer−colloid complexes has been elucidated.[28−31] The structural behavior of the typical cationic surfactant, that is, cetyltrimethylammonium bromide, is compared with that of cetyldimethylhydroxyethylammonium and cetyldimethylhydroxyethylammonium bromides, with the critical micelle concentrations (cmc's) and thermodynamic parameters of the micellization determined.[17] Similar investigations have been carried out for the dodecyl analogues with the successive introduction of hydroxyalkyl substituents into the head groups.[32] These studies demonstrated an increase in the aggregative capacity with hydroxyalkylation, as well as the advantages of such functionalization from the viewpoint of nanotechnological applications, that is, the design of nanocontainers, nanoreactors, and so forth. However, the understanding of the role of hydroxyalkyl groups in the physicochemical properties of surfactants is unclear until now. In some cases their effects are treated in terms of the increase in the volume of head groups inducing the shielding effect around the charged atom, while another viewpoint assumes the contribution of hydrogen bonds to the interactions of head groups with each other and solubilized compounds. In addition, upon their functionalization, changes in the micropolarity of the surface layer occur, which can strongly affect the surfactant interactions with different guest molecules. To elucidate the mechanism of the hydroxylalkyl groups' effect on both the supramolecular structure and the functional activity of surfactants more experimental data are necessary.

Our recent investigations are focused on the catalytic activity of organized systems in the nucleophilic substitution in phosphorus acid esters.[33−37] Micellar surfactant solutions are known to strongly influence the properties of solubilized

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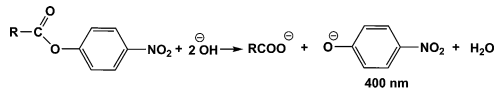
compounds including their reactivity,[38−41] thereby resulting in considerable changes in the mechanism and rate of reactions. The micellar rate effect of surfactants is mainly determined by noncovalent binding of reagents, which results in concentrating the reactants in micelles and changes in their environment. The functionalization of head groups allows us to invoke additional binding mechanisms, that is, the H-bonding that may enhance catalytic effect.

Herein, the influence of the structure of cationic surfactants with hydroxyalkyl fragments in head groups on their aggregation behavior and catalytic activity in the hydrolysis of carbonic acid esters has been systematically studied. Two homological series of ammonium surfactants differing in the distance of their OH-groups from the cationic center, that is, $R(CH_3)_2N^+(CH_2CH_2OH)Br^-$ (**1a−d**) and $R(CH_3)_2N^+(CH_2CH_2CH_2OH)Br^-$ (**2a−d**), in which R = n-$C_{12}H_{25}$ (**a**), n-$C_{14}H_{29}$ (**b**), n-$C_{16}H_{33}$ (**c**), and n-$C_{18}H_{37}$ (**d**) has been investigated and compared with nonfunctionalized cationic surfactants of trimethylammonium (TMA) series $R(CH_3)_3N^+Br^-$ (**3a−d**). Apart from their aggregation behavior, the kinetics of basic hydrolyses of *p*-nitrophenyl esters of carbonic acids differing in hydrophobicity has been measured (Scheme 1). It can be expected that the substrates were displaced from the outside to the nonpolar core with an increase of their alkyl chain length, which would affect their reactivity.

Scheme 1. Schematic Representation of the Hydrolysis of *p*-Nitrophenyl Esters of Carbonic Acids



R = CH_3 (PNPA), n-C_7H_{15} (PNPC), n-C_9H_{19} (PNPCn), n-$C_{11}H_{23}$ (PNPL), n-$C_{13}H_{27}$ (PNPM)

EXPERIMENTAL SECTION

Chemicals. Commercial alkyltrimethylammonium bromides **3a−d** (Sigma), *p*-nitrophenol, *p*-nitrophenyl acetate (PNPA), *p*-nitrophenyl caprilate (PNPC), *p*-nitrophenyl caprinate (PNPCn), *p*-nitrophenyl laurate (PNPL), and *p*-nitrophenyl myristate (PNPM) (Fluka) of 99 % purity were used. Hydroxyalkylated surfactants **1a−d** and **2a−d** were synthesized through the reaction of dimethylaminoethanols with corresponding alkyl bromides.[17,42] The structure of surfactants synthesized was proved by elemental analysis, IR, and H^1 NMR spectroscopy.

Surface tension measurements were performed with the du Nouy ring detachment methods using tensiometer K6 (Kruss).[43]

Acid−base properties of *p*-nitrophenol (PNP) were investigated by spectrophotometry. A Specord UV−vis instrument supplied by a temperature-controlled module with quartz cuvettes of a 1 cm path length was used. Absorption spectra of PNP were collected for the λ ranging from (250 to 600) nm, with pH value varying. The observed pK_a values (p$K_{a,obs}$) of PNP were determined using eq 1[44]

$$pK_{a,obs} = pH + \log \frac{[PNP]}{[PNP^-]} \quad (1)$$

where [PNP] and [PNP^-] are the molar concentrations of the neutral form and *p*-nitrophenolate ion, respectively. Each value of pK_{obs} is the mean of three to five independent determinations obtained at different pH values.

The reaction kinetics was monitored through changes in the *p*-nitrophenolate anion absorption at 400 nm. The initial substrate concentration of $5\cdot10^{-5}$ mol·kg^{-1} was maintained throughout the kinetic study. The observed rate constants (k_{obs}) were determined as follows: $\ln(A_\infty - A) = -k_{obs}t$ + const; here A and A_∞ are the absorbances 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 (Figures S4 and S5 of the Supporting Information, SI). The k_{obs} values were triply or fourfold measured, and the mean value was taken into consideration, with the experimental error being within 4 %.

Kinetic theory and quantitative treatment of kinetic data are given in the SI, Figures S1−S5. The reaction under study, that is, the nucleophilic substitution in the carbonic acid esters, is a bimolecular reaction, and generally it is second-order. A commonly used approach for the kinetic study of such processes is to carry out them under the excess of one of reagents, thereby reducing processes to the first-order reactions. This transformation is supported by the linearity in the $\ln(A_\infty - A)$ versus t coordinates (Figures S4 and S5 of the SI). To provide pseudofirst rate conditions, we carried out the reaction in basic buffer solution, in which the concentration of OH-ions is much higher as compared to that of substrate. In these conditions, only the substrate concentration determines the reaction rate.

