

Evidence of Hydronium Ion Complexation by 18-Crown-6 at the Surface of Hydrogen Dodecyl Sulfate Micelles

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Received: April 10, 1997; In Final Form: July 10, 1997[⊗]

The effect of 18-crown-6 (18C6) on the decomposition of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) by N_3^- and H_3O^+ in micelles of tetradecyltrimethylammonium azide (TTAN₃) and hydrogen dodecyl sulfate (HDS) has been studied. The crown ether solubilizes in TTAN₃ micelles only in its uncomplexed form due to hydrophobic effects because the positively charged TTAN₃ micellar surface avoids incorporation of 18C6 complexed with cations. In HDS, besides hydrophobic effects, 18C6 binds to the micelles by complexing H_3O^+ counterions. The hydronium complexation constant of 18C6 in the micellar phase is much larger than its corresponding value in water, which was explained on the basis of changes in the microenvironment of the reagents at the water–micelle interface. The results obtained allowed us to discuss the different locations of the micelle-bound crown ether both in its free and complexed forms: the uncomplexed crown ether is located in an inner region of the micelle, whereas 18C6· H_3O^+ is preferentially located in the Stern layer acting like a counterion and modifying the bimolecular rate constant of MNTS decomposition in the micellar phase.

Introduction

Crown ethers are macrocyclic compounds which form inclusion complexes with a large number of ionic and even neutral species.¹ Hence, due to the possibility of these polyethers complexing the counterions of anionic micelles^{2–4} the surfactant–polyether-mixed systems show some differences when compared to mixtures of surfactants and other additives such as alcohols,^{5–7} amines,⁸ or ureas.⁹ In general, as the complexation constant between macrocyclic polyether and micellar counterions increases, larger effects are observed in some micellar properties like aggregation number, cmc, and micellar charge. Some studies show the influence of macrocyclic polyethers with different complexing ability on those properties of anionic micelles.^{10–14}

On the other hand, it is interesting to know the location of these polyethers in micellar aggregates. Electron spin resonance (ESR) studies showed that 15-crown-5 (15C5) and 18-crown-6 (18C6) are located at the micellar–water interface of sodium dodecyl sulfate (SDS) and lithium dodecyl sulfate (LDS).^{15,16} Small-angle neutron scattering (SANS) experiments on the effect of 18C6 in SDS micelles¹⁷ are inconclusive since they are unable to distinguish whether the crown ether complexing the sodium counterions is either in the Stern layer or in the micellar core. Fluorescence¹³ and NMR¹⁸ studies on the effect of cryptand 222 (C222) in SDS micelles showed that C222· Na^+ counterions, more hydrophobic than Na^+ , are located among the head groups acting like spacers, whereas the uncomplexed counterions are in the outer side of the micelle head groups region. Therefore, the micellar surface is less compact allowing a larger extent of water penetration and reducing the repulsive interactions among the head groups.

This paper on the effect of 18C6 on chemical reactivity in micellar media was carried out in cationic and anionic micelles both of them possessing reactive counterions (tetradecyltrimethylammonium azide (TTAN₃) and hydrogen dodecyl sulfate

(HDS), respectively). In both these cases the bifunctional substrate *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS), which binds to micelles of TTAN₃ and HDS with a similar constant and reacts with both N_3^- and H_3O^+ ,^{19,20} was used. We have chosen functionalized TTAN₃ and HDS for simplicity as it is not necessary to take into account possible ionic exchange equilibria between reactive and unreactive counterions. We have also avoided addition of other cationic species which could be complexed by the crown ether.

18C6 only has the possibility of binding the micellar phase of TTAN₃ in its uncomplexed form due to hydrophobic effects because the trimethylammonium head groups are too large to be complexed by 18C6, and association of a cationic complex of 18C6 is prevented by the positive potential which exists at the micellar surface. This has allowed us to study the effect of the uncomplexed macrocyclic polyether in MNTS decomposition in micellar media. In the case of HDS we are most interested in studying the possibility of hydronium complexation by 18C6 at the micellar interface and comparing the results to those of an aqueous phase in which the hydronium complexation constant was estimated²¹ as 0.4 M^{-1} .

