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Kinetics of the pH-independent hydrolysis of 4-nitrophenyl chloroformate in aqueous micellar solutions: effects of the charge and structure of the surfactant

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ABSTRACT: The pH-independent hydrolysis of 4-nitrophenyl chloroformate in the presence of aqueous micelles of sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, alkyltrimethylammonium chlorides, alkyldimethylbenzylammonium chlorides (alkyl group = cetyl and dodecyl) and polyoxyethylene (9) nonylphenyl ether was studied spectrophotometrically. The observed rate constants, k_{obs}, decrease in the following order: cationic micelles > bulk water > non-ionic micelles > anionic micelles. Surfactant–substrate association constants, K_s, were determined from the dependence of k_{obs} on surfactant concentration, and were found to be only slightly dependent on the charge of the surfactant and, for similarly charged micelles, on the length of their hydrophobic tail. A ^{1}H NMR study of the solubilization of a model compound, 4-nitrophenyl chloroacetate, showed that all surfactant segments are affected by the solubilizate and the effect is more pronounced toward the middle of the hydrocarbon chain. The average solubilization site of the acetate ester does not depend on the charge of the micelle or the length of the surfactant hydrophobic tail. Micellar effects on observed rate constants are analyzed in terms of a 'medium' effect and an 'electrostatic' effect. The lower microscopic polarity at the reaction site retards the reaction, whereas electrostatic interactions of the polar transition state with the charged interface result in a rate decrease by anionic micelles and a rate enhancement by cationic micelles. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: 4-nitrophenyl chloroformate; hydrolysis; aqueous miceller solutions; surfactants; kinetics

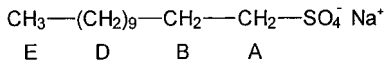
INTRODUCTION

Organized assemblies affect the rates of chemical and photochemical reactions and the position of chemical equilibria.[1–5] There are several reasons for interest in studying effects of aqueous micelles on water-catalyzed reactions, e.g. their mechanisms are simple and have been studied in water and aqueous solvents in sufficient detail, micellar effects on observed rate constants can be quantitatively accounted for in terms of distribution of the substrate between water and micelle and the first-order rate constant in each pseudo-phase and these hydrolytic reactions can be used to probe the properties of interfacial water.

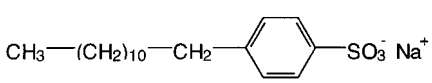
The pH-independent hydrolysis of several acid anhydrides, aromatic carbonates, acyl halides, 4-nitrophenyl chloroformate and alkylaryl halides have been studied in the presence of micelles of cetyltrimethylammonium salts, CMe_3AX, where X = Br, Cl, mesylate and sulfate, and sodium dodecyl sulfate (SDS). All these reactions have been studied at a single temperature, 25 °C [50 °C for bis(4-nitrophenyl) carbonate]; aqueous micelles decrease the observed rate constants, except for 4-nitrophenyl chloroformate, whose rate of hydrolysis increases in the presence of cationic micelles. The results obtained were rationalized in terms of solubilization site of the substrate in the micellar pseudo-phase and interactions between the surfactant headgroup and the polar transition state.[6,7]

As a part of our interest in studying the dependence of properties of interfacial water on the charge and structure of the surfactant headgroup,[8] in this work we studied the kinetics of the pH-independent hydrolysis of 4-nitrophenyl chloroformate (hereafter referred to as 'formate ester') in micellar solutions of the following surfactants:

Anionic:
Sodium dodecyl sulfate (SDS):



sodium dodecylbenzene sulfonate (SDBS):



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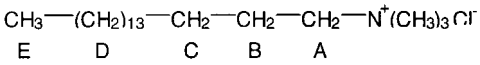
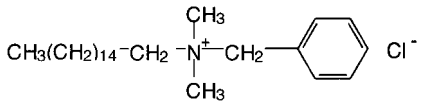
Cationic:

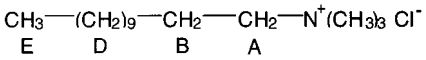
cetyltrimethylammonium chloride (CMe_3ACl):



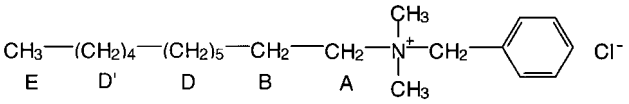
cetyldimethylbenzylammonium chloride (CMe_2BzACl):



dodecyltrimethylammonium chloride (DMe_3ACl):

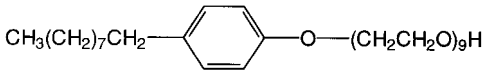


dodecylbenzydimethylammonium chloride (DMe_2BzACl):



Non-ionic:

polyoxyethylene (9) nonylphenyl ether (Arkopal N-090):



We found that the reaction rate is enhanced by cationic micelles and retarded by anionic and non-ionic micelles. For ionic surfactants, the micellar effect is clearly dependent on the structure of the headgroup. These results are rationalized in terms of the low polarity at the reaction site and electrostatic interactions between the polar transition state and the surfactant headgroup.