Micellar catalysis assumes the distribution of reagents between two phases (Scheme S1 of the SI).[1,45] Herein, kinetic data were treated in terms of the pseudophase model, which assumes that micellar solution consists of two pseudophases, that is, volume phase and a micellar phase. The reagents (substrate, S, and nucleophile, OH) are distributed between the two phases in accordance with the partition coefficients expressed as follows:

$$P_S = [S]_m/[S]_0 \qquad P_{Nu} = [OH]_m/[OH]_0$$

in which the lower indices m and 0 denote the micellar and bulk phases, respectively.

Depending on the ratio between these contributions, two types of kinetic plots can be observed. In the case of the moderate binding of the reagents a plateau is observed in kinetic curves. In the case of the effective binding of reagents, the contribution of the reaction in bulk phase is minor, and an extremum type dependence occurs. The first case is usually described by eq 2, which is analogous to Michaelis−Menten equation, while the second type kinetics obeys eq 3. The maximum in kinetic curves is due to the complete binding of reagents at low surfactant concentrations, so that the dilution is observed with further increase in surfactant concentrations resulting in the decrease in the reaction rate.

$$k_{obs} = \frac{k_m K_S C + k_0}{1 + K_S C} \quad (2)$$

here K_S is the binding constant of substrate (S) associated with the partition coefficient $P_S = [S]_m/[S]_0$ as follows: $K_S = (P_S - 1)V$; indices 0 and m denote the water and micelles, respectively; V is the molar volume of micellar pseudophase; k_0 and k_m (s^{-1}) are the pseudofirst rate constants in water and micelles, respectively; C is the surfactant concentration minus cmc.

$$k'_{obs} = \frac{k_{2,0} + k_m K_S K_{OH} C}{(1 + K_S C)(1 + K_{OH} C)} \quad (3)$$

in which k'_{obs} is the second-order rate constant obtained by division of the observed pseudofirst rate constant (k_{obs}) by the total nucleophile concentration; $k_{2,0}$ is the second-order rate constant of the reaction in water, k_m (= $k_{2,m}/V$) characterizes the reactivity in the micellar phase; C is the total surfactant concentration minus cmc. To determine the true bimolecular rate constant for the reaction in the micellar phase, $k_{2,m}$, a value for the volume of the micellar pseudophase, should be estimated. The value V of 0.3 kg·mol^{-1} is taken for the surfactants based on their molecular weight and density,[46] with no corrections introduced for the water in solvation shells. K_S and K_{OH} are the binding constants of the substrate and nucleophile.

To differentiate factors responsible for the micellar effects eq 3 is reduced to eq 4.[45] Equations 3 and 4 are valid for the systems with the extremum type of the k_{obs} versus C curve. In this case, a considerable acceleration of reactions occurs in micellar systems as compared to molecular solution, that is, the contribution of the reaction in the bulk phase, is neglected. The maximum rate acceleration can be calculated as the ratio between the pseudofirst rate constants in the micellar system and water, respectively (eq 4):

$$\left(\frac{k_{obs}}{k_0}\right)_{max} = \frac{k_{2,m}}{k_{2,0}} \cdot \frac{K_S K_{OH}}{V(\sqrt{K_S} + \sqrt{K_{OH}})^2} \quad (4)$$

The first multiplier on the right characterizes the influence of the micellar microenvironment (F_m), and the second factor determines the concentration of the reagents in micelles (F_c).

NMR experiments were performed with a Bruker AVANCE-600 spectrometer (14.1 T) equipped with a 5 mm diameter gradient inverse broad band probehead and a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 0.535 T·m^{-1}. Frequencies are 600.13 MHz in ^{1}H and 150.90 MHz in ^{13}C experiments. Chemical shifts are reported in the δ (ppm) scale relative to the residual signal of solvents [HDO (4.7 ppm); CD_3OD (3.31 and 49.0 ppm, for ^{1}H and ^{13}C, respectively)]. Experiments were carried out at (30 ± 0.2) °C. To avoid temperature fluctuations owing to the sample heating by the magnetic field pulse gradients high airflow was used (0.149 s^{-1}). The Fourier transform pulsed-gradient spin−echo (FT-PGSE)[47−49] experiments were performed by the BPP-STE-LED sequence.[47] Data were acquired with a (50.0 or 120.0) ms diffusion delay, with bipolar gradient pulse duration from (2.2 to 6.0) ms, 1.1 ms spoil gradient pulse (30 %), and a 5.0 ms eddy current delay. The bipolar pulse gradient strength was incremented from (0.01 to 0.32) T·m^{-1} in 32 steps.

The FT-PGSE experiments were performed in triplicate, and only the data with the high (>0.999) correlation coefficients of ln I/I_0 versus b were included [I/I_0, the normalized signal attenuation; $b = \gamma^2\delta^2g^2(\Delta - \delta/3)$; γ, the gyromagnetic ratio; g, the pulsed gradient strength; Δ, the interval between the pulsed-gradients; δ, the pulsed gradient duration]. All peaks were analyzed, and the values were averaged.

