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pH-independent hydrolysis of 4-nitrophenyl 2,2-dichloropropionate in aqueous micellar solutions: relative contributions of hydrophobic and electrostatic interactions

Omar A. EI Seoud,[1]* Marie-Françoise Ruasse[2] and Shirley Possidonio[1]

[1]Instituto de Química, Universidade de São Paulo, C.P. 26077, 05513-970 São Paulo, S.P., Brazil
[2]Institut de Topologie et de Dynamiques des System, Université de Paris VII–CNRS, 1 Rue Guy de la Brosse, F-75005 Paris, France

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ABSTRACT: The pH-independent hydrolysis of 4-nitrophenyl 2,2-dichloropropionate (NPDCP) in the presence of aqueous micelles of sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, alkyltrimethylammonium chlorides, alkyldimethylbenzylammonium chlorides (alkyl = cetyl and dodecyl) and polyoxyethylene(9) nonylphenyl ether was studied spectrophotometrically. The observed rate constants, k_{obs}, decrease in the following order: bulk water >cationic micelles >anionic micelles >non-ionic micelles. This order is different from that observed for pH-independent hydrolysis of 4-nitrophenyl chloroformate (NPCF), whose reaction is faster in cationic micelles than in bulk water. A proton NMR study on solubilization of a model ester, 4-nitrophenyl 2-chloropropionate, showed that the methylene groups in the middle of the surfactant hydrophobic chain are most affected by the solubilizate. Lower polarity and high ionic strength of interfacial water decrease the rates of hydrolysis of both NPCF and NPDCP, but the fraction of the former ester that diffuses to the interface is probably higher than that of the latter. Therefore, whereas the (negatively charged) transition state of NPCF is stabilized by cationic interfaces and destabilized by anionic interfaces, that of NPDCP is negligibly affected by ionic interfaces, which explains the observed rate retardation by *all* ionic micelles. Calculated activation parameters corroborate our explanation. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: 4-nitrophenyl 2,2-dichloropropionate; hydrolysis; aqueous micellar solutions; hydrophobic interactions; electrostatic interactions

INTRODUCTION

The effects of organized assemblies on chemical reactivity have been rationalized in terms of differences between the properties of interfacial and bulk water and, for ionic micelles, local concentrations of reactants in the Stern region and electrostatic interactions between the charged interface and reactants and/or transition states.[1–6] Micelle-mediated, pH-independent hydrolyses offer insights into the subtle interactions that affect chemical reactivity in organized assemblies because their mechanisms are simple and have been studied in sufficient detail, and because they can be used to probe properties (e.g. polarity and ionic strength) of interfacial water.[7–9]

Recently, we studied the pH-independent hydrolysis of 4-nitrophenyl chloroformate (NPCF), in the presence of the aqueous micelles of the following surfactants: *anionic*, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS); *cationic*, cetyltrimethylammonium chloride (CMe_3ACl), cetyldimethylbenzylammonium chloride (CMe_2BzACl), dodecyltrimethylamminium chloride (DMe_3ACl), dodecyldimethylbenzylammonium chloride (DMe_2BzACl); *non-ionic*, polyoxyethylene(9) nonylphenyl ether, Arkopal N-090. The reaction was enhanced by cationic micelles and retarded by anionic and non-ionic micelles. These results were explained in terms of electrostatic stabilization/destabilization of the reaction transition state (TS), by charged interfaces and by differences between the properties of interfacial and bulk water.[9]

We report here on the pH-independent hydrolysis of 4-nitrophenyl 2,2-dichloropropionate (NPDCP) in the presence of the above-mentioned aqueous micelles. We were interested in determining how pH-independent hydrolyses are affected by increasing reactant chain length and hydrophobicity. In contrast to the hydrolysis of NPCF, the corresponding reaction of NPDCP is retarded by *all* micelles. Hydrophobic interactions of the reactant state (RS) with the surfactant and micellar

**Correspondence to:* O. A. EI Seoud, Instituto de Química, Universidade de São Paulo, C.P. 26077, 05513-970 São Paulo, S.P., Brazil.
Email: elseoud@iq.usp.br
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'medium' effect cause rate retardation. Negligible interactions of the (negatively charged) TS with the ionic interface explain the small dependence of reaction rates on the charge of the latter, and rate retardation by cationic micelles.