Experimental Section

HDS was prepared from SDS solutions by ion exchange using the cationic resin Amberlite IR-120PLUS (from Sigma) as described elsewhere.²² TTAN₃ was similarly prepared from tetradecyltrimethylammonium bromide (TTABr) using the anionic resin Amberlite IRA-410 (from Sigma). MNTS, SDS, TTABr, and 18C6 were products of the highest commercially available purity (either from Merck or Aldrich). Solutions of MNTS were prepared in acetonitrile (and stored at low temperature in the dark to avoid decomposition). Kinetic experiments were started by addition of small volumes of MNTS solutions to the reaction mixtures. The proportion of organic solvent in the final mixture was never greater than 2%.

All kinetic experiments were carried out at 25 °C in Kontron Uvikon 930 or Milton Roy Spectronic 3000 diode array spectrophotometers equipped with thermostated cell holders. First-order conditions were ensured in all cases by using ionic

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[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

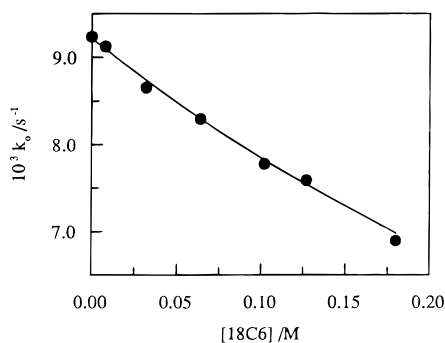


Figure 1. Influence of 18C6 concentration, [18C6], on the rate of MNTS decomposition k_o in TTAN₃ micelles: [TTAN₃] = 1.60×10^{-2} M, cmc = 1.20×10^{-3} M, [NaN₃] = 1.50×10^{-2} M.

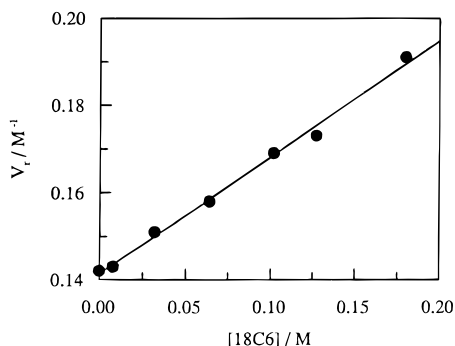


Figure 2. Influence of 18C6 concentration, [18C6], on the molar reaction volume per mole of micellized surfactant V_r for reaction in the micellar phase of TTAN₃: [TTAN₃] = 1.60×10^{-2} M, [NaN₃] = 1.50×10^{-2} M.

reagent concentrations (H_3O^+ or N_3^-) very much greater than the MNTS concentration. Kinetic runs were followed by monitoring the absorbance of MNTS at 250–270 nm. In all cases the experimental absorbance–time data fitted very well the first-order integrated equation, and first-order rate constants k_o were reproducible within 3%.

Results and Discussion

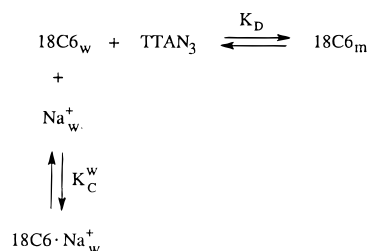
Influence of 18C6 on MNTS Decomposition in TTAN₃ Micelles. Figure 1 shows the inhibition on the observed first-order rate constant k_o due to 18C6 addition on MNTS decomposition by azide ion in TTAN₃ micelles.

MNTS reacts with N_3^- in both aqueous and in micellar pseudophases.¹⁹ By applying the kinetic model of the pseudophase to micellar solutions with reactive counterions,^{23,24} the following equation for k_o is obtained, which is similar to the one obtained in a previous paper:⁵

$$k_o = \frac{k_w[\text{N}_3^-]_t + \left(\frac{k_2^m}{V_r} K_S - k_w \right) m_{\text{N}_3^-} [\text{D}_n]}{1 + K_S [\text{D}_n]} \quad (1)$$

where k_w and k_2^m are the bimolecular rate constants in the aqueous and micellar pseudophases, respectively, V_r is the molar reaction volume per mole of micellized surfactant for reaction in the micellar phase, K_S is the micelle–MNTS binding constant, $[\text{D}_n]$ is the concentration of micellized surfactant ($[\text{D}_n] = [\text{D}] - \text{cmc}$), and $m_{\text{N}_3^-} = [\text{N}_3^-]_m / [\text{D}_n]$ is the concentration of N_3^- bound to the micelle, expressed as a mole ratio, which, in this case, is identified as β (the degree of micellar charge neutralization). Values used for these parameters are $k_w = 3.39 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, $k_2^m = 2.32 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $K_S = 150 \text{ M}^{-1}$, cmc = $1.20 \times 10^{-3} \text{ M}$, and $\beta = 0.8$, all of them were obtained in a