RESULTS AND DISCUSSION

Tensiometry data exemplified by the surface tension isotherms for cationic surfactants **1a−d** (Figure 1) show that they exhibit a marked surface activity, with all σ vs C dependences being

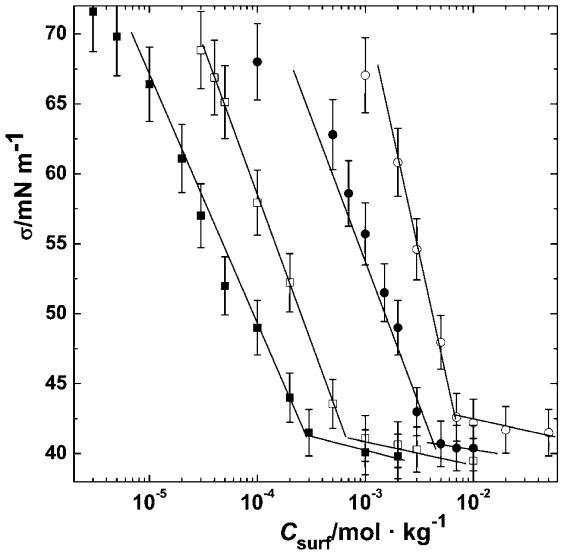


Figure 1. Surface tension isotherms of hydroxyethylated cationic surfactants; 25 °C. ○, **1a**; ●, **1b**; □, **1c**; ■, **1d**.

discontinued at a definite concentration, which is generally called a critical micelle concentration (cmc). Hydroxyalkylated surfactants demonstrate lower cmc values as compared to reference compounds **3a−d** (Table 1). This trend agrees well with refs 23 and 50 which indicates that micellization is probably favored by the H-bonding between head groups and their more effective solvation. Meanwhile, the main factor contributing to the aggregation is the hydrophobicity of surfactants controlled by the alkyl chain length. Indeed, for all of the surfactant series the cmcs decrease by a factor of 10 with the transition from dodecyl to octadecyl tails (Table 1).

The micellar solutions of cationic surfactants provide a wide range of possibilities for the control of the rate of ion-molecular reactions, including the basic hydrolysis of esters. These processes generally proceed in the Stern layer of micelles and strongly depend on the sign and magnitude of the micellar surface potential. In the case of cationic surfactants, the concentration of anionic nucleophiles can occur in the reaction zone, which results in the acceleration of the reaction. Figures 2 to 5 summarize kinetic data on the hydrolyses of esters in the cationic surfactants studied. The catalytic effect is manifested on reaching the cmc and increases with an increase in the alkyl chain length of surfactants, which is typical for the reactivity in micellar systems. For all the surfactants studied the micellar rate effect increases by an order of magnitude on transition from dodecyl to octadecyl derivatives (e.g., see Figures 2 and 3 for PNPA and PNPC, respectively). Surfactants with hydroxyethylated head groups are markedly more effective than their nonfunctionalized analogues, while hydroxypropylated surfactants are intermediate. The catalytic effect expressed as the ratio k_{obs}/k_0 is markedly higher for hydroxyalkylated surfactants as compared to TMA analogues (Figure 6: exemplified by hexadecyl derivatives) and changes as follows: **1c** > **2c** > **3c**.

It is noteworthy that, due to a certain acidity of hydroxyalkyl groups (pK_a (12.4 to 12.6)), these surfactants can exist in the form of zwitterions in strong alkali solutions, thus showing a nucleophilic activity.[51,52] However under the experimental conditions maintained in this study (pH 9.0) hydroxyalkylated surfactants behave as typical cationic compounds. The above-mentioned advantages of their catalytic activity over non-

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Table 1. Values of cmc, the Surface Potential, Binding Constants, and p$K_{a,m}$ of *p*-Nitrophenol for Micelles of Cationic Surfactants 1a−d and 2a−d

surfactant	R	cmc/mol·kg^{-1}	K_A/kg·mol^{-1}	K_B/kg·mol^{-1}	p$K_{a,m}$	Ψ/mV
1a	$C_{12}H_{25}$	0.0071				
1b	$C_{14}H_{29}$	0.0049	600	13700	5.79	107
1c	$C_{16}H_{33}$	0.00070[a]	620	26600	5.52	123
1d	$C_{18}H_{37}$	0.00012	1320	67600	5.42	129
2a	$C_{12}H_{25}$	0.0068				
2b	$C_{14}H_{29}$	0.0034	290	6150	5.83	105
2c	$C_{16}H_{33}$	0.00065[a]	395	22800	5.39	131
2d	$C_{18}H_{37}$	0.000096	1100	78600	5.30	136
3c	$C_{16}H_{33}$	0.00080	230	17300	5.32	133

[a]cmc values for **1c** equal 0.0072 mol·kg^{-1} (fluorometry), 0.0078 mol·kg^{-1} (conductometry), 0.0083 mol·kg^{-1} (microcalorimetry);[43] cmc for **2c** equals 0.008 mol·kg^{-1} (conductometry).[23]