EXPERIMENTAL

Materials. The reagents were obtained from Aldrich, Fluka, Merck and Clariant (SDBS and Arkopal N-090) and were purified by standard procedures.[10]

NPDCP was prepared by reacting the corresponding acyl chloride with sodium 4-nitrophenoxide under phase-transfer conditions. First, 2,2-dichloropropionic acid was generated from its sodium salt by acidification with sulfuric acid, followed by extraction of the aqueous solution with dichloromethane. The solvent was removed and the acid distilled, b.p. 80–81 °C/10 mmHg (90–92 °C/14 mmHg).[11] A mixture of 2,2-dichloropropionic acid (13.16 g, 0.09 mol) and thionyl chloride (12.24 g, 0.1 mol) was refluxed for 3 h and the acyl chloride was purified by distillation, b.p. 117–119 °C (117.4 –117.8 °C/753 mmHg).[11] Equal amounts (0.03 mol) of 4-nitrophenol and NaOH were dissolved in 25 ml of water. After agitation for 30 min, solid tetrabutylammonium hydrogensulfate (0.2g) was added, followed by a solution of 2,2-dichloropropionyl chloride (3.20 g, 0.02 mol) in 25 ml of dichloromethane. The mixture was vigorously stirred for 30 min and the organic phase was separated, washed with cold water, and dried over anhydrous $MgSO_4$. After solvent evaporation the ester was purified with flash column chromatography, using hexane as eluent; yield, 30%; IR (KBr, Perkin-Elmer FT-1750), 1771 cm^{-1} ν_{CO}; 1528 and 1348 cm^{-1}, ν_{NO_2} (asymmetric and symmetric, respectively). The ester 4-nitrophenyl 2-chloropropionate was prepared by a similar procedure from the corresponding acyl halide and sodium 4-nitrophenoxide; yield 38%; IR (KBr), 1774 cm^{-1}, ν_{CO}; 1532 and 1347 cm^{-1}, ν_{NO_2} (asymmetric and symmetric, respectively)

The purity of the esters and surfactants was established by microanalysis (Microanalysis Laboratory, Instituto de Química, Universidade de São Paulo) and, for surfactants, by surface tension measurement (Lauda TE 1C digital ring tensiometer). Their critical micelle concentrations (c.m.c.) were determined at 30 °C in the presence of 0.01 M HCl.

Kinetic measurements. The apparatus was that employed previously.[9] All experiments were carried out in triplicate, under pseudo-first-order conditions, in the presence of 0.01 M HCL and 4% (v/v) acetonitrile. Preliminary runs showed that the observed rate constant, k_{obs}, is independent of [NPDCP] in the range $(0.5–5) \times 10^{-5}$ M. In subsequent work, the final [NPDCP] was 0.6 to 2×10^{-5} M. The reaction was followed by monitoring the liberation of 4-nitrophenol at 320 nm as a function of time. The relative standard deviation for k_{obs}, i.e. (standard deviation/k_{obs}) × 100 was ≤0.2%, and when the experiment was run 3 times, the difference between any two k_{obs} was ≤2%.

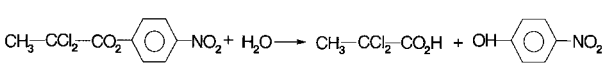
^1H NMR spectra. Proton NMR spectra were obtained with a Bruker DRX-500 instrument at a digital resolution of 0.05 Hz per data point. Chemical shifts were measured at 30 °C, relative to internal dioxane (5×10^{-3} M), then transformed into the TMS scale by using $\delta_{dioxane} = 3.53$ ppm.[12]

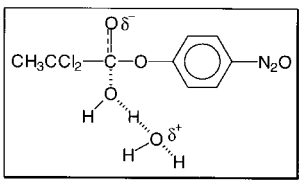
RESULTS AND DISCUSSION

We found that the reaction under consideration is independent of solution pH in the range 1.0–4.0 (4% acetonitrile in water). The pH-independent hydrolysis of the structurally similar 4-nitrophenyl dichloroacetate is associated with a sizeable solvent deuterium kinetic isotope effect, $k_{H_2O}/k_{D_2O} = 3.1$.[7a,b] These results are compatible with reaction Scheme 1 and the TS structure depicted.[7]