SCHEME 1: 18C6 Distribution between Water and TTAN₃ Micelles



previous study of MNTS decomposition in TTAN₃ micelles with no 18C6 added (unpublished results). In this study, k_w is not affected by 18C6 addition because the low 18C6 concentrations used do not change the properties of the aqueous phase, and 18C6 does not complex the reactive anionic N_3^- . The micellar parameters (k_2^m , K_S , cmc, and β) were assumed the same as in absence of 18C6 in view of (i) the low distribution constants of this crown ether measured in positively charged micelles of DTABr,² (ii) the absence of counterion complexation (in this case the anionic species N_3^-), and (iii) the observation that the binding constants of MNTS to several micelles do not change significantly even in the presence of additives like alcohols.^{5,25} We have confirmed these assumption and the distribution constant of MNTS in SDS:18C6 in (1:1) and (1:4) ratios was 116 and 132 M^{-1} , respectively. Similarly, β changes from 0.58 in the absence of 18C6 to 0.63 (1:1 ratio) and 0.66 (1:4 ratio) in SDS micelles measured by conductivity. (Note that in SDS micelles the binding constant of 18C6 is about 30 times larger than in cationic micelles as DTABr² and no significant effects were found in the micellar parameters of SDS, hence our assumption about TTAN₃.) These initial approximations allowed us to obtain a good fit of the results and a distribution constant for 18C6 which agrees with the one obtained by other methods (see discussion below).

Progressive incorporation of 18C6 to the micelle is responsible for k_o inhibition due to a change in the micellar volume V_r , diluting the reagents in this pseudophase as it was reported for the addition of alcohols.^{5,26} In the absence of 18C6, $V_r = V_o$, where V_o is the molar reaction volume of the Stern layer in the absence of additives which was estimated as 0.14 M^{-1} .^{27,28} Considering the molar reaction volume in the micellar phase as the sum of V_o plus the molar volume of the bound crown ether, V_r can be expressed as

$$V_r = V_o + \frac{[18\text{C6}]_m}{[\text{D}_n]} V_{18\text{C6}} \quad (2)$$

where $V_{18\text{C6}}$ is the molar volume of 18C6, estimated²⁹ as 0.23 M^{-1} and $[18\text{C6}]_m / [\text{D}_n]$ is the mole ratio of bound crown ether.

In order to obtain the binding constant of 18C6 to the micelle K_D , we must consider that 18C6 can participate in two equilibria as is described in Scheme 1: (i) Na^+ complexation in the aqueous phase from added NaN₃ and (ii) association of uncomplexed 18C6 to the micellar phase (the electrostatic association of $18\text{C6} \cdot \text{Na}^+$ to the micelle is prevented because TTAN₃ is a cationic micelle, and hence, the binding should be only due to hydrophobic effects).

Nevertheless, considering that the Na^+ complexation constant of 18C6 in water, $K_C^w(\text{Na}^+)$, was measured³⁰ as 6.6 M^{-1} and that the amount of Na^+ present (from added NaN₃) is low, in a first analysis we do not consider the complexation process in water. In this way, from eq 2 and writing $[18\text{C6}]_m$ as a function of K_D and $[18\text{C6}]_t$ we obtain

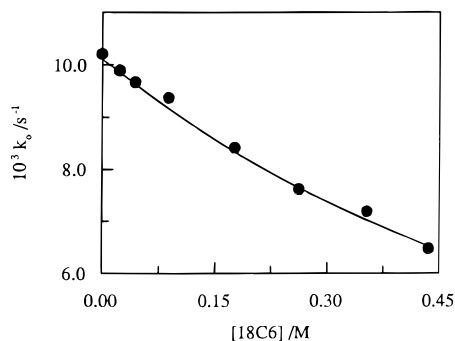


Figure 3. Influence of 18C6 concentration, [18C6], on the rate of MNTS decomposition k_o in TTAN₃ micelles: [TTAN₃] = 4.35×10^{-2} M, cmc = 1.20×10^{-3} M, [Na₃] = 1.50×10^{-2} M.