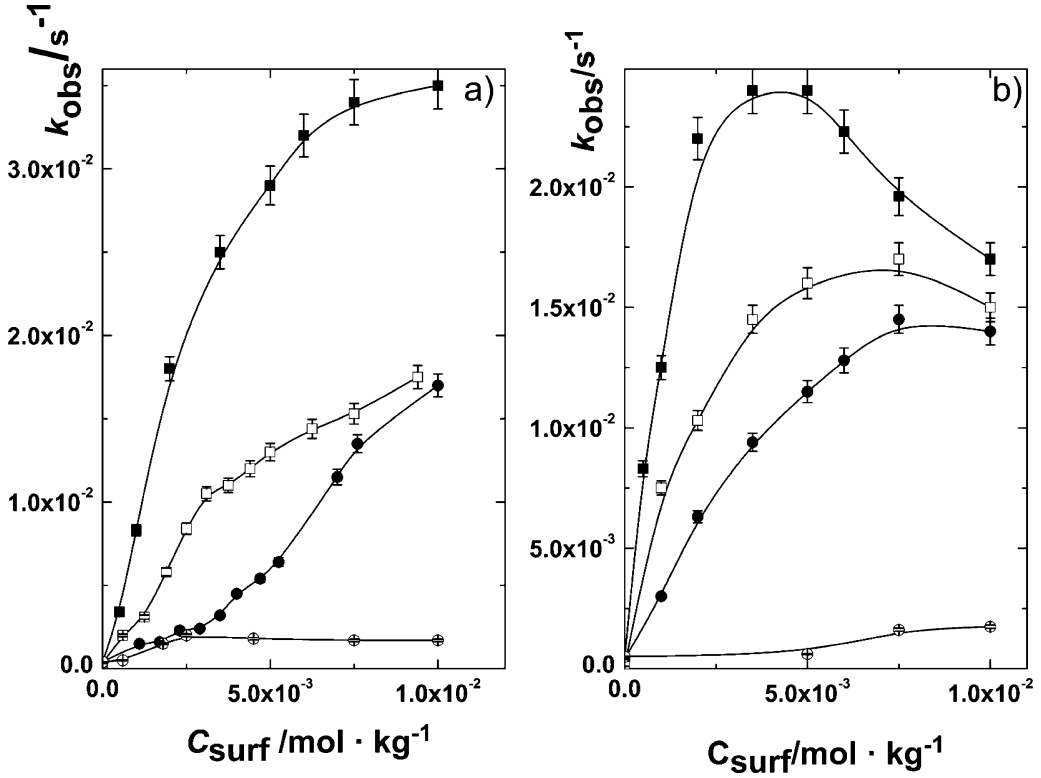

Figure 2. Observed rate constants of basic hydrolyses of PNPA (a) and PNPC (b) as a function of the concentration of cationic surfactants; pH 9.0; 25 °C; ○, **1a**; ●, **1b**; □, **1c**; ■, **1d**.

functionalized analogues can be due to the differences in the surface potential, which is responsible for the concentration of hydroxide-ions in the reaction zone. The surface potential was determined from the p$K_{a,obs}$ values of *p*-nitrophenol (PNP) by the spectrophotometry method.[23,53] Neutral form of PNP demonstrates a lower affinity toward a micelle as compared to the anionic form. The latter can be effectively bound by cationic micelles by electrostatic interactions, which results in a decrease in the observed pK_a value in cationic micelles (Figure 7). The observed constant of the acid−base dissociation K_{obs} depends on the surfactant concentration as follows:[45]

$$K_{obs} = \frac{1 + K_B C}{1 + K_A C} \cdot K_{a,0} \quad (5)$$

where $K_{a,0}$ is the constant of the acid−base dissociation in water; K_A and K_B are the binding constants of the acid and base forms of the compound; C is the surfactant concentration minus cmc. The quantitative analysis of the $(K_{a,0} - K_{obs})/C$ vs K_{obs} dependence by the least-squares method gives the values of binding constants. With an increase of the surfactant concentration p$K_{a,obs}$ approximates to p$K_{a,m}$; here p$K_{a,m}$ is the pK_a in the micelle. Table 1 summarizes the cmc values and binding constants of neutral and anionic forms of PNP calculated by eq 5.

Equation 6 gives the relation between the p$K_{a,m}$ value and the surface potential:

$$pK_{a,m} = pK_{a,i} - \frac{F\psi}{2.303RT} \quad (6)$$

where p$K_{a,i}$ is the intrinsic pK_a of the probe in the absence of an electrostatic field, and F is the Faraday constant. The p$K_{a,i}$ value can be equated to nonionic surfactants or modeled by addition of electrolytes to the surfactant solutions. Herein the pK_a value of 7.6 for PNP in the Triton-X-100 solution is used.

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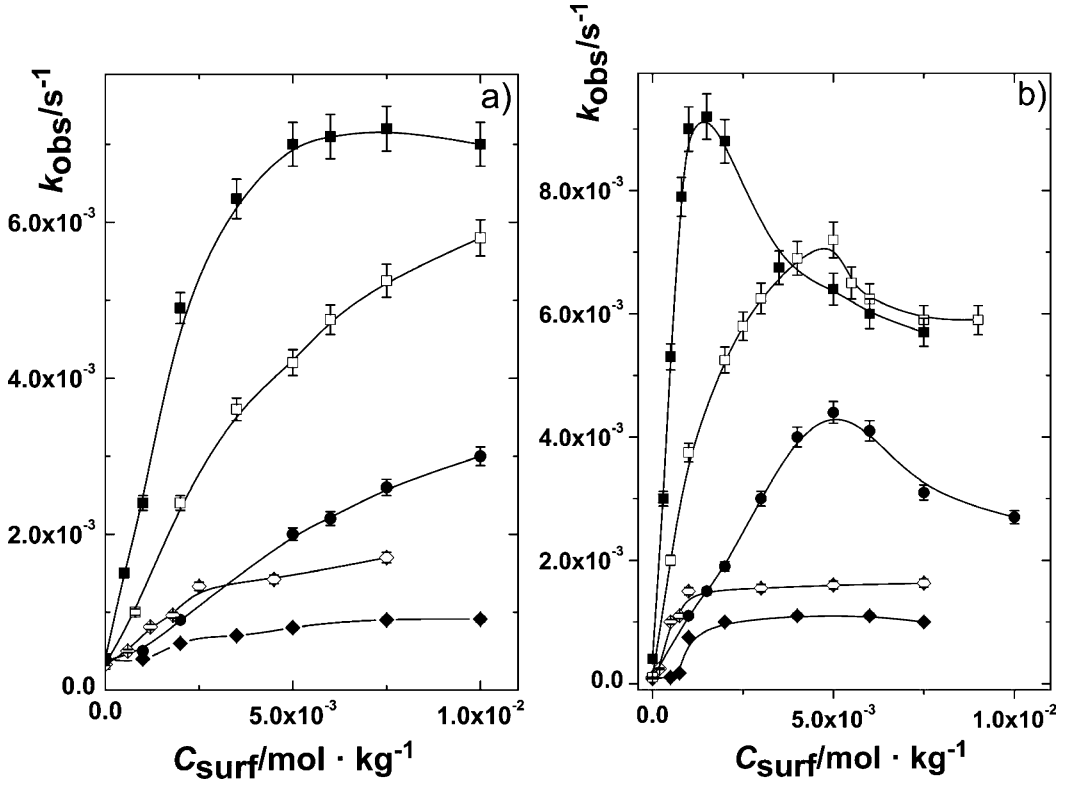

Figure 3. Observed rate constants of basic hydrolyses of PNPA (a) and PNPC (b) as a function of the concentration of cationic surfactants; pH 9.0; 25 °C; ●, **2b**; □, **2c**; ■, **2d**; ◆, **3b**; ◇, **3c**.