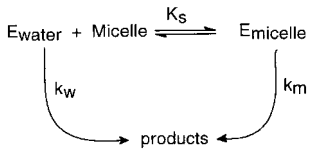
In the TS, shown a second 'general base' water molecule abstracts a proton from the attacking 'nucleophilic' water molecule, leaving the organic moiety with a net negative charge.[7] In the presence of 0.1 mol l^{-1} SDS or CMe_3ACl the micellar reaction was found to be independent of [HCl] in the range 0.001–0.1 mol l^{-1} and showed a sharp isosbestic point at 288 nm. Additionally, the kinetics were rigorously first order; identical k_{obs} were obtained in the presence or absence of 4×10^{-5} mol l^{-1} 4-nitrophenol; an initial rapid release of 4-nitrophenol was not observed. Hence the reactions in bulk aqueous medium and in micellar pseudo-phases have similar mechanisms, with water attack being the rate-limiting step. This conclusion is similar to that reached for other micellar, pH-independent hydrolysis reactions.[8,9]

In presence of the micelle, the reaction is represented by Scheme 2, where E refers to NPDCP, k_w and k_m are pseudo-first-order rate constants in bulk water and in the micelle, respectively, and the binding constant K_s is





Scheme 1



Scheme 2

written in terms of the molarity of micellized surfactant, i.e. (C_D − c.m.c.), where C_D is the analytical concentration of surfactant.

From scheme **2**, the following equation was derived:[8]

$$k_{obs} = [k_w + k_m K_s(C_D - \text{c.m.c})]/[1 + K_s(C_D - \text{c.m.c})] \quad (1)$$

Figures 1 and 2 show the dependence of k_{obs} on [surfactant], where the points are experimental and the curves were calculated from Eqn. (1) by iteration, by using *experimentally* determined k_w and c.m.c. The results for k_m and K_s are given in Table 1.

The dependence of k_{obs} on temperature was studied at [surfactant] in the plateau region of the rate constant–surfactant plots (Figs 1 and 2). The results are given in Table 2, and the corresponding activation parameters are given in Table 3. Plots of log k_{obs} versus $1/T$ were rigorously linear, which shows that micellar structural changes, if they do occur in the temperature range employed, have no measurable effects, e.g. on the heat capacity of the TS. Tables 2 and 3 also show data for hydrolysis in electrolyte solutions in aqueous dioxane; this will be addressed later.

We measured ^{1}H NMR chemical shifts of the surfactant discrete protons, $\delta_{surfactant}$, as a function of [ester] in order to determine its average solubilization site in the micellar pseudo-phase. Model ester- 1, 4-nitrophenyl 2-chloropropionate, was used instead of NPDCP, because the latter would have undergone extensive hydrolysis during sample preparation and spectra acquisition. The structures presented show the relevant surfactant protons of SDS, CMe_3ACl, CMe_2BzACl, and DMe_2BzACl. The reason for the additional splitting of protons D of the last two surfactants is the presence of interfacial benzyl group, as discussed elsewhere.[9]

SDS CH_3—$(CH_2)_9$—CH_2—CH_2—SO_4^- Na^+
E D B A

CMe_3ACl CH_3—$(CH_2)_{13}$—CH_2—CH_2—CH_2—$N^+(CH_3)_3$ Cl^-
E D C B A

CMe_2BzACl CH_3—$(CH_2)_8$—$(CH_2)_5$—CH_2—CH_2—$N^+(CH_3)_2$—CH_2—Ph Cl^-
E D' D B A

DMe_2BzACl CH_3—$(CH_2)_4$—$(CH_2)_5$—CH_2—CH_2—$N^+(CH_3)_2$—CH_2—Ph Cl^-
E D' D B A

Plots of $\Delta\delta_{surfactant} = \delta_{surfactant}$ in D_2O − $\delta_{surfactant + model\ ester\ 1}$ in D_2O were found to be linear, and the slopes are given in Table 4, which shows that model ester 1 is solubilized (on average) in the region of surfactant protons C and D.