$$V_r = V_o + \frac{K_D V_{18C6}}{1 + K_D [D_n]} [18C6]_t \quad (3)$$

Figure 2 shows the good fitting of V_r values (calculated from eq 1) to eq 3. The intercept yields $V_o = 0.141 \pm 0.001 \text{ M}^{-1}$ in accordance with the literature value mentioned above. From the slope a value of $K_D = 1.1 \pm 0.1 \text{ M}^{-1}$ is obtained. This value of K_D is comparable with that obtained by Stilbs² ($K_D = 1.1 \pm 0.1 \text{ M}^{-1}$) in dodecyltrimethylammonium bromide micelles (DTABr) using a different experimental technique, showing the validity of the kinetic method used here to calculate the binding constant of 18C6. Moreover, Figure 1 shows the good fit of k_o to eq 1 taking the value of $K_D = 1.1 \text{ M}^{-1}$.

Further experiments were carried out using larger TTAN₃ concentrations. Analysis of such data showed a value $K_D = 1.2 \pm 0.1 \text{ M}^{-1}$ and, again, the good fit of the experimental plot of k_o vs 18C6 is shown in Figure 3.

In order to check the validity of the approximation used above (where Na⁺ complexation is ignored), a complete analysis, as shown in Scheme 1, has been made by considering both Na⁺ complexation in the aqueous phase and micellar binding of 18C6. The obtained K_D results were within the error limits calculated previously ($K_D = 1.2 \pm 0.1 \text{ M}^{-1}$ and $K_D = 1.0 \pm 0.1 \text{ M}^{-1}$ in TTAN₃ concentrations 1.60×10^{-2} and 4.35×10^{-2} M, respectively).

Effect of 18C6 on the Acid Hydrolysis of MNTS in HDS Micelles. Figures 4 and 5 show the effect of addition of 18C6 to HDS micelles in a constant ratio ([HDS]:[18C6] = 1:1 and 1:4, respectively) on the observed rate constant k_o for the acid hydrolysis of MNTS.

In order to explain these results, the data were similarly analyzed as those described above for TTAN₃, assuming 18C6 to be distributed between the aqueous and micellar pseudophases. In this case, the only cation in the reaction media is the proton, which is present as its hydronium form both in the aqueous phase and at the HDS micellar interface.³¹ H₃O⁺ complexation by different crown ethers has been reported in the literature,³² although some doubts arise as to whether it is easy to differentiate between a H₃O⁺ complex and a complex of ether + H₂O + acid.³³ Nevertheless, in the case of H₃O⁺, similar to the cases in other ions of similar structure such as NH₄⁺ and several RNH₃⁺,³⁴ the aqueous hydronium complexation constant by 18C6 is quite small, being estimated as 0.40 M^{-1} .²¹ Consequently, in a first approach, we assumed that 18C6 is only distributed in its uncomplexed form between the aqueous and the micellar pseudophases with $K_D = 1.1 \text{ M}^{-1}$ equal to that calculated by Stilbs² in DTABr and coincident with our own results in TTAN₃ micelles.

Therefore, the application of the kinetic model of the pseudophase to HDS micellar solutions enables us to calculate

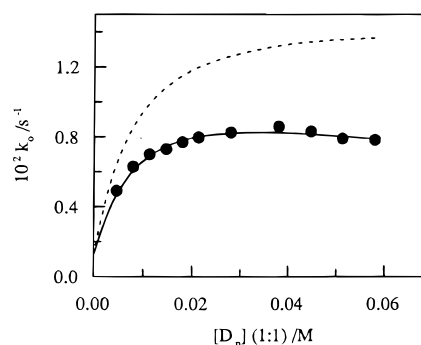


Figure 4. Influence of micellized HDS concentration $[D_n]$ in HDS: 18C6 (1:1) mixture on the pseudo-first-order rate constant of acid hydrolysis of MNTS: [HCl] = 4.14×10^{-2} M, cmc = 2.0×10^{-3} M. See text for interpretation of the lines.