EXPERIMENTAL

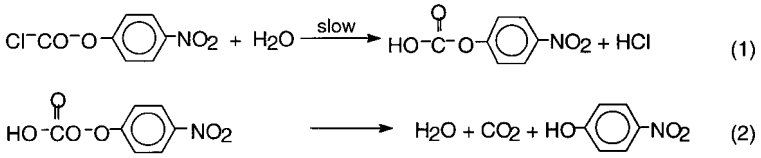
Materials. The reagents were obtained from Aldrich, Fluka, Merck and Hoechst (SDBS and Arkopal N-090) and were purified by standard procedures.[9] The formate ester was purified by several sublimations under reduced pressure. The impurity, 4-nitrophenol, sublimes, leaving a pale yellow pure formate ester which gave a satisfactory microanalysis (Perkin-Elmer CHN-2000 apparatus, Microanalysis Laboratory, Instituto de Química, Universidadede São Paulo). The surfactants were purified as follows: SDS, extraction with absolute ethanol; SDBS (aqueous slurry, 50% surfactant), drying under reduced pressure, followed by extraction with absolute ethanol; CMe_3ACl (aqueous solution, 25% surfactant), drying under reduced pressure and recrystallization from acetone–methanol; DMe_3ACl, recrystallization from acetone–methanol; Arkopal N-090 was used as received. All-glass, doubly distilled water was used throughout; D_2O was used as received.

The ester 4-nitrophenyl chloroacetate (hereafter referred to as 'acetate ester') was prepared as follows: chloroacetyl chloride was prepared by reacting 4.73 g of chloroacetic acid (50 mmol) with 7.2 ml of thionyl chloride (0.1 mol) under reflux for 4 h. Excess thionyl chloride was distilled off and the crude acid chloride was dissolved in 30 ml of dichloromethane. The organic solution was vigorously stirred for 30 min with an equal volume of a 0.1 M aqueous NaOH solution containing 0.86 g of tetra-*n*-butylammonium hydrogensulfate (2.5 mmol) and 10.4 g of 4-nitrophenol (75 mmol). The organic layer was separated, washed with water, dried and the solvent evaporated. The solid acetate ester was recrystallized from acetone–hexane and dried; m.p. 96–97 °C (lit.[10] m.p. 97–98 °C); calculated for $C_8H_6ClNO_4$, C 44.57, H 2.81, N 6.50; found, C 44.58, H 2.81, N 6.27%.

CMe_2BzACl and DMe_2BzACl were prepared by reacting *N*,*N*-dimethylalkylamine (alkyl group-cetyl or dodecyl) with benzyl chloride in tetrahydrofuran under reflux for 4 h. The solvent was evaporated under reduced pressure and the remaining solid extracted with diethyl ether, then recrystallized from acetone–methanol.

Purified surfactants were dried under reduced pressure over P_2O_5 to a constant weight. SDS (as barium salt) and the cationic surfactants (as perchlorate salts) gave satisfactory microanalyses. Their critical micelle concentrations (cmc) were determined at 25 °C by surface tension measurement (Lauda TE 1C digital ring tensiometer) and were in agreement with literature values.[11] Cmc values were also determined at 30 °C in the presence of 0.01 M HCl. The aqueous dioxane which was used to mimic the medium effect (see below) was 50% (w/v), i.e. 50.0 g of dioxane in 100 ml of aqueous binary mixture.

Kinetic measurements. Kinetic runs were carried out with an Applied Photophysics SX-18 MV stopped-flow spectrophotometer, interfaced to a microcomputer and equipped with a thermostated cell holder whose temperature was kept constant to within ±0.05 °C. All runs were carried out in triplicate, under pseudo-first-order conditions, in the presence of 0.01 M HCl and 4% (v/v) acetonitrile. The surfactant aqueous solution and the formate ester stock solution in dry acetonitrile were introduced into the mixing chamber of the stopped-flow spectrophotometer with the aid of Accudil syringes (Hamilton Microsyringe, Reno, NV, USA) of unequal volumes (0.1 and 2.5 ml, respectively). Preliminary experiments showed that the observed rate constant, k_{obs}, is independent of [formate ester] in the range $(2–8) \times 10^{-5}$ M. In subsequent kinetic runs the final [formate ester] was 4×10^{-5} M. The reaction was followed by



Scheme 1.

monitoring the liberation of 4-nitrophenol at 320 nm as a function of time. Values of k_{obs} were calculated from log(absorbance) versus time plots; these were rigorously linear over more than five half-lives. The relative standard deviation in k_{obs}, i.e. (standard deviation/k_{obs}) $\times$ 100, was $\leq$0.2% and that between k_{obs} of a triplicate was $\leq$2%.