Table 1 shows that the reaction is retarded by *all* surfactants (k_m/k_w from 0.02 to 0.11), is only slightly affected by micellar charge ($k_{DMe_3}ACl/k_{SDS} = 2.2$) and, for similarly charged surfactants, is almost insensitive to variations of the structure of the hydrophilic group ($k_{DMe_2}BzACl/k_{DMe_3}ACl = 1.2$). This is at variance with the hydrolysis of NPCF in the presence of the same surfactants, where the reaction shows catalysis by cationic micelles (k_m/k_w between 1.7 and 2.7) and a stronger dependence on micellar charge ($k_{DMe_3}ACl/k_{SDS} = 13.5$).

The question now arises of what the reasons are for the different micellar effects on hydrolysis of NPCF and NPDCP. At the outset, we emphasize that the rate-limiting step of both reactions is the same, namely attack on the ester carbonyl group by a 'nucleophilic' water molecule catalyzed by a second 'general base' water

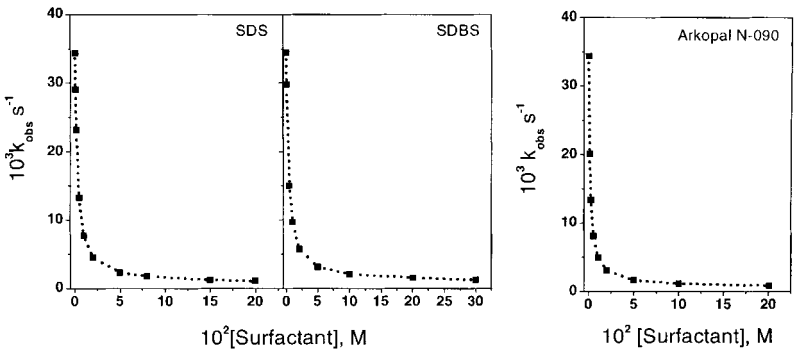


Figure 1. Dependence of observed rate constants, k_{obs}, on [surfactant] for anionic and non-ionic micelles at 35 °C. The points are experimental and the curves were calculated using Eqn. (1)

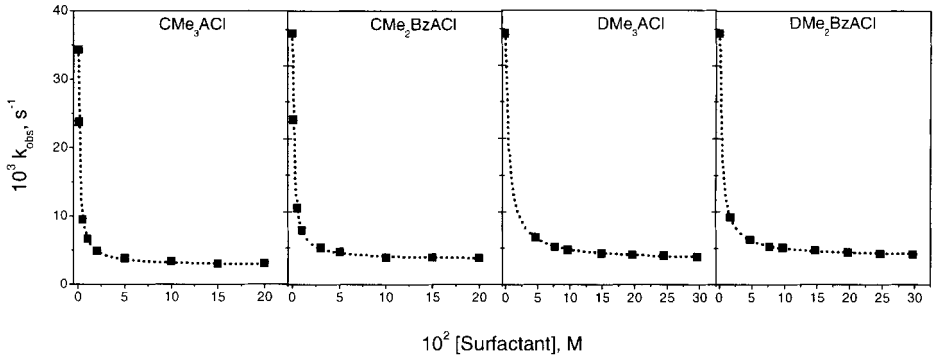


Figure 2. Dependence of observed rate constants, k_{obs}, on [surfactant] for cationic micelles at 35 °C. The points are experimental and the curves were calculated using Eqn. (1)

Table 1. Results of the application of Eqn. (1) to rate constants for the hydrolysis of 4-nitrophenyl 2,2-dichloropropionate in the presence of ionic and non-ionic aqueous micelles at 35 °C

Surfactant	10^4 c.m.c. (mol l^{-1})[a]	K_s, (mol l^{-1})[b]	10^3 k_m (s^{-1})[b,c]	k_m/k_w[d]
SDS	31	848 ± 96	1.5	0.04
SDBS	2.6	274 ± 11	0.8	0.02
CMe_3ACl	2.3	673 ± 34	2.7	0.08
CMe_2BzACl	0.024	650 ± 13	3.4	0.10
DMe_3ACl	19.0	189 ± 6	3.3	0.10
DMe_2BzACl	28.7	268 ± 6	3.9	0.11
Arkopal N-090	0.62	677 ± 6	0,0007	0.02