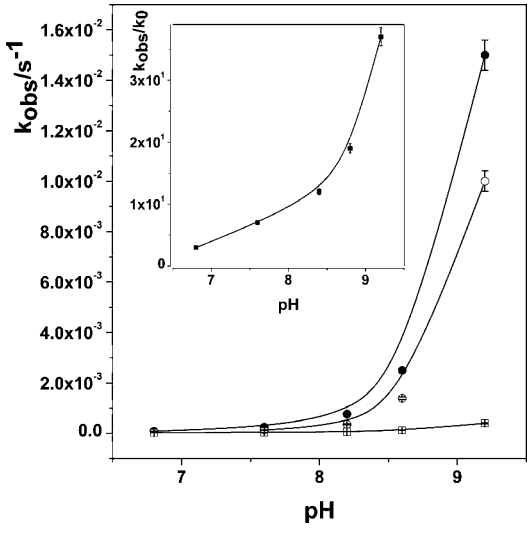

Figure 4. Observed rate constants of basic hydrolyses of PNPA as a function of solution pH without any cationic surfactants (□) and in the presence of 0.0025 mol·kg^{-1} (○) and 0.005 mol·kg^{-1} (●) of **1c**; 25 °C. Inset shows the effect of pH on the catalytic effect of **1c** toward the basic hydrolyses of PNPA.

For T = 298 K eq 6 can be transformed to:

$$\Psi = 0.0591(pK_{a,i} - pK_{a,m}) \quad (7)$$

The binding constants of the anionic form of PNP by micelles of the surfactants studied are ca. (20 to 70)-fold higher as compared to the neutral form (Table 1). This fact is responsible for the lower pK_a values of PNP in the micellar phase versus water by the (1.4 to 1.9) logarithmic unity. The binding constants of both forms increase with the alkyl chain length of surfactants, which is probably due to the increase in their solubilization capacity. Surface potentials somewhat increase with an increase in the alkyl chain length, demonstrating only a slight dependence on the presence of hydroxyalkyl groups. These data somehow disagree with the assumption[29] that the decrease in the cmcs of hydroxyalkylated surfactants is due to the shielding effect of head groups toward the charged nitrogen. To compare the surface potentials and observed rate constants of the hydrolysis of PNPA and PNPC for three surfactants with the same alkyl chain length (e.g., for **1c**, **2c**, and **3c**, see Table 1 and Figures 2 and 3) it is clear that the Ψ value is slightly lower in the case of hydroxyethylated surfactant versus the conventional TMA-analogue, while the observed rate constants for the latter are ca. 10-fold lower. Thus the surface potential is not the main factor determining the catalytic activity of hydroxyalkylated surfactants. We assume that the electrophilicity of the carbon atom in the carbonyl group and hence the reactivity of substrates can increase due to their H-bonding with the hydroxyalkyl fragment of surfactants. To gain an insight into the substrate−surfactant interactions, hexadecyl derivatives of hydroxyalkylated surfactants **1c** and **2c** and conventional TMA analogue **3c** were investigated by NMR self-diffusion coefficient (D_s) measurements in both the presence and the absence of substrates.

The effective method for characterization of association of amphiphiles is NMR self-diffusion.[54,55] The association process can be monitored through the difference in the self-diffusion coefficients (D_S) for the amphiphile monomers and aggregates. The translational mobility of an amphiphilic species decreases by 1−2 orders of magnitude, when it is bound by the micelle. Due to a fast exchange in the NMR time scale between

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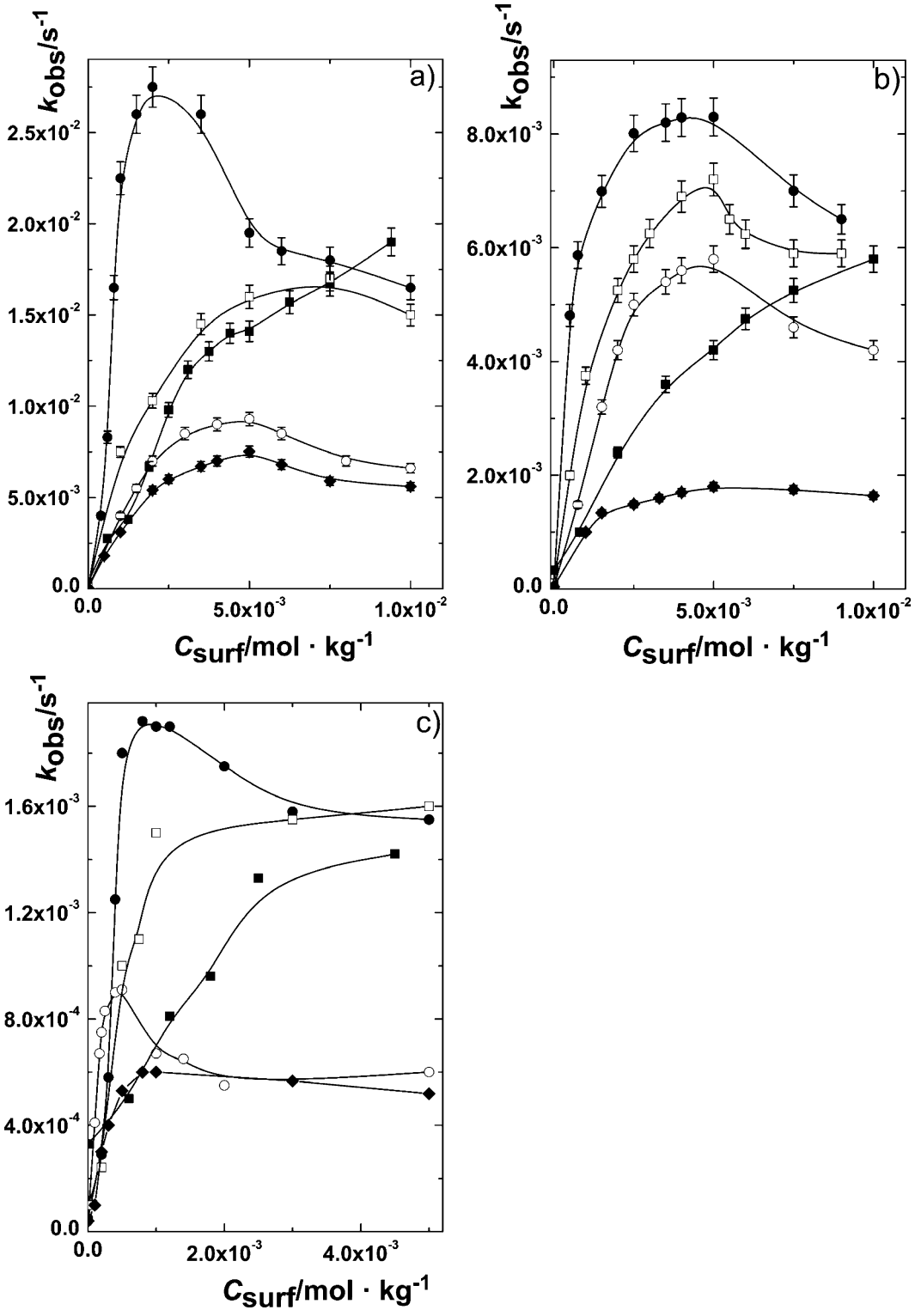