^{1}H NMR Spectra. A Labquake tube agitator (VWR Scientific, Chicago, IL, USA) was used to solubilize the acetate ester in the surfactants solutions in D_2O; *ca* 60 min were sufficient to obtain clear solutions. Proton NMR spectra were obtained with a Bruker DPX-300 instrument operating at 300.13 MHz for proton, at a digital resolution of 0.05 Hz per data point. Chemical shifts were measured relative to internal dioxane (5×10^{-3} M) and then transformed into the TMS scale.

RESULTS AND DISCUSSION

Choice of surfactants

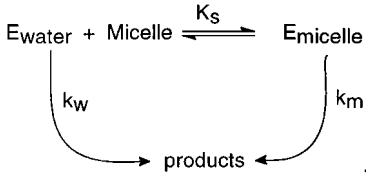
We are interested in investigating the effects of anionic, cationic and non-ionic surfactants on a pH-independent reaction; the relevant structural features include micellar charge and, for surfactants with the same charge, length of the hydrophobic tail and structure of the headgroup. Regarding micellar charge, it has been shown that alkyltrimethylammonium bromides form micelles that are 'drier' than those of SDS, and a switch from —OSO_3^- to —NMe_3^+ headgroup influences the hydration of the attached hydrophobic tail.[12] These differences in hydration may affect a water-catalyzed reaction, e.g. because of differences in solvation of the reactant state and/or transition state. Regarding headgroup structure, it is interesting that very little work has been done on the effects of SDBS and CMe_2BzACl on the rates and equilibria of chemical reactions.[1–4] The former is extensively used in household products, whereas the latter is a major component of 'benzalkonium chloride,' a product which is widely used as an antiseptic in pharmaceutical preparations.[13] In view of the practical importance of the known interaction between aromatic compounds and micellar interfaces,[14] it was deemed important to include SDBS and CMe_2BzACl in the present study in order to investigate how a change in the structure of surfactant headgroup, e.g. from trimethylammonium of CMe_3ACl to benzyldimethylammonium of CMe_2BzACl, may affect the results. Additionally, ^{1}H NMR data indicated that whereas the benzenesulfonate headgroup of SDBS is perpendicular to the micellar interface,[8] the benzyl headgroup of CMe_2BzACl lies more or less parallel to it;[15] this difference in the (average) conformation of the aromatic ring at the interface may affect interactions of reactant state and/or transition state with the surfactant headgroup. Finally, substrate–micelle association constants usually increase as afunction of increasing chain length of the surfactant,[1–3] a factor whose importance can be determined by varying the length of the surfactant hydrophobic group, e.g. CMe_2BzACl and DMe_2BzACl.

Micellar effects on the reaction rate constant

The reaction under investigated is shown in Scheme 1.

Our results indicate that the micellar reaction is independent of pH because k_{obs} is independent of [HCl] in the range 0.001–0.1 M. Hydrolysis of the formate ester gives one equivalent of 4-nitrophenol and the reaction shows a sharp isosbestic point at λ = 285 nm. Additionally, we always observed rigorous pseudo-first-order kinetics; identical rate constants were obtained in the presence or absence of 4×10^{-5} M 4-nitrophenol; an initial rapid release of 4-nitrophenol was not observed. That is, the intermediate of the first step, the monoester of carbonic acid [Eqn. (1)], does not accumulate, and the first step is rate limiting, in agreement with the conclusions of other studies in bulk aqueous phase.[7,16] Additionally, we obtained similar solvent kinetic isotope effects (k_{H_2O}/k_{D_2O}) for the reaction occurring in bulk water, 1.6, and in micellar solutions of SDS, 1.9, CMe_3ACl, 1.9, and Arkopal N-090, 1.7.

In the presence of the micelle, the reaction is represented as shown in Scheme 2, where E refers to formate ester and k_w and k_m refer to pseudo-first-order rate constants in bulk water and in the micelle, respectively. The binding constant, K_s, is written in terms of the molarity of micellized surfactant, i.e.



Scheme 2.