[a] Experimental c.m.c., determined at 30 °C in the presence of 0.01 M HCl by surface tension (see Experimental).
[b] Calculated from Eqn. (1) by iteration, by using experimental c.m.c.
[c] Relative standard deviations in k_m are ≤1%.
[d] At 35 °C, the rate constant in water, k_w, is 0.0344 s^{-1}.

molecule.[7,13] We address the question raised by considering the following: (i) strength of ester–micelle association, (ii) average micellar solubilization site of the ester, (iii) medium effects arising from the low polarity and the high ionic strength of interfacial water relative to bulk water and (iv) stabilization/destabilization of RS and/or TS by different mechanisms, including electrostatic and hydrophobic interactions.

With regard to point (i), we note that NPDCP binds efficiently to all micelles, and K_s for NPDCP ≈ $10K_s$ for NPCF. Therefore, part of the micellar effect on hydrolysis of both esters may arise from this large difference in substrate–micelle association.

Concerning point (ii), our NMR data show that model ester 1 is located, on average, in the region occupied by surfactant protons C and D, i.e. the same solubilization site of 4-nitrophenyl chloroacetate (model ester 2) that has been employed (in a similar NMR experiment) instead of NPCF. Log$P_{octanol}$ [the partition coefficient of a substrate between water and *n*-octanol, a measure of its

Table 2. Dependence on temperature of observed rate constants, k_{obs}, for hydrolysis of 4-nitrophenyl 2,2-dichloropropionate in different reaction media

	10^3 k_{obs} (s^{-1})								
T (°C)	Water	SDS (0.2 M)	CMe_3ACl (0.2 M)	CMe_2BzACl (0.2 M)	DMe_3ACl (0.3 M)	DMe_2BzACl (0.3 M)	Arkopal N-090 (0.2 M)	CH_3SO_3Na (1.0 M)[a]	$(CH_3)_4NCl$ (0.1 M)[a]
15	13.4	0.31	0.95	1.18	1.18	1.39	0.29	0.39	0.50
25	21.6	0.58	1.76	2.04	2.15	2.47	0.52	0.67	0.89
35	34.4	1.09	3.11	3.64	3.79	4.18	0.85	1.10	1.46
45	51.8	1.85	5.14	5.88	5.97	6.4	1.36	1.72	2.30

[a] In 50% (w/v) aqueous dioxane.

Table 3. Activation parameters for the pH-independent hydrolysis of 4-nitrophenyl 2,2-dichloropropionate in different reaction media[a,b]

Reaction medium	$\Delta\ddagger H$ (kcal mol^{-1})	$\Delta\ddagger S$ (cal K^{-1}mol^{-1})	$\Delta\ddagger G$ (kcal mol^{-1})
Water	7.7	−40.4	19.7
SDS, 0.2 M	10.5	−38.1	21.9
CMe_3ACl, 0.2 M	9.7	−38.6	21.2
CMe_2BzACl, 0.2 M	9.2	−39.8	21.1
DMe_3ACl, 0.3 M	9.3	−39.5	21.0
DMe_2BzACl, 0.3 M	8.7	−41.3	21.0
Arkopal N-90, 0.2 M	8.8	−44.2	21.9
$CH_3SO_3^-Na^+$[a]	8.4	−44.7	21.8
$(CH_3)_4N^+Cl^-$[b]	8.7	−43.5	21.6

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

hydrophobicity,[14] calculated using the LogP program (ACD, Toronto, Canada)] are 1.66, 1.65, 2.17 and 3.24 for model ester 2, NPCF, model ester 1 and NPDCP, respectively. That is, the first two esters have practically the same hydrophobicity and are expected to be solubilized (on average) in the same region of the micellar pseudo-phase. NPDCP partitions into n-octanol 11.7 times more than model ester 1 and is expected, therefore, either to be solubilized deeper within the micelle or to associate more strongly with it. Hence part of the micellar effect on both hydrolysis reactions may arise from different solubilization sites of NPCF and NPDCP within the micellar pseudo-phases.