Figure 5. Observed rate constants of basic hydrolyses of carbonic acid esters as a function of the concentration of cationic surfactants **1c** (a); **2c** (b); **3c** (c); pH 9.0; 25 °C; ■, PNPA; □, PNPC; ●, PNPCn; ○, PNPL; ◆, PNPM.

amphiphiles in the micelles and the bulk phase two-site model can be used

$$D_{sur} = D_{mic}P_{mic} + D_{free}(1 - P_{mic}) \quad (8)$$

in which D_{sur} is the time-averaged diffusion coefficient of the surfactant, P_{mic} is the fraction of micellized surfactant molecules, D_{mic} is the diffusion coefficient of the micelle, and D_{free} is the diffusion coefficient of the "free" surfactant in the aqueous phase.

First, the 0.005 mol·kg^{-1} surfactant solutions **1c**, **2c**, and **3c** were investigated (Table 2). Then to these samples, PNPA was added, and similar NMR measurements were also carried out (Table 2). Thus the sizes of aggregates were estimated based on self-diffusion coefficients both prior to and after the substrate

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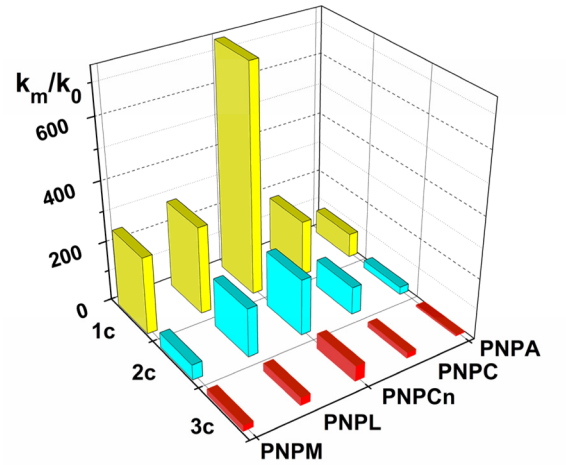

Figure 6. Micellar rate effect of cationic surfactants **1c**, **2c**, and **3c** toward the basic hydrolyses of *p*-nitrophenyl esters of carbonic acids.

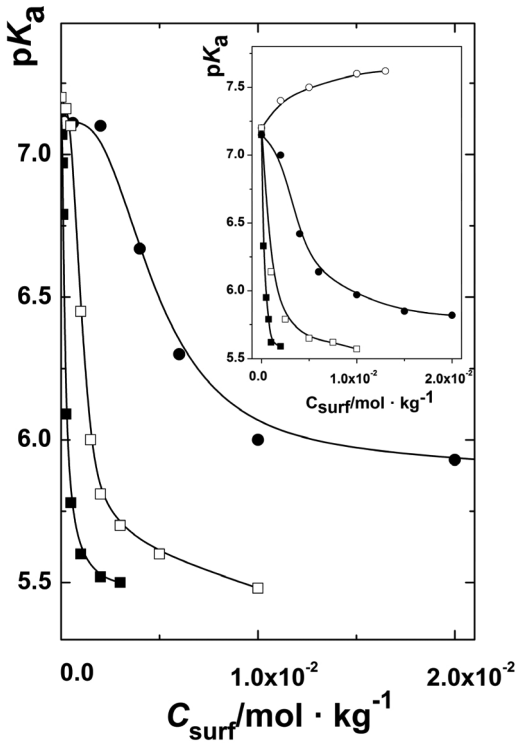

Figure 7. Dependence of pK_a of *p*-nitrophenol on the hydroxypropylated surfactant concentration ●, **2b**; □, **2c**; ■, **2d**. Inset shows dependence of pK_a of *p*-nitrophenol on the concentration of ○, Triton-X-100 and ●, **1b**; □, **1c**; ■, **1d**.

addition. In single surfactant solutions, the hydrodynamic radius of micelles lies within the interval of (2.2 to 2.4) nm, which corresponds to the aggregation numbers of (31 to 39) in spherical approximation. The addition of the substrate PNPA results in the increase of the size of aggregates by (5 to 15) %. The D_S value of the substrate upon its solubilization by surfactant micelles should decrease due to the contribution of self-diffusion coefficients of the bound substrate (eq 7). Therefore the comparison of the D_S value of free substrate (i.e., in the absence of surfactants or below the cmc) with that in micelles makes it possible to estimate the fraction of the bound substrate, P_b (Table 2). As can be seen, P_b reaches 24 % at the surfactant concentration of 0.005 mol·kg^{-1}. This value exceeds the cmc (Table 1) but lies below the plateau k_{obs} region in Figures 2, 3, and 5. Therefore P_b can considerably increase with an increase in the surfactant concentration in the case of PNPA and especially for the more hydrophobic esters, for which the complete binding can occur. At the same time, the self-diffusion coefficients of the substrate and hence its solubilization by micelles practically do not depend on the structure of head groups. The lack of any specific interaction between the substrate and surfactant head groups is also supported by the ^{13}C chemical shifts. Namely, the electrophilicity of the carbon atom is mostly determined by the polarization of carbonyl group, which can be monitored in its ^{13}C chemical shift.[56] Essentially similar chemical shifts observed for carbonyl group of acetate in D_2O (172.4 ppm) and surfactant (171.9 to 172.4) ppm solutions indicate that there is the lack of change in charge density at carbon atom upon substrate solubilization.