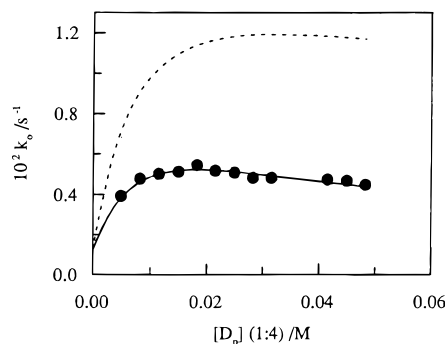


Figure 5. Influence of micellized HDS concentration $[D_n]$ in HDS: 18C6 (1:4) mixtures on the pseudo-first-order rate constant of acid hydrolysis of MNTS: [HCl] = 4.14×10^{-2} M, cmc = 1.8×10^{-3} M. See text for interpretation of the lines.

k_o vs [HDS]:[18C6] using

$$k_o = \frac{k_w [H^+]_t + \left(\frac{k_2^m}{V_r} K_S - k_w \right) m_{H^+} [D_n]}{1 + K_S [D_n]} \quad (4)$$

where the parameters have the same meaning as in TTAN₃, but in this case k_w and k_2^m are the bimolecular reaction rate constants for acid hydrolysis of MNTS in water and micellar pseudophases, respectively. Values of $k_w = 2.76 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and $k_2^m = 3.78 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ were taken from independent studies on the acid hydrolysis of MNTS in H₂O and HDS micelles,²² respectively, while cmc values of 2.0×10^{-3} and $1.8 \times 10^{-3} \text{ M}$ were kinetically measured for the 1:1 and 1:4 ratios (HDS:18C6), respectively. K_S values of 116 M^{-1} (1:1 ratio) and 132 M^{-1} (1:4 ratio) were obtained from previous experiments on the basic hydrolysis of MNTS in SDS:18C6 mixtures of the same ratios. We used SDS whose counterions could be complexed by 18C6, and we found that K_S did not differ from the value in the absence of 18C6²⁵ or in the presence of alcohols.⁵ Moreover, m_{H^+} (or β) values have been determined from conductivity measurements in mixtures SDS:18C6 yielding $\beta = 0.63$ (1:1 ratio) and $\beta = 0.66$ (1:4 ratio). These values of β do not appear to be largely modified by 18C6 as was also found by Caponetti et al.¹⁷ in SDS micelles. Finally, the molar reaction volume per mole of micellized surfactant for the reaction in the micellar phase V_r is given by eq 3, used to explain the above TTAN₃ results.

Use of eqs 3 and 4, together with the above parameters, allowed us to calculate k_o for different [HDS]:[18C6] ratios. These results are shown in Figures 4 and 5 (dotted line) for 1:1 and 1:4 ratios, respectively. These figures clearly show the large

TABLE 1: Influence of 18C6 Concentration, [18C6], on the Bimolecular Rate Constant of MNTS Decomposition in Media with Different Composition MeCN:H₂O (v/v)

[18C6]/M (pure water) ^a	$k_2^w/\text{M}^{-1} \text{ s}^{-1}$	[18C6]/M (25:75) ^a	$k_2^{25:75}/\text{M}^{-1} \text{ s}^{-1}$	[18C6]/M (50:50) ^b	$k_2^{50:50}/\text{M}^{-1} \text{ s}^{-1}$	[18C6]/M (75:25) ^c	$k_2^{75:25}/\text{M}^{-1} \text{ s}^{-1}$
1.72×10^{-3}	2.77×10^{-2}	1.70×10^{-3}	7.35×10^{-3}	2.04×10^{-2}	1.77×10^{-3}	7.40×10^{-2}	1.14×10^{-3}
5.15×10^{-3}	2.60×10^{-2}	1.70×10^{-2}	7.24×10^{-3}	4.08×10^{-2}	2.06×10^{-3}		1.01×10^{-3}
1.72×10^{-2}	2.84×10^{-2}	7.48×10^{-2}	6.82×10^{-3}	7.40×10^{-2}	1.86×10^{-3}		

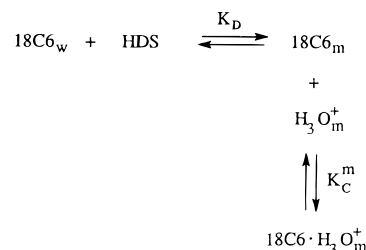
^a [HCl] = 1.70×10^{-3} M. ^b [HCl] = 1.70×10^{-2} M.

difference between the experimental (full circles) and calculated (dotted line) results, the former being much smaller than the latter for all [HDS]. The low experimental values of k_0 suggest that in HDS micelles a larger amount of