In considering point (iii), we take into account the dynamic nature of the micelle and the binding process itself; both result in RS/TS sampling interfacial water whose properties are akin to those of electrolyte solutions in aqueous organic solvents.[15–17] The low microscopic polarity and high ionic strength of this water (relative to bulk water) is expected to affect the present reactions because their TS differ in polarity and solvation from their RS. Aqueous dioxane has been proposed as a model for interfacial water and we employed 1.0 M Me_4NCl and/or 1.0 M $MeSO_3Na$ in 50% (w/v) aqueous dioxane in order to mimic the polarity and ionic strength of interfacial water of cationic and anionic micelles, respectively. Solubility constraints precluded the use of more concentrated electrolyte solutions. Table 3 shows that the reaction in these model media is slower than that both in bulk water and the corresponding ionic micelles. Although the ionic strength in the Stern layer is >1.0 M,[16] rates of other pH-independent hydrolyses decrease as a function of increasing [electrolyte].[7a–c,8a,c] That is, hydrolysis of NPDCP in these models solvents would have been even slower had we been able to use [electrolyte] >1.0 M. Although the results in these media and in micellar solutions show the same trend, i.e. the reaction in both is slower than in bulk water, rate retardation does not seem to have the same origin, as shown by considering the contributions of $\Delta\Delta\ddagger H$ (= $\Delta\ddagger H$ in micelles or electrolyte solution $-\Delta\ddagger H$ in bulk water) and $T\Delta\Delta\ddagger S$ to $\Delta\Delta\ddagger G$ of the reaction in ionic micelles. Whereas $\Delta\Delta\ddagger H$ contributes 1–2.8 kcal mol^{-1}, the $T\Delta\Delta\ddagger S$ term makes a minor contribution, from 0.3 to 0.7 kcal mol^{-1} (1 kcal = 4.184 kJ). On the other hand, for the reaction in model media both terms contribute almost equally to $\Delta\Delta\ddagger G$, and $T\Delta\Delta\ddagger S$ is negative. It is interesting that the data for Arkopal-N090 are similar to those for model media, i.e. $\Delta\Delta\ddagger H$ and (negative) $T\Delta\Delta\ddagger S$ contribute equally to $\Delta\Delta\ddagger G$.

Table 4. Dependence of chemical shift differences, $\Delta\delta = \delta_{\text{surfactant}} - \delta_{(\text{surfactant + model ester1})}$ of the surfactant discrete protons on [4-nitrophenyl 2-chloropropionate] at 30 °C[a,b]

	Slope (Hz / mol 4-nitrophenyl 2-chloropropionate)								
Surfactant	Me_3N^+	Me_2N^+	CH_2 (A)	CH_2 (B)	CH_2 (C)	$(CH_2)_5$ (D)	$(CH_2)_n$ (D′)	CH_3 (E)	$C_6H_5CH_2$
SDS			576 ± 34	1075 ± 38		2025 ± 41		1131 ± 59	
CMe_3ACl	355 ± 72		870 ± 83	1195 ± 106	1757 ± 142	1665 ± 70		543 ± 70	
CMe_2BzACl		215 ± 24	489 ± 52	1528 ± 193		1759 ± 34	−160 ± 27	−319 ± 34	952 ± 29
DMe_2B-zACl		185 ± 52	212 ± 15	1248 ± 34		1659 ± 48	103 ± 33	−64 ± 31	694 ± 47

[a] Measurements were carried out at 500.13 MHz (see Results and Discussion for designation of the discrete surfactant protons).
[b] 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, 0.661 and 1.088 for protons (A), (B), (D) and (E), respectively; CMe_3ACl (0.1 M), 2.944, 3.150, 1.556, 1.157, 1.089 and 0.671 for protons (Me_3N^+), (A), (B), (C), (D) and (E), respectively; CMe_2BzACl (0.1 M), 2.811, 2.761, 1.502, 1.002, 1.107, and 0.701 for protons (Me_2N^+), (A), (B), (D), (D′) and (E), respectively; DMe_2BzACl (0.1 M), 2.820, 2.772, 1.531, 1.032, 1.064 and 0.681 for protons (Me_2N^+), (A), (B), (D), (D′) and (E), respectively.

The large K_s and $\Delta\delta_{surfactant}$ indicate that RS of NPDCP is stabilized by hydrophobic interactions with the surfactant tail [point (iv)]. On the other hand, the small dependence of k_m on micellar charge [$k_m(DMe_3ACl)/k_m(SDS) = 2$ and 13.5 for NPDCP and NPCF, respectively] indicates that TS does not interact significantly with the ionic interface. It is tempting to use an analogy to the 'spatiotemporal hypothesis' introduced by Menger.[18] In order to rationalize the fast rates of certain intramolecular reactions and the high catalytic efficiency of enzymes, he argued that 'the rate of reaction between functionalities A and B is proportional to the time that A and B reside within a critical distance.' Evidence has been given to show that this distance should be <3 Å. For the reaction studied, the analogy to this idea, is as follows: (a) because both micelle and substrate solubilization are dynamic in nature, some RS/TS should diffuse to the ionic interface and are affected by electrostatic interactions; (b) the TSs of concern carry a net negative charge, so that electrostatic interactions with the micellar interface are much more important for TS than for RS. These are stabilizing for cationic micelles (rate increase) and destabilizing for anionic micelles (rate decrease), provided that the TS comes within a certain distance from the interface. The contribution of electrostatic interactions depends, therefore, on the fraction of TS that comes within this distance. If this fraction is insignificant, the micelle-mediated reaction will be dominated by other (retarding) effects, e.g. stabilization of the RS and medium effects. (Although the rate variations that are being discussed here are very modest compared with those discussed by Menger,[18] the analogy employed is useful, provided that the dynamic nature of the micellar system is taken into account.)

The preceding discussion agrees with contributions of $\Delta\Delta\ddagger H$ and $T\Delta\Delta\ddagger S$ to $\Delta\Delta\ddagger G$ of hydrolysis of both esters, and we concentrate on cationic micelles. For example, RS/TS of NPCF diffuse easily within the micelle, so that the reaction is sensitive to charge of the interface ($k_{DMe_3}ACl/k_{SDS} = 13.5$) and $k_m > k_w$. The reaction is associated with negative $\Delta\Delta\ddagger H$ (−2.9 to −3.4 kcal mol^{-1}) due to electrostatic stabilization of the TS, and negative $T\Delta\Delta\ddagger S$ (−2.5 to −3.0 kcal mol^{-1}) due to decrease in the number of degrees of freedom on going from RS to TS (the latter is associated with the interface). Hydrolysis of NPDCP is associated with a positive $\Delta\Delta\ddagger H$ whereas $T\Delta\Delta\ddagger S$ makes a smaller contribution. Both quantities agree with an RS that is stabilized by hydrophobic interactions with the surfactant tail, a reaction occurring in an aqueous medium of low water activity, and a TS whose stability is little affected by the ionic interface. (The question of water activity is important because the reaction is second order in water, i.e. $k_m/k_{bulk\ water} = k_{3m}$ [interfacial water]$^2/k_{3w}$ [bulk water]^2, where k_3 refers to the third-order rate constant. Consequently, the effect of decreased water activity is expected to be larger for NPDCP because it diffuses less readily than NPCF to the micellar interface where such activity is relatively high. Uneven hydration of the oxyethylene units[19] and uncertainty about the localization of NPDCP in the non-ionic micelle preclude detailed interpretation of the inhibition by Arkopal N-090.)

CONCLUSIONS

In contrast to micelle-mediated pH-independent hydrolysis of NPCF, the reaction of NPDCP is slower than that in bulk water and shows little dependence on the structure and charge of the surfactant. We explain our results in terms of a combination of hydrophobic stabilization of the RS, low water activity at the reaction site and negligible contribution of electrostatic effects of the ionic interface to the stability of TS. This explanation agrees with the higher enthalpies and entropies of activation of the micellar reaction relative to that in bulk water (Table 3). Experimental determination of the average solubilization site of the substrate and of the activation parameters is important for understanding the subtle interactions that affect chemical reactivity in organized assemblies.

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