The nature of the micellar Stern region as studied by reaction kinetics

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The nature of the rate retarding effects of cationic, anionic and nonionic micelles on the water-catalysed hydrolysis reactions of 1-benzoyl-3-phenyl-1,2,4-triazole (**1**) and *p*-methoxyphenyl dichloroacetate (**2**) has been studied by kinetic methods using UV/VIS spectroscopy. A comparison was made between medium effects in micellar solutions and in solutions of a model compound, in which the model compound is a small molecule resembling the surfactant headgroup. The rate retarding effect of micelles on the hydrolysis of **1** and **2** was shown to be largely caused by the high concentration of headgroups in the Stern region where **1** and **2** bind to the micelle. Other factors which contribute to the rate inhibition are also briefly discussed.

Introduction

Numerous reactions are accelerated in water-rich environments[1] relative to organic solvents. This is obviously true for hydrolysis reactions, but also for other organic reactions that are less expected to show rate enhancements in aqueous media, the Diels–Alder reaction[2] and Claisen rearrangements[3] being the best known examples. Apart from the possible beneficial effect on rate constant, water is a cheap, nontoxic and readily available reaction medium. These factors make water an environmentally and economically attractive solvent. However, one of the main problems in performing reactions in water is the fact that many organic substrates are quite hydrophobic. In order to solubilise hydrophobic compounds in aqueous media, several approaches are possible; one of which is carrying out the reaction in aqueous micellar solutions.

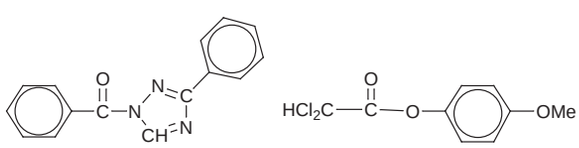
In micellar solutions, reactions can be both accelerated and inhibited compared to the reaction in pure water.[4,5] Until now, however, the exact mechanism of micellar acceleration and deceleration has remained rather obscure. The aim of this study was to investigate mechanistic aspects of micellar effects on pH-independent hydrolytic reactions.

Gruen has described a realistic model for a micelle.[6] This model involves a rather sharp interface between a dry[6,7] hydrophobic hydrocarbon core and a region filled with surfactant headgroups, part of the counterions and water, *viz.* the Stern region. This model has been validated using molecular dynamics simulations[8,9] and is valid for both ionic and nonionic micelles.

A micelle offers several binding sites for relatively apolar molecules. These include the hydrophobic core and hydrophobic binding sites located in the Stern region. The latter region is particularly flexible in binding molecules as it contains the highly hydrophilic surfactant headgroups and hydrophobic domains due to backfolding of the surfactant tails[6,8,9] as well as water molecules.

It has previously been estimated that the concentration of headgroups in the Stern region lies in the range of 3 to 5 M,[10–12] though recent work also suggested lower values.[13,14a] The concentration of counterions is slightly less due to incomplete counterion binding, creating an electrically non-neutral environment. In order to study the nature of the micellar Stern region, two approaches were followed. One involved kinetic measurements of the rates of the water-catalysed hydrolysis of an activated amide and ester in micelles and in electrolyte solutions mimicking the local environment in the Stern region. The second involved spectroscopic studies employing the well-known solvatochromic $E_T(30)$ micropolarity indicator.[15]

The hydrolytic reactions were the pH-independent hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole **1** and *p*-methoxyphenyl dichloroacetate **2** (Scheme 1).



1 **2**

Scheme 1

Both reactions are water-catalysed between pH 3 and 5, and pH 1 and 5.5, respectively. These reactions proceed *via* a dipolar activated complex in which two water molecules, one of which is acting as a general base, are involved with three protons in flight[16–18] (Scheme 2). In aqueous solutions, the reactions show pseudo-first-order kinetics.

Reactions and reaction product distributions have been frequently used in order to investigate micellar properties, *e.g.* the Romsted arenediazonium probe.[13,14] The kinetic approach used in the present study is less common. Work aimed at identifying the noncovalent interactions determining micellar catalysis and inhibition has been performed on purely micellar solutions[4,12,19–23] but also on, *e.g.*, mixtures of both polymers and surfactants[24] to study polymer surfactant interactions.

Results

The results from the kinetic experiments are summarised in Table 1, Table 2, Fig. 1 and Fig. 2. The results for the experiments using the $E_T(30)$ probe are given in Tables 1 and 4.