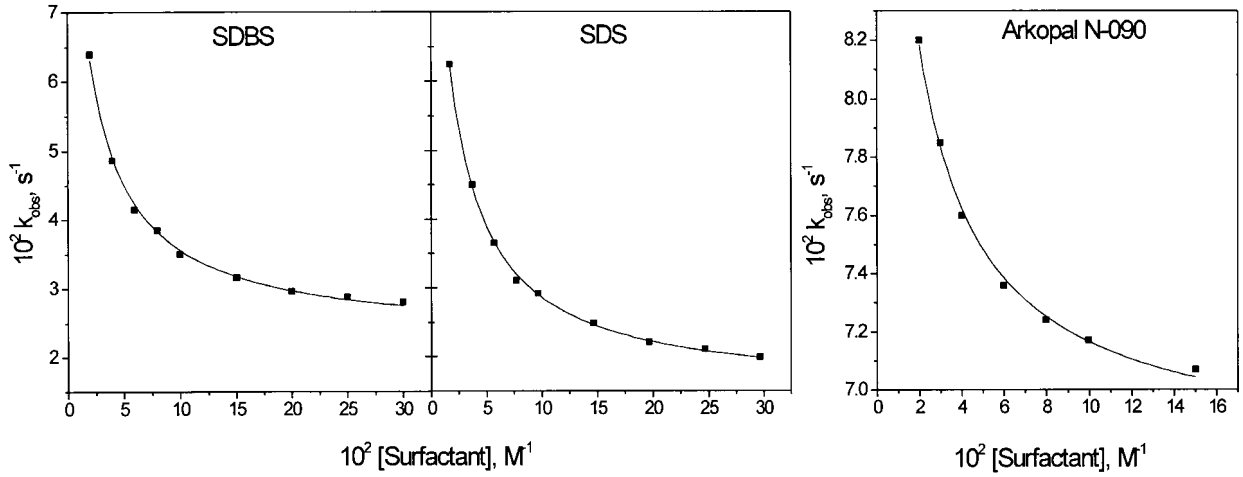


Figure 1. Dependence of observed rate constants, k_{obs}, on [surfactant] for anionic and non-ionic micelles at 30 °C. The points are experimental and the curves were calculated using Eqn. (3)

(C_D − cmc), where C_D is the analytical concentration of surfactant. K_s could equally be written in terms of the molarity of the micelle, i.e. (C_D − cmc)/N, where N is the micelle aggregation number. The latter expression of K_s is less convenient, however, because it requires a knowledge of N under reaction conditions. Equation (3) was derived from Scheme 2:[3a, 17]

$$k_{obs} = [(k_w + k_m)K_s(C_D - cmc)/[1 + K_s(C_D - cmc)] \quad (3)$$

Figures 1 and 2 show the dependence of k_{obs} on [surfactant]. The points are experimental and the curves were calculated from Eqn. (3) by iteration, by using the experimentally determined k_w and cmc. The goodness of fit of Eqn. (3) to our data can be judged visually and from the small values of the statistical parameter χ^2, e.g. 10^{-6} for CMe_2BzACl and DMe_2BzACl. The results of this non-linear regression are given in Table 1.

In principle, Eqn. (3) can be used to calculate values of k_m, K_s and cmc; this was done and the results are also included in Table 1. Interestingly, there is good agreement between k_m calculated by the two methods (differences between k_m range from −2.5 to 15%), although the K_s values differ by a much wider range, namely from −38% for CMe_3ACl to 56% for DMe_3ACl. The results in Table 1 show, however, that this equation is unsuitable to obtain even a rough estimate of cmc, and consequently reliable K_s values cannot be obtained from Eqn. (3) by using cmc as an adjustable parameter.

The most important information from Table 1 is the effect of micellar charge and structure on the observed rate constants. Relative to the reaction in water, anionic and non-ionic micelles retard the reaction, whereas cationic micelles enhance it [$k_m(DMe_2BzACl)/k_m(SDS) = 19.7$]. The effect of headgroup structure is, however, more important than that of the length of the hydrophobic tail. Thus k_m/k_w is almost the same for CMe_2BzACl and DMe_2BzACl and increases by 8% on going from CMe_3ACl to DMe_3ACl. The corresponding figures for CMe_3ACl and CMe_2BzACl, for DMe_3ACl

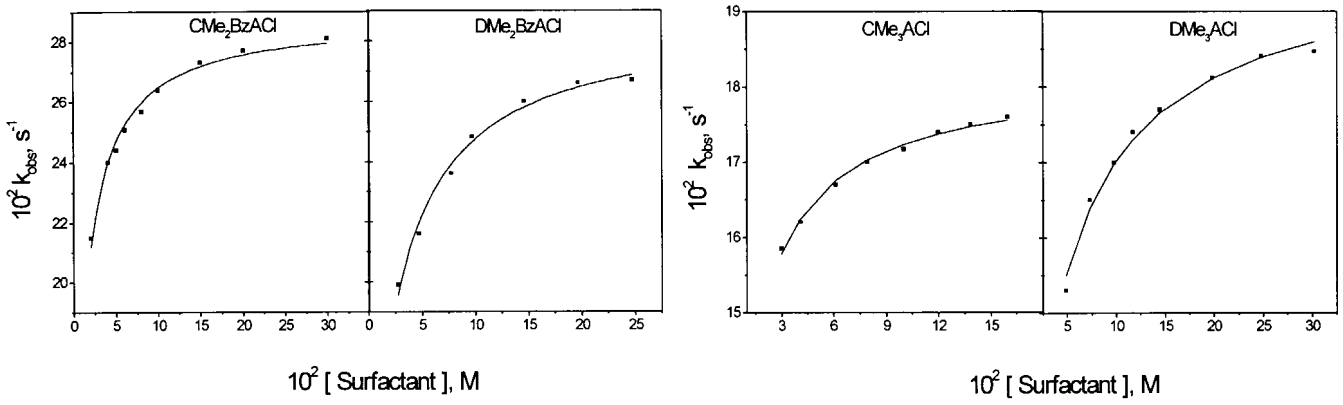


Figure 2. Dependence of observed rate constants, k_{obs}, on [surfactant] for cationic micelles at 30 °C. The points are experimental and the curves were calculated using Eqn. (3)

Table 1. Results of the application of Eqn. (3) to rate constants for the hydrolysis of 4-nitrophenyl chloroformate in the presence of ionic and non-ionic aqueous micelles[a]

Surfactant	10^4 cmc[b] (M)	K_s[c] (M^{-1})	k_m[c,d] (s^{-1})	k_m/k_w[e]	10^4 cmc[f] (M)	K_s (M^{-1})	k_m (s^{-1})
SDS	31	57 ± 1	0.0146	0.13	37	59 ± 2	0.0149
SDBS	2.6	56 ± 2	0.0228	0.21	31	65 ± 3	0.0237
CMe_3ACl	2.3	70 ± 3	0.1816	1.68	—	43 ± 4	0.1851
CMe_2BzACl	0.024	68 ± 4	0.288	2.67	—	50 ± 4	0.2931
DMe_3ACl	19.0	23 ± 1	0.197	1.82	180	36 ± 4	0.192
DMe_2BzACl	28.7	35 ± 3	0.2872	2.66	—	28 ± 6	0.293
Arkopal N-090	0.62	93 ± 3	0.0677	0.63	32	111 ± 13	0.0682

[a] All experiments were carried out at 30 °C.
[b] Experimental values, determined at 30 °C, in the presence of 0.01 M HCl by surface tension (see Experimental). Our cmc values agree with those calculated from an equation which describes the effect of simple, i.e. non-aggregated, electrolytes on cmc.[18]
[c] Values calculated from Eqn. (3) by iteration, using experimental cmc.
[d] Relative standard deviations in k_m are $\leq 1\%$.
[e] At 30 °C, the rate constant in water is 0.1080 s^{-1}.
[f] Calculated by iteration from Eqn. (3). In some cases, calculations gave physically meaningless negative cmc values and these are not reported.

and DMe_2BzACl and for SDS and SDBS are 58, 46, and 64%, respectively.

We discuss our results in terms of (i) the strength of the substrate–micelle interactions, (ii) average solubilization/reaction site of the substrate in the micellar pseudo-phase and (iii) interactions of the reactant state and/or transition state with the ionic interface. Regarding the first point, it is clear from K_s that all micelles bind the substrate reasonably efficiently (Table 1). Although the formate ester–micelle association constant increases as a function of increasing chain length of the hydrophobic tail, there is no clear correlation between K_s and k_m, i.e. the observed micellar effects on the reaction rate do not appear to be due to differences in the strength of their binding of the substrate.

^{1}H NMR spectroscopy is an appropriate technique to investigate point (ii), i.e. the average solubilization site of the formate ester in the micellar pseudophase. The problem, however, is that the hydrolysis reaction is too fast to permit solution preparation and subsequent spectrum acquisition [the reaction half-lives at 30 °C range from 2.4 to 34.8 s (Table 1)]. We employed 4-nitrophenyl chloroacetate as a model compound because although both esters differ widely in reactivity towards pH-independent hydrolysis, their hydrophobic character and molecular volumes do not differ much. Thus values of log P_{oct}[19] (the partition coefficient of a substance between *n*-octanol and water, calculated by the ACB/LogP program, ACD, Toronto, Canada) are 1.647 and 1.658, whereas the corresponding molecular volumes are 204 and 227 Å^3,[20] for formate ester and acetate ester, respectively. Based on these data, one expects similar solubilization sites for both esters in the micelle. Figure 3 shows the dependence of ^{1}H NMR chemical shifts of the discrete protons of SDS and DMe_2BzACl on [acetate ester]. For clarity, we plotted our data as chemical shift differences, $\Delta\delta = \delta_{surfactant} - \delta_{surfactant\ +\ acetate\ \ ester}$. All plots are linear and the slopes, along with those for CMe_3ACl and $DoMe_3ACl$, are given in Table 3.

Before addressing these results, we discuss the

Table 2. Observed rate constants, k_{obs} (s^{-1}) for the pH-independent hydrolysis of 4-nitrophenyl chloroformate in different reaction media[a,b,c]

T (°C)	Water	SDS	SDBS	CMe_3ACl	CMe_2BzACl	DMe_3ACl	DMe_2BzACl	Arkopal N-090	CH_3SO_3Na	$(CH_3)4NCl$
10				0.051						
15			0.0075					0.0287	0.0203	0.038
20		0.0089		0.099		0.0709	0.143			
25	0.0728		0.0194			0.134		0.0515	0.050	0.074
30	0.108	0.0199	0.0277	0.177	0.285	0.184	0.266	0.0711	0.066	0.108
35	0.159		0.0399		0.427[c]		0.405[c]	0.094	0.095	0.145
40	0.227	0.0422		0.319	0.57[d]	0.337				
45			0.0859				0.628	0.164	0.169	0.278
50		0.0843			0.86					

[a] Average of three rate constants. The relative standard deviation in k_{obs} is <0.2% and that between k_{obs} of a triplicate is $\leq 2\%$.
[b] Concentrations used were 0.3 M for SDS, SDBS and CMe_2BzACl, 0.25 M for DMe_2BzACl and 0.15 M for CMe_3ACl and Arkopal N-090. The concentration of the simple, i.e. non-aggregated, salts was 1.0 M in aqueous dioxane (50%, w/v).
[c] This experiment was carried out at 37.1 °C.
[d] This experiment was carried out at 41.9 °C.

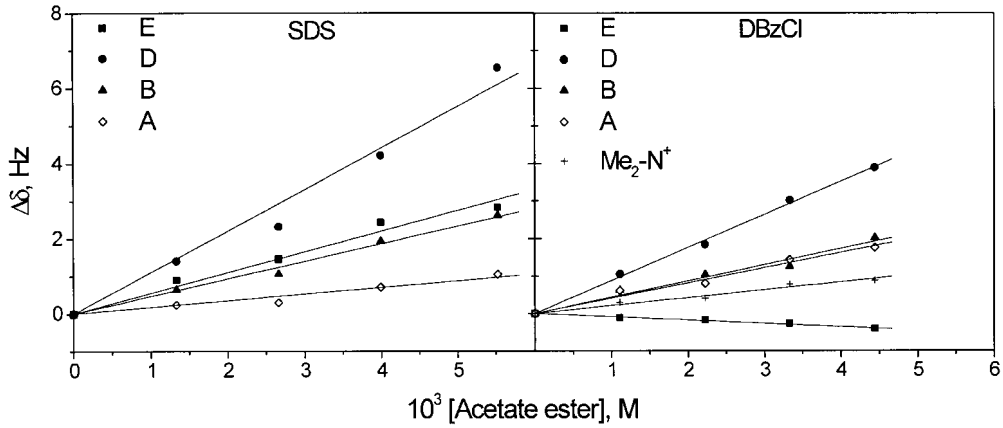


Figure 3. Dependence of chemical shift differences, $\Delta\delta = \delta_{\text{surfactant}} - \delta_{\text{surfactant + acetate ester}}$ for the surfactant discrete groups on [acetate ester] for SDS and DMe_2BzACl, at 300 MHz

problem of splitting of the peak of methylene protons (D), which for most surfactants appears as a broad singlet because of virtual coupling.[22] Solubilization of a substrate bearing an anisotropic group (e.g. an aromatic ring) sometimes results in splitting of protons (D) singlet, and this has been used to indicate the average solubilization site in the micellar pseudo-phase.[23] Surfactants whose headgroup contains a benzyl moiety show, however, a different behavior because protons (D) appear as a doublet, in the absence of solubilizate. This splitting has not been observed in spectra recorded at a low spectrometer frequency (60 MHz),[22] but was later alluded to (100 MHz), although no information was given with regard to the number of methylene groups in each peak.[24] We observed two peaks for the middle methylene groups of DMe_2BzACl and CMe_2BzACl; the high–field peak corresponds to five CH_2 units. Diamagnetic shielding of the outer (D) methylene groups is most certainly due to the presence of the benzyl headgroup more or less parallel to the micellar interface, as discussed previously.[15] It is interesting that solubilization of the acetate ester did not result either in further splitting of the two peaks of DMe_2BzACl and CMe_2BzACl or in splitting of the (D) proton singlet of the other surfactants. This may be due to the small [solubilizate]/[surfactant] range which we used.

The results in Table 3 can be explained by considering the average solubilization site of the acetate ester in the micelle, and the consequent effect on chemical shifts of the surfactant segments. The dynamic nature of the micelle has to be borne in mind, i.e. the micellar 'interface' fluctuates because of movement of the monomers, the discrete segments of the hydrophobic tail have different mobilities and sample the aggregate interface and the micellar conformation of the surfactant hydrophobic tail is not a fully stretched, *all-trans* form[25,26].

The following can be deduced from our ^{1}H NMR results: (a) solubilization of the acetate ester results in an upfield shift (i.e. toward TMS) of all surfactant protons, except those of the terminal methyl group (protons E) of DMe_2BzACl, whose peak is slightly shifted downfield; (b) the slopes of plots of protons C and D are larger than those of other protons. This shows that the acetate ester is

Table 3. Dependence of chemical shift differences, $\Delta\delta = \delta_{\text{surfactant}} - \delta_{\text{surfactant + acetate ester}}$ of the surfactant discrete protons on 4-nitrophenyl chloroacetate concentration[a,b,c]

	Slope (Hz mol^{-1} 4-nitrophenyl chloroacetate)								
Surfactant	Me_3N^+	Me_2N^+	CH_2 (A)	CH_2 (B)	CH_2 (C)	$(CH_2)_5$ (D)	$(CH_2)_4$ (D′)	CH_3 (E)	CH_2 benzyl
SDS			175 ± 13	466 ± 14		1104 ± 53		550 ± 23	
CMe_3ACl	264 ± 18		583 ± 18	440 ± 20	941 ± 24	670 ± 17		251 ± 17	
DMe_3ACl	93 ± 12		424 ± 31	553 ± 19	958 ± 17	822 ± 14		356 ± 12	
DMe_2BzACl		209 ± 11	214 ± 20	432 ± 21		880 ± 13	362 ± 22	-90 ± 3	414 ± 12

[a] The slopes are from linear plots, e.g. Fig. 3. Measurements were made at 300.13 MHz, at room temperature. See Introduction for designation of the discrete surfactant protons.
[b] Chemical shifts were measured from internal dioxane (5×10^{-3} M) and then transformed into the TMS scale by using $\delta_{\text{dioxane}} = 3.53$ ppm.[21]
[c] The following values of δ (ppm) were observed for the surfactant discrete protons in the absence of solubilizate: SDS (0.1 M), 3.801, 1.459, 1.088, 0.661 for protons A, B, D and E respectively; CMe_3ACl (0.1 M), 2.944, 3.15, 1.556, 1.157, 1.089, 0.671 for protons Me_3N^+, A, B, C, D and E, respectively; DMe_3ACl (0.1 M), 2.919, 3.117, 1.551, 1.149, 1.080, 0.671 for protons Me_3N^+, A, B, C, D and E, respectively; DMe_2BzACl (0.1 M), 2.820, 2.772, 1.531, 1.032, 1.064, 0.681 for protons Me_2N^+, A, B, D, D and E, respectively.

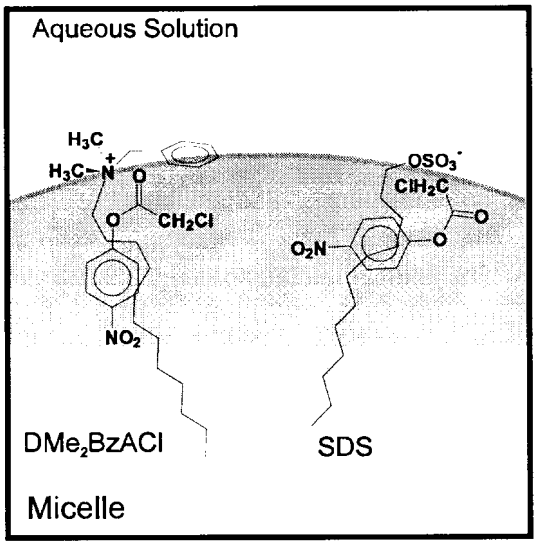
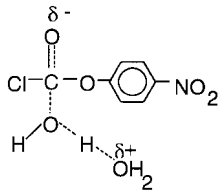


Figure 4. Schematic representation of the solubilization of the acetate ester in aqueous micelles of DMe_2BzAC and SDS. For simplicity, we show the average solubilization site with respect to a single monomer of each surfactant and do not show the corresponding counterion

neither adsorbed at the micellar interface (as in the case of polycyclic aromatic compounds)[23b,e] nor penetrates deep within the micellar 'core.' It is predominantly present in a region that covers protons C and D, as is shown in Fig. 4. Our results also show that the average solubilization site of the acetate ester is not critically dependent on the micellar charge or the length of the hydrophobic tail. Therefore, the dependence of k_m on the surfactant charge and structure (Table 1) is not due to very different micellar reaction sites, provided that acetate and formate esters are solubilized in the same region in the micelle, and that solubilization and reaction sites are similar.

In analyzing point (iii), we note that the rate-limiting step for the micelle-mediated reaction seems to be the same as that for the reaction in water, i.e. attack by water on the carbonyl group of the ester, leading to the following transition state:



Transfer of this polar transition state from bulk water to the micelle induces destabilization because of the 'medium' effect and stabilization/destabilization due to electrostatic interactions with the charged interface. The former effect results from the fact that the polarity and dielectric constant at the site of the micelle-mediated reaction are lower than those of bulk water.[3–5] Both non-

Table 4. Activation parameters for the pH-independent hydrolysis of 4-nitrophenyl chloroformate in different reaction media[a]

Reaction medium	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal K^{-1} mol^{-1})	$\Delta G^{\neq}$ (kcal mol^{-1})
Water	13.5	−18.4	19.0
SDS, 0.30 M	13.5	−21.7	20.0
SDBS, 0.30 M	14.1	−19.3	19.9
CMe_3ACl, 0.15 M	10.1	−28.6	18.6
CMe_2BzACl, 0.30 M	10.2	−27.4	18.4
DMe_3ACl, 0.25 M	10.6	−27.0	18.7
DMe_2BzACl, 0.25 M	10.4	−26.9	18.4
Arkopal N-090, 0.15 M	10.0	−30.8	19.2
CH_3SO_3Na–aq. dioxane[b]	12.2	−23.8	19.3
$(CH_3)_4NCl$–aq. dioxane[b]	11.5	−25.1	19.0

[a] The errors are ±0.1 kcal mol^{-1} ($\Delta H^{\neq}$ and $\Delta G^{\neq}$) and 0.5 cal K^{-1} mol^{-1} ($\Delta S^{\neq}$).
[b] Salt concentration, 1.0 M in aqueous dioxane (50%, w/v).

ionic micelles and binary solvent mixtures have been used to mimic the micellar medium effect;[4,27–29] therefore, we used aqueous dioxane (50%, w/v) as a model for interfacial water of micellar Arkopal N-090 and a 1.0 M electrolyte solution in the same solvent mixture as a model for interfacial water of ionic micelles.[28]

Although the ionic strength in the Stern layer is probably higher than 1.0 M,[3,7] solubility constraints precluded use of more concentrated electrolyte solutions. At 30 °C, the reaction rate constant is slightly retarded by 50% aqueous dioxane ($k_{aq.\ dioxane}/k_w = 0.9$), and by sodium methanesulfonate ($k_{obs\ CH_3SO_3^-Na^+}/k_w = 0.61$), and is unaffected by tetramethylammonium chloride [$k_{obs\ (CH_3)_4N^+Cl^-}/k_w = 1$]. Although these results show that the medium effect is small, the following should be borne in mind: probes which have been used to investigate the medium effect, e.g. solvatochromic probes and acid–base indicators, are usually localized at the micelle interface,[4,28] i.e. they report on a medium whose polarity and dielectric constant are higher than those at the average solubilization/reaction site of the formate ester. Therefore, the medium effect, as mimicked by the models which we used, is almost certainly underestimated.

Electrostatic interactions between the negatively charged carbonyl oxygen of the above shown transition state and the surfactant headgroup are attractive (stabilizing) for cationic micelles and repulsive (destabilizing) for anionic micelles. The degree of dissociation, and hence the surface potential, of the former micelles increases on going from alkyltrimethylammonium chlorides to alkyldimethyl benzylammonium chlorides (alkyl group = cetyl and tetradecyl).[15,30] This is one reason for expecting a higher catalytic effect for surfactants bearing a benzyl moiety in the headgroup. These electrostatic interactions affect the activation parameters in a complex manner (Table 4). Compare, for example, the effects of SDS and SDBS on the activation enthalpy and entropy. Interaction

of the formate ester with the phenyl ring of the latter surfactant seems to stabilize the reactant state, leading to $\Delta H_{SDBS}^{\neq} - \Delta H_{SDS}^{\neq} = 600$ cal mol;[7] this difference is more than compensated for by the $T\Delta S^{\neq}$ term ($T\Delta S_{SDBS}^{\neq} - T\Delta S_{SDS}^{\neq} = 715$ cal mol)$^{-1}$ due to loss of degrees of freedom of the reactants. In the case of cationic micelles, electrostatic stabilization of the transition state seems to be the dominant factor. Thus the reaction is faster than that in water because of the favorable activation enthalpy (e.g. $\Delta H_{water}^{\neq} - \Delta H_{DMe2BzACI}^{\neq} = 3100$ cal mol)$^{-1}$ which is caused by electrostatic stabilization of the transition state, not fully compensated for by the $T\Delta S^{\neq}$ term ($T\Delta S_{water}^{\neq} - T\Delta S_{DMe2BzACI} = 2534$ cal mol)$^{-1}$ owing to loss of degrees of freedom in the transition state–micelle complex.

CONCLUSIONS

The mechanism of the pH-independent hydrolysis of 4-nitrophenyl chloroformate is the same in water and in ionic and non-ionic micelles. Relative to the reaction in water, the rate constant increases in the presence of cationic micelles and decreases in the presence of anionic and non-ionic micelles, and is more sensitive to the structure of the headgroup than to the length of the surfactant hydrophobic tail. These effects are not due either to sizeable differences in the micelle–ester association constants or to very different average solubilization/reaction sites in the micellar pseudo-phases. They arise mainly from the medium effect, interaction of the reactant state with the phenyl group of SDBS and electrostatic stabilization/destabilization of the transition state by the charged interface.

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