Above investigations were carried out in aqueous solution. Meanwhile, in the presence of micelles, the reaction in the micellar pseudophase, that is, in the nonpolar microenvironment, mainly contributes to the observed rate constant. Therefore the above conclusion on the lack of the headgroup/substrate interactions may be invalid in nonpolar microenvironment. Besides, hydrogen bonds between carbonyl oxygen and OH groups of the substrate in water will be suppressed by competitive interactions of these species with water. Therefore the ^{13}C NMR- and IR-spectroscopy studies were carried out for 0.001 mol·kg^{-1} PNPA single solution ($CDCl_3$) and for (0.005 and 0.01) mol·kg^{-1} solutions of **1c** and **3c** ($CDCl_3$). It turned out that there are almost no differences in the ^{13}C spectra of single substrate and micellar (**1c** and **3c**) substrate solutions. Similarly, in the IR spectrum of the substrate the carbonyl stretching absorption is observed at 1720 cm^{-1} regardless of the presence and type of surfactants added. Therefore, this experiment contradicts the assumption that the activation of substrates occurred by hydroxyalkylated surfac-

Table 2. NMR Self-Diffusion Data (Self-Diffusion Coefficients D_S, Hydrodynamic Radius R_h, Fraction of the Bound Substrate P_b, and Aggregation Number N_{agg} for Components of the Systems Based on Cationic Surfactants in the Presence and Absence of PNPA; 30 °C

surfactant	C_S/mol·kg^{-1}	D_S/(10^{10} m^2·s^{-1}) (surfactant)	D_S[a]/(10^{10} m^2·s^{-1}) (substrate)	R_h/A (micelle)	P_b	N_{agg}
1c	0	1.18		23.5		39
	0.001	1.14	7.32	24.4	0.19	43
2c	0	1.26		22.0		32
	0.001	1.06	6.95	26.2	0.24	54
3c	0	1.27		21.9		31
	0.001	1.15	7.36	24.0	0.18	42

[a] D_S of free (nonmicellized) PNPA equals 8.76·10^{-10} m^2·s^{-1}.

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Table 3. Quantitative Treatment of Kinetic Data of the Reaction of the Esters in Surfactant Solutions of 1c, 2c, and 3c (Figure 5) in Terms of Equation 2 (pH 9.0, 25 °C)

surfactant	substrate	k_m/s^{-1}	$K_S/kg\cdot mol^{-1}$	cmc/(10^4 mol·kg^{-1})	k_m/k_0[a]
1c	PNPA	0.0263	260	2.07	80
	PNPC	0.0185	1050	3.75	185
	PNPCn	0.0375	1900	3.4	750
	PNPL	0.0116	990	4.86	290
	PNPM	0.0102	600	1.58	255
2c	PNPA	0.0082	240	5.7	25
	PNPC	0.0092	720	1.2	92
	PNPCn	0.0093	2350	0.34	186
	PNPL	0.00655	2000	1.97	161
	PNPM	0.00201	1450	3.11	50
3c	PNPA	0.00168	960	4.67	5.1
	PNPC	0.0017	4500	1.80	17
	PNPCn	0.00208	18400	2.81	50
	PNPL	0.00103	19100	0.69	26
	PNPM	0.00074	5100	0.82	19

[a] k_m/k_0 is the acceleration of the reaction as compared to basic hydrolyses of the substrates under a solution pH of 9.0.

Table 4. Results of the Quantitative Treatment of Kinetic Data for Hydrolyses of PNPCn and PNPL in Micellar Solutions of Cationic Surfactants 1c, 2c, and 3c (Figure 5) in Terms of eq 3; pH 9.0; 25 °C

substrate	surfactant	$k_{2,m}/kg\cdot mol^{-1}\cdot s^{-1}$	$K_{OH}/kg\cdot mol^{-1}$	$K_S/kg\cdot mol^{-1}$	$(k_{obs}/k_0)_{max}$	F_m	F_c	$F_m\cdot F_c$
PNPCn	**1c**	10	100	6100	550	2.0	266	531
PNPL	**1c**	7.4	45	4200	232.5	1.25	124	230
PNPCn	**2c**	5.8	40	7100	172	1.45	116	170
PNPL	**2c**	3.9	44	5650	145	0.96	123	118
PNPCn	**3c**	0.52	130	10300	38.4	0.10	346	36
PNPL	**3c**	0.39	140	10100	22.8	0.01	247	24

tants through H-bonding. Another explanation of the influence of hydroxyalkyl moieties on the reactivity of alkanoates may be based on accompanying changes in the micropolarity of the reaction site. However, as the monitoring of the steady-state fluorescence emission spectra revealed, the I_1/I_3 ratio as a measure of the micropolarity only slightly changes by introducing one-by-one hydroxyalkyl moieties into the head groups of **3c**.[28]

It can be concluded that none of the above factors, that is, changes in the surface potential or micropolarity and the activation of the substrate by the OH-group of the head groups, are responsible for the rate enhancement induced by the functionalization of the surfactant head groups. Probably, more detailed investigations involving modeling the transition state of the reaction are required.