The kinetic data for the micellar solutions were analysed using the Menger–Portnoy equation[25] [eqn. (1)].

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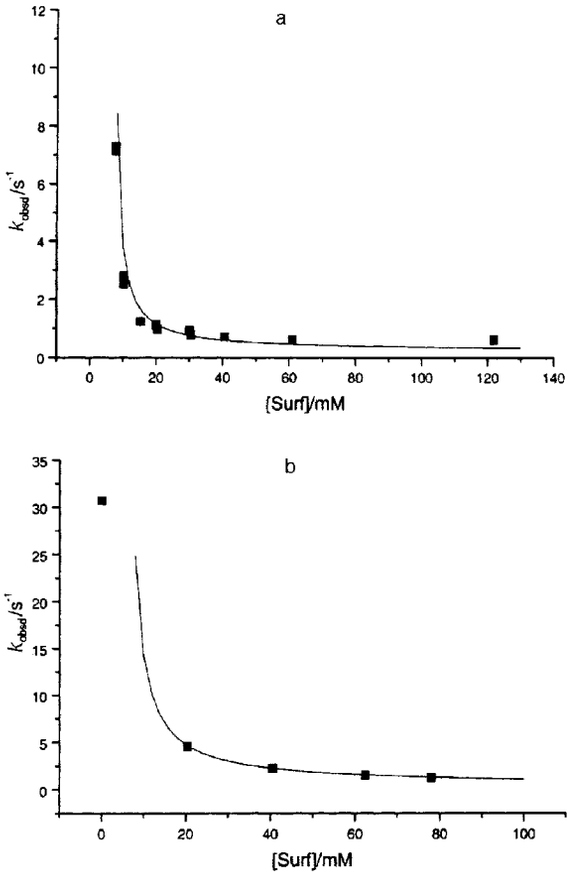
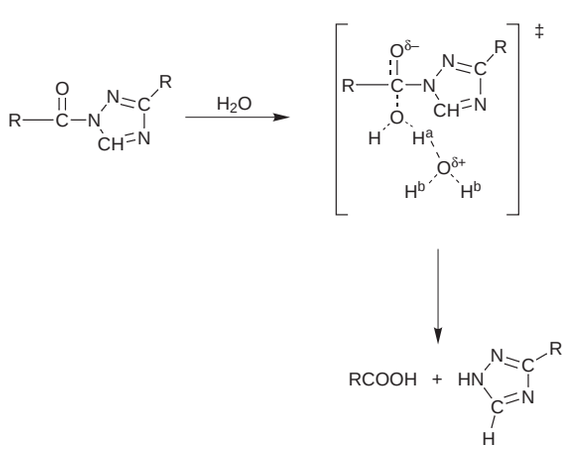


Fig. 1 Representative examples of k_{obsd} *vs.* [Surf]. a) **1** in SDS, b) **2** in SDS.



Scheme 2

$$(k_w - k_{obsd})^{-1} = (k_w - k_{mic})^{-1} + (k_w - k_{mic})^{-1}(N/K)([Surf] - cmc)^{-1} \quad (1)$$

Herein k_{obsd} is the observed rate constant at a certain surfactant concentration [Surf], k_w is the rate constant in pure water (pH = 4.0) and k_{mic} is the rate constant for complete binding of the substrate to the micelles. N is the aggregation number of the micelle, K is the binding constant of the kinetic probe to the micelle, cmc is the critical micelle concentration of the surfactant. This equation follows from an analysis in terms of the pseudophase model. A plot of $(k_w - k_{obsd})^{-1}$ *versus* ([Surf] − cmc)$^{-1}$ yields $(k_w - k_{mic})^{-1}$ as the intercept, and therefore k_{mic} can be calculated if k_w is known. From the intercept and the slope of the Menger–Portnoy plot the micellar binding constant K can be calculated. In this treatment, k_w is set equal to the rate constant in pure water. However, the monomeric surfactant concentration in the bulk water phase equals the cmc so that there is a possibility that hydrophobic interactions between probe molecules and monomeric surfactant molecules could exert an effect on the rate of hydrolysis in bulk water.[23] For the present reactions, the minor decrease in rate constant before the cmc indicates that these effects are small. Moreover, the Menger–Portnoy treatment is not particularly sensitive to the precise value of k_w, as k_{mic} is determined from the intercept. Furthermore, we note that the micellar rate constant for substrates bound to spherical micelles can be determined as long as one works with surfactant concentrations below the concentration at which wormlike micelles start to form.