The high catalytic activity of hydroxyethylated surfactants **1c** and **1d** let us to carry out kinetic studies in mild alkali conditions (about pH 9.0), thereby eliminating side reactions contributed by the hydroxyl-groups of surfactants. According to these data (Figure 4) the observed rate constants of hydrolysis of PNPA in alkali solutions increase with the addition of hydroxyethylated surfactant **1c**, with the catalytic effect (k_{obs}/k_0) depending on the solution pH. A rather sharp increase in the catalytic activity with an increase in pH can be due to the contribution of the nucleophiliciy of hydroxyethyl groups of the surfactant at strong alkali conditions.

Apart from nonassociated substrates PNPA and PNPC the kinetic studies of PNPCn, PNPL, and PNPM prone to aggregation were also carried out in micellar solutions of surfactant series **1**−**3** at pH 9.0. It can be assumed that with an increase in the hydrophobicity of substrates their dislocation may occur toward the micellar interior, thus affecting the reaction rate. As a whole, an increase in the surfactant hydrophobicity results in the increase in the observed rate constants and the catalytic effect (Figure 2, 3, and 5). The increase in the substrate hydrophobicity exerts a non-monotonous effect, so that the decrease in the reactivity occurs in the case of the most hydrophobic esters, which can be due to the micellization of high homologues.[57] In the presence of cationic surfactants, mixed micelles are formed instead of individual substrate associates, thus influencing the reactivity of amphiphilic esters.[23,40] The micellar rate effect on the hydrolysis of substrates differing in their hydrophobicity is exemplified by hexadecyl derivatives of surfactants **1**−**3** (Figure 5). For all of the substrates their reactivity changes in the following order **1c** > **2c** > **3c**; that is, the highest catalytic effect is observed in the case of the hydroxyethylated surfactant **1c**.

Further information can be obtained from the quantitative treatment of kinetic data (Figures 2, 3, and 5) in terms of the pseudophase model (eq 2). The results of analysis (Table 3) reveal that the so-called kinetic cmc's extracted from the fitting procedure are lower than those obtained by tensiometry. This discrepancy can be due to (i) the contribution of the premicellar assemblies to the micellar rate effect and (ii) the promotion of the micellization by the additives of organic substrates. Indeed, the more marked decrease in the kinetic cmc is observed for the more hydrophobic esters. It is noteworthy that the binding constants of substrates with hydroxyalkylated surfactants **1c** and **2c** are similar, while those with TMA analogues are (3 to 4)-fold higher. This is another argument in favor of the conclusion that the higher catalytic

activity of hydroxyalkylated surfactants is not related to their higher binding capacity toward the substrates.

Equation 2 describes the reaction kinetics for the first-order rate constants demonstrating the plateau-type concentration dependence. In this case only the substrate distribution between two phases is taken into account, and therefore the reaction kinetics is treated in terms of the substrate binding constant and the first-order rate constant in the micellar phase. However, basic hydrolysis is related to the bimolecular reaction, although the pseudofirst conditions were maintained. Indeed, many concentration dependences in Figures 2, 3, and 5 exhibit an extremum-type shape, which is typical for ion-molecular reactions in cationic micelles in the case of the strong binding of the substrate.[45] These dependences were also treated in terms of eq 2, with part of the curves before maximum being considered. To obtain a deeper insight into the catalytic mechanism, eq 3 was used for the quantitative analysis of selected dependences. The calculated values of binding constants for both reagents and second order rate constants for reactions of hydrophobic substrates PNPCn and PNPL are summarized in Table 4. The effective binding of substrates is supported by the high values of K_S ranging from (4000 to 10000) kg·mol^{-1}, while the binding of hydrophilic nucleophile is much weaker. The above-mentioned reverse correlation between the binding constants and catalytic activity obtained by fitting eq 2 to the kinetic data has been confirmed by calculations with eq 3; that is, higher binding constants are obtained for nonfunctionalyzed surfactants of the TMA type, while their catalytic effect is lower as compared to their hydroxyalkylated analogues.

In aqueous micellar solutions, the concentration factor F_c (eq 4) is the main contributor to the micellar rate effect, while the micellar microenvironment exerts a negative effect upon the nucleophilic substitution, with the F_m decreasing with the substrate hydrophibicity.[45] Such behavior is actually observed in the case of the nonfunctionalized surfactant (Table 4); namely, the concentration factor exceeds by 2 orders of magnitude. However due to the decrease in the second-order rate constant in the micellar pseudophase as compared to water the resulting effect ranges from (20 to 45) times depending on the substrates. For the case of the hydroxyalkylated surfactant similar values of the concentration factor are also observed (Table 4), while unlike the TMA series, $F_m > 0$, which results in a marked increase in catalytic effects (550-fold acceleration). This clearly indicates that the advantage in catalytic activity of hydroxyalkylated surfactants is due to the activation of the substrates. Probably, hydroxyalkyl fragments provide more polarity in the reaction site as compared to the TMA series.

CONCLUSIONS

A systematic study of the aggregation behavior and catalytic activity toward the cleavage of *p*-nitrophenyl esters of carbonic acids of different hydrophobicity (acetate, caprilate, caprinate, laurate, myristate) has been carried out for two homological series of cationic surfactants bearing hydroxyalkyl fragment in the head groups $R(CH_3)_2N^+(CH_2CH_2OH)Br^-$ and $R(CH_3)_2N^+(CH_2CH_2CH_2OH)Br^-$. The catalytic effect increases with the alkyl chain length of surfactants and depends on the structure of the headgroup as follows: trimethylammonium (TMA) < hydroxypropylated < hydroxyethylated surfactants. NMR and IR spectroscopy studies and the surface potential calculations revealed that the higher catalytic effect of hydroxyalkylated surfactants is not due to their higher surface potential and binding capacity toward substrates. This is in line with the simulation of kinetic data in framework of pseudophase model, which demonstrated the higher binding constants for the TMA series as compared to hydroxyalkylated analogs. Fitting parameters showed that microenvironment factor rather than concentrating effect is responsible for the advanced catalytic properties of hydroxyalkylated surfactants.

ASSOCIATED CONTENT

Supporting Information

Kinetic theory, calculations of the rate constants, and the binding constants of reagents in the micellar pseudophase. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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