A refinement of eqn. (1) consists of including the possibility of different reaction domains within the micelle. The pseudophase model, only distinguishing between a micellar phase and an aqueous phase, then turns into a three[26] (or multiple[27]) domain model in which, for example, the Stern region and the hydrophobic micellar core are treated as separate regions. Hydrolysis in the first domain, *i.e.* the core of the micelle, then occurs with a rate constant k_c, hydrolysis in the Stern region, a second domain, occurs with a rate constant k_s and the hydrolysis in bulk water, the third domain, has rate constant k_w. In the limit of an infinite number of domains this model provides the exact rate constant as the integral over the domains with their local rate constant of hydrolysis.

If we use the three domain model and assume that in the anhydrous, hydrophobic core no hydrolysis takes place (setting k_c to zero), k_{obsd} is given by eqn. (2).

$$k_{obsd} = \frac{k_w + k_{mic}K_m(V_m/V_w)}{1 + K_m(V_m/V_w)} \quad (2)$$

This relation still resembles the ordinary Menger–Portnoy equation, but k_{mic} is now given by eqn. (3).

$$k_{mic} = k_s\left\{\frac{V_mK_m - V_cK_{ws}K_{sc}}{V_mK_m}\right\} = k_s\left\{\frac{V_sK_{ws}}{V_mK_m}\right\} \quad (3)$$

Herein, V_m and K_m are the micellar volume and partition coefficient, respectively, V_c is the micellar core volume, K_{ws} is the water–Stern region partition coefficient, K_{sc} the partition coefficient for the Stern region–core equilibrium and V_s is the Stern region volume.

It turns out that the micellar rate constant is, under the above conditions, given by the rate constant for the hydrolysis in the Stern region multiplied by a factor which represents the fraction of the total amount of micellar-bound probe that resides in the Stern region.

In the present study, the following surfactants were used: cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), dodecyltrimethylammonium chloride (CTACl), sodium dodecylsulfate (SDS) and dodecylheptaoxyethylene glycol ether ($C_{12}E_7$).

For every probe–micelle combination, the rate constant for hydrolysis of the probe bound to the micelle, k_{mic}, was determined, using the "conventional two domain" Menger–Portnoy equation. These values are given in Table 1.

In addition to the micellar rate constants, the micellar binding constants K were determined, as outlined above, as well as the transition state pseudo-equilibrium constants K^{TS}, as given by eqn. (4).[28]

$$K^{TS} = \frac{k_{mic}K}{k_w} = \frac{k^3_{mic}[H_2O]^2_mK}{k^3_w[H_2O]^2_w} \quad (4)$$

In eqn. (4) k^3 are the third-order rate constants in the aqueous and the micellar pseudophase, $[H_2O]_w$ the water concentration in bulk water and $[H_2O]_m$ the water concentration in the Stern region (assuming $\gamma = 1$). The data are collected in Tables 2 and 3.

Table 1 Micellar rate constants and $E_T(30)$ values for different micelle–probe combinations[a]

	$k_{mic}/10^{-5}$ s^{-1}		
	1	**2**	$E_T(30)$/ kcal mol^{-1}
CTAB	6.7 ± 0.8	1.6 ± 0.5	53.5
DTAB	12.6 ± 0.5	—	53
CTACl	14.5 ± 1.5	—	
SDS	4.8 ± 0.9	4.7 ± 1.8	57
SDS[b]	2.4 ± 0.2	—	
$C_{12}E_7$	5.8 ± 0.3	0.6 ± 0.4	

[a] Water values are: k_w(**1**): (125.5 ± 1.5) × 10^{-5} s^{-1} and k_w(**2**): (307 ± 6) × 10^{-5} s^{-1}. [b] In the presence of 0.5 M of NaCl.

Table 2 Micellar binding constants for different micelle–probe combinations

	$K/10^4$ M^{-1}	
	1	**2**
CTAB	7 ± 2	11 ± 2
SDS	11 ± 1	3.1 ± 0.3
$C_{12}E_7$	11 ± 1	5.2 ± 0.4

In calculating the binding constants, the following aggregation numbers were used: N_{CTAB} = 110, N_{SDS} = 64 and $N_{C_{12}E_7}$ = 100.

Table 3 Transition state pseudo-equilibrium constants for different micelle–probe combinations

	$K^{TS}/10^3$ M^{-1}	
	1	**2**
CTAB	3.7 ± 1.2	0.6 ± 0.2
SDS	4.2 ± 0.9	0.5 ± 0.2
$C_{12}E_7$	5.1 ± 0.6	0.1 ± 0.07

As a model system for the Stern region of the micelle, a concentrated solution of a model solute was used. These solutes were chosen on the basis of their resemblance to the micellar headgroup.[12,29] For both CTAB and DTAB, tetramethylammonium bromide (TMAB) was chosen. For SDS, sodium monomethylsulfate (NMS) was employed. As a model for $C_{12}E_7$, both tetra- and heptaethyleneglycol (TEG and HEG) were used.

Plots of the rate constants for the two probes as a function of model-solute concentration are given in Fig. 2.

Interestingly, the micellar rate constant matches (for **1**) or nearly matches (for **2**) the rate constant for hydrolysis in the model compound solutions at rather high concentrations. The matching for **1** occurs at a 4.3 M aqueous solution of NMS for the SDS micelles, at 4.2 M TEG for $C_{12}E_7$ micelles and around 5 M (from extrapolation, at least >4.2 M) for CTAB micelles.

The nature of the micellar binding places was also compared on the basis of the $E_T(30)$ solvatochromic probe. This dye indicator is regarded as one of the most useful polarity indicators.[15] One of the reasons for this is the appreciable sensitivity of the visible absorption spectrum to small changes in the medium surrounding the betaine dye. Comparison of the $E_T(30)$ value of micellar solutions with those for the same model compound solutions (Table 4) as used in the kinetic experiments, shows that matching occurs in a completely different region of model compound concentration (Table 5). In terms of the solvatochromic comparison, the micellar Stern region does not resemble a 4–5 M model compound solution.

Table 4 $E_T(30)$ values of salt solutions

[TMAB]/ mM	$E_T(30)$/ kcal mol^{-1}	[NMS]/ mM	$E_T(30)$/ kcal mol^{-1}
995	61.8	1989	63.8
2185	61.2	4248	62.6
3178	60.3		
3686	59.5		

Discussion

The hydrolysis of **1** and **2** is not severely inhibited upon binding to the micelles ($k_{mic} \neq 0$). Therefore we conclude that the reaction has to take place in a relatively "wet" region of the micelle. Since the hydrocarbon core of micelles has been shown to be dry,[6–9] the hydrolyses take place in the Stern region. Our conclusion is strengthened by the fact that addition of salt to the micellar solution, leading to increased counterion binding and thereby affecting the Stern region, causes a further decrease in hydrolysis rate. It should be noted, however, that, in view of the multiple domain model suggested above, the hydrolysis in the micellar media can also be explained in another way—*i.e.*, a weakly retarded hydrolysis of the micellar-bound probe molecules that reside in the Stern region can be combined with completely inhibited hydrolysis of the probe molecules bound in the micellar core. This could also result in a significantly reduced overall micellar rate constant for the hydrolysis. This possibility is unlikely though, as it is commonly assumed that polar molecules preferably bind to the micelles in the Stern region.[30–34] Moreover, it is also commonly assumed that, up to a critical concentration, aromatic molecules bind in the Stern region as well.[35] Since the hydrolytic probes are slightly polar aromatic molecules, the Stern region will be the most favourable binding site.

The notion that the polar probe molecules bind to the Stern region is strengthened by the fact that the order of micellar reaction rates for **1** can be accounted for by simple electrostatics.[36] First we note that the negative charge developed on the carbonyl moiety during the activation process will be stabilised by the net positive charge of the Stern region of CTAB-micelles. The formation of negative charge will be disfavoured by the negative charge at the surface region of the SDS-micelles. The positive charge evolving on the water molecule that acts as a general base is dispersed into other water molecules.[36] These electrostatic effects are relatively small as in all cases the hydrolysis is considerably retarded, but they will show up as small differences in the observed rate constants for the fully micellar-bound hydrolytic probe. The rate constant for the nonionic micelle, lying exactly in between those for the anionic and cationic micelles, is in accord with this idea. The difference in hydrophobic character of the binding site of the hydrolytic probe molecules resulting from the difference in surfactant tail length, hardly seems to influence the kinetics.

The rate decrease in the micellar solutions relative to the reaction in bulk water can be caused by several effects. First of all, the water activity will be decreased. Secondly, the substrate is stabilised by hydrophobic interactions at the micellar surface, whereas the transition state is destabilised (or less stabilised). The kinetic probe molecule can also be stabilised by interactions with the surfactant headgroups. Another possibility would be an unfavourable orientation of the hydrolytic probe in the Stern region, *e.g.* with the reactive ester functionality lying closer to the micellar core. This, however, is not expected as previous work on hydrolysis of micellar bound probes yielded no evidence for specific probe orientation.[37] Finally, it has been demonstrated by molecular dynamics simulations[38] that the rate of reaction critically depends on the water configuration around the amide functionality. In the Stern region, the surfactant molecules, particularly the headgroups, will probably reduce chances for finding water molecules in the positions

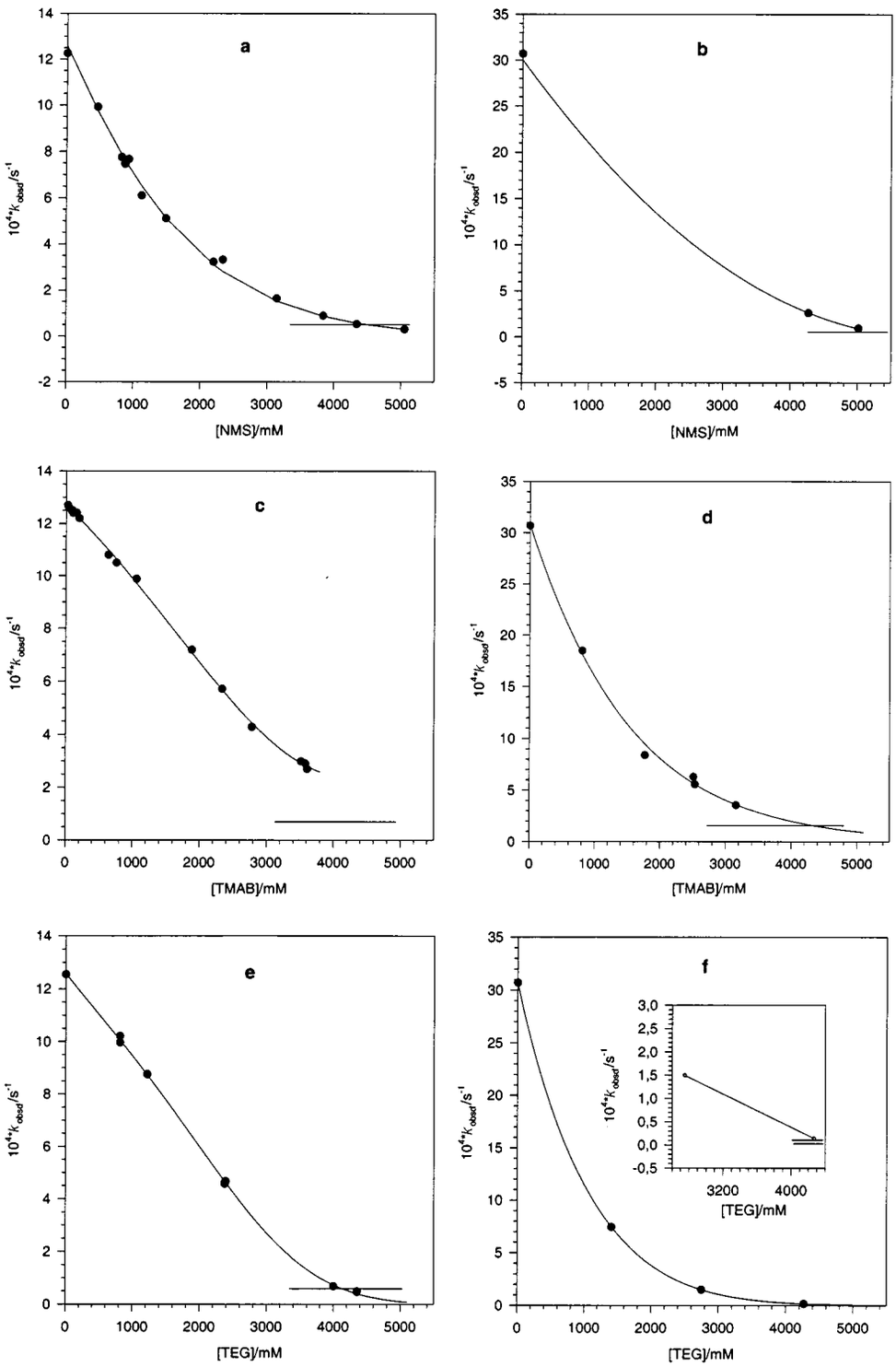


Fig. 2 Matching and near-matching of the rate constants. Horizontal lines give micellar rate constants. a) **1** in NMS–SDS, b) **2** in NMS–SDS, c) **1** in TMAB–CTAB, d) **2** in TMAB–CTAB, e) **1** in TEG–$C_{12}E_7$, f) **2** in TEG–$C_{12}E_7$.

needed for the hydrolysis reaction as a result of the conformational requirements on the water molecules in the hydration shells of the headgroups. This effect will be most pronounced in the case of the ionic micelles.

The observation that the rate of hydrolysis of **1** is constant up to higher kinetic probe concentrations in a 1.6 M solution of TMAB than in pure water, suggests that the alkyltrimethylammonium group is able to solubilise the hydrolytic probe.

An analysis based on the transition state pseudo-equilibrium approach,[28] as used before in micellar catalysis and inhibition,[27,39] yields insight into the stabilisation of the activated complex, as compared to the initial state. Unfortunately, as can be seen from eqn. (4), the difference in water activity between bulk water and water as bound to the micelle in this analysis also determines K^{TS}/K. This means that, in the system under study, the activated complex is stabilised to a much lesser extent than the initial state by binding to the micelle or the water activity in the Stern region is considerably lower than that in bulk water, or, a combination of these two effects occurs.

One can estimate the headgroup concentration in the Stern region. From known micellar and molecular dimensions, one can make an educated guess as to the volume of the micellar Stern region.[40] Together with the aggregation number and counterion binding,[41] the headgroup concentration in the Stern

Table 5 Calculated[a] and experimental salt concentrations in the micellar Stern region

Surfactant	[Headgroup]/M		
	Calculated	Kinetics	$E_T(30)$
SDS	2.7–5.4	4.3	17
CTAB	2.9–5.7	>4.2	10
DTAB	2.6–5.3	>4.1	10
$C_{12}E_7$	7–10[b]	16.8	
	15–18[c]		

[a] The following parameters were used in the estimation of headgroup concentrations in the Stern region: SDS: l_c = 16.7 Å, d_{Stern} = 3.7–6.5 Å, N = 64, β = 0.65; CTAB: l_c = 21.7 Å, d_{Stern} = 4.0–6.6 Å, N = 110, β = 0.8; DTAB: l_c = 16.7 Å, d_{Stern} = 4.0–6.6 Å, N = 60, β = 0.75; $C_{12}E_7$: l_c = 16.7 Å, d_{Stern} = 3.6 Å, N = 64–100. See ref. 38. [b] Monomer concentration of the completely stretched ethyleneglycol chain. [c] Monomer concentration of a backfolded ethyleneglycol chain.

region can be calculated. These concentrations are given in Table 5. They can be compared to the electrolyte compound concentrations for which the substrate hydrolyses with the same rate constant in this model compound solution and under conditions of 100% binding to the micelles (k_{mic}).

The fact that the salt concentrations, as they are deduced from the kinetic experiments, match the calculated salt concentrations so closely, can be regarded as evidence that the dominating effect in the rate inhibition is primarily a salt effect. Presumably, differences in stabilisation of the initial state and the activated complex by hydrophobic interaction with surfactant tails are of minor importance. Even if these interactions would have some importance, the salt concentrations would still denote an upper limit for the Stern region headgroup concentration. In these salt effects, all possible interactions with the headgroup mimic are included. It is worth mentioning, however, that compounds such as TMAB or TMACl possess hydrophobic hydration shells as has been shown by a neutron diffraction study.[42] This means that the molecule is probably involved in hydrophobic interactions as well. These hydrophobic interactions are, in the current definition, included in the salt effect. For the nonionic compound, the term salt effect is rather misplaced, as oligoethyleneglycol is not ionic, but the term is used for convenience. Curiously, it has been shown[43] that rate effects on reactions occurring in the aqueous phase of micellar solutions can be explained by a salt effect as well. In this case, the rate effect is explained by modelling complete micelles by single ions, thus creating a diluted solution of highly valent ions.

It is found that the order of rate constants of **2** in different surfactant solutions cannot be explained in terms of the Stern region electrolyte effects. In this case, the order is opposite to what would be expected on the basis of simple electrostatics. Apparently, the influence of the hydrophobic chains is more pronounced for **2** than for **1**. It has been observed before[44] that the hydrolysis of **2** is more sensitive to hydrophobic interactions than the hydrolysis of **1** and is more strongly retarded by hydrophobic co-solutes.[45]

The order of sensitivity of the reaction rate towards hydrophobic interactions does not follow the order of hydrophobicity of the substrates. Even though **1** is the more apolar compound, as can be seen from the micellar binding constants, the match in rate constants is better for this compound, which leads to the conclusion that the influence of the hydrophobic tails on the rate of reaction is smaller than that in the case of **2**. Consequently no link between hydrophobicity of the substrate and sensitivity of the hydrolysis reactions towards hydrophobic interactions appears to be present.

In order to check the generality of the results obtained with the kinetic probes, a second type of probe was employed, *viz.* the solvatochromic $E_T(30)$ probe. The $E_T(30)$-probe shows completely different behaviour from that of the hydrolytic probes (Tables 1 and 4). This suggests that the spectroscopic probe is sensitive to or experiencing other types of interactions than the kinetic probes **1** and **2**. Assuming that the dipolar $E_T(30)$ probe binds in the Stern region as well, the Stern region seems to show hydrophobic character in these measurements. The mismatch in the Stern region headgroup concentration as found from comparing micellar and salt solutions can be understood from the large difference between the hydrolytic probes on the one hand and the $E_T(30)$ probe on the other. Considering the fact that, compared to a micelle, the $E_T(30)$ solvatochromic probe is a huge dipolar molecule, a strong perturbation of the micellar structure upon binding of this molecule is anticipated.

The overall way the Stern region manifests itself will be the result of a subtle interplay between the interactions a probe molecule (*e.g.* a hydrolytic probe or a solvatochromic probe) can have with either the hydrophobic tails or with the headgroups and water molecules present in the Stern region. This, of course, can be expected for a region that constitutes a concentrated aqueous solution of surfactant headgroups and counterions next to the hydrophobic micellar core.

For the nonionic surfactant, initially both tetraethyleneglycol and heptaethyleneglycol solutions in water were used as models for the Stern region. As heptaethyleneglycol gave the same results as tetraethyleneglycol, eventually tetraethyleneglycol was chosen as it was available in the purest form.

Remarkably, the seven ethyleneoxide units of the $C_{12}E_7$ surfactant headgroup have a similar effect on the hydrolysis of both probes to the ionic headgroups of the other surfactants used in this study. When we compare kinetic results obtained for the micellar solutions to those for tetraethyleneglycol solutions, we see that no match in rate constant occurs until an ethyleneoxide monomeric unit concentration of 16 M, suggesting that the concentration of ethyleneoxide units in the Stern region has a similar value.

A calculation of the Stern region concentration of ethyleneoxide headgroup units suggests a value of 8 M in the case that the ethyleneglycol chain is fully extended. The discrepancy by a factor of two can be explained by taking into account back folding or meandering of the heptaethyleneglycol units of the surfactant molecules, as has been observed in other studies as well.[7,46]

The decreased water activity in the Stern region of SDS, estimated by others[47] to be about 0.6, coincides with the decreased water-concentration in the model compound solutions corresponding to the Stern region, *viz.* around 33 M. This means that only a deceleration factor of three can be attributed to the decreased water activity. The rest of the deceleration has to be attributed to reaction-specific requirements on probe and water configuration[38] not being met as a result of the presence of surfactant headgroups or model compound molecules forcing the water molecules in certain configurations. For CTAB, the water concentration in the Stern region has been estimated to be 45 M,[13,14a] meaning that almost the entire rate deceleration is caused by restricted motion (lower activity coefficient) of the water molecules as found in the Stern region.

Hydrophobic interactions do not seem to play an active role in decelerating the water-catalysed hydrolysis reactions as can be concluded from the fact that the model compounds, lacking the hydrophobic chains, decelerate the reaction as well. It has been shown before that the hydrolysis of **1** and **2** is able to respond strongly to hydrophobic interactions as has been demonstrated convincingly for a range of hydrophobic co-solutes.[44,48] This effect is different for the ethyleneglycol solutions. Here the concentration of water in solution for the matching solutions is so low (approx. 15 M) that a large part of the deceleration, *viz.* a factor of 13.4 (assuming γ = 1 at all concentrations), can be directly attributed to the reduced availability of water molecules in the solution, without invoking

reduced mobility of the water molecules. Alternatively, the water concentration in the Stern region can be estimated to be approximately 48 M, from the hydration number of ethyleneoxide moieties of three.[14d,41] However, creating a solution that is 48 M in water and 16 M in ethyleneglycol is impossible. Therefore it appears to be reasonable to conclude that the hydration of the ethyleneglycol units varies over the Stern region with the innermost ethyleneglycol units, close to the hydrophobic core and presumably also to the binding location of the hydrolytic probe, least hydrated. In the case of the ionic solutions, the water molecules are available, but are now much more restricted in their movements as a result of stronger interactions with the ions.

Conclusion

From the match in the CTAB and SDS micellar rate constant with the rate constant in a concentrated headgroup model compound solution, we contend that the micellar retardation of the hydrolysis of **1** and **2** is dominated by a salt effect with the hydrophobic substrate being bound in the Stern region of the micelle. This salt effect includes the effect of the hydrophobic moieties in the surfactant headgroup. For nonionic $C_{12}E_7$ micelles, the term 'salt effect' denotes the effect of the oligoethyleneoxide moieties in the $C_{12}E_7$ headgroup, even though these are not ionic. We conclude that the Stern region can be regarded as a separate phase with a high surfactant headgroup and counterion concentration.

The kinetic effect of hydrophobic stabilisation, the reason for substrate binding to the micelle, is comparatively small. This must mean that the stabilisation by the hydrophobic parts of the micelle is similar for the reactant state and for the activated complex. Even though **1** is the more hydrophobic compound and binds more strongly to the micelle, the effect of the hydrophobic surfactant tails seems largest for the hydrolysis of **2**. This can be deduced from the fact that in the case of the hydrolysis of **2**, the discrepancy between micellar rate constant and rate constant in the model compound solution is largest. Contrastingly, the solvatochromic $E_T(30)$ probe indicates a much more hydrophobic environment for binding of the probe as a result of the closeness of the Stern region to the hydrophobic core of the micelle.

The present results clearly indicate that characterisation of the Stern region as a medium for kinetic or spectroscopic probes is hampered by the complexity of noncovalent interactions acting upon the probe. The highly dynamic nature of the micelle and the possibilities for probe-induced changes of the micellar structure further complicate a general marking of the distinguishing features of the Stern region.

Experimental

SDS was obtained from BDH Chemicals, CTAB and TMAB from Merck and DTAB from Sigma. $C_{12}E_7$ was from Nikko Chemicals Co., 1-benzoyl-3-phenyl-1,2,4-triazole **1** and *p*-methoxyphenyl dichloroacetate **2** were synthesised according to literature procedures.[49] The $E_T(30)$-probe was kindly provided by Prof. Chr. Reichardt. Sodium monomethylsulfate was synthesised by hydrolysis of dimethyl sulfate and subsequent neutralisation with NaOH. Tetraethyleneglycol was obtained from Merck Schuchardt. Micellar solutions were 1×10^{-4} M in HCl, model compound solutions were acidified to pH 4. All solutions were made in water that was distilled twice in an all-quartz apparatus. Surfactants and salts were dried before use. Solutions were made volumetrically, the mass of all components of the solutions was determined in order to know both solute and solvent concentration.

Reactions were followed at 273 nm (for **1**) and 288 nm (for **2**) at 25.0 ± 0.2 °C for at least six half-lives using a Perkin-Elmer λ2 or λ5 spectrophotometer. Good to excellent pseudo-first-order kinetics were obtained, the error in the rate constants being 2% or less for the micellar solutions and the dilute salt solutions, but up to 10% for the concentrated salt solutions.

The probes were injected as 2–5 μl of a stock solution of **1** or **2** in acetonitrile into a 1 cm quartz cuvet of *ca.* 2.5 ml yielding a total probe concentration during the reaction of *ca.* 10^{-5} M. These concentrations were chosen in order to have absorbance changes not larger than 0.6.

Kinetics in concentrated model compound solutions were checked for salting out of the hydrolytic probes by doing a number of experiments with different probe concentrations to exclude possible effects due to rate-determining dissolution of the probe.

The measurements involving the $E_T(30)$-probe were performed at pH 11, using a Perkin-Elmer λ2-spectrophotometer. The $E_T(30)$ probe was injected as <6 μl of a stock solution of the solvatochromic probe in EtOH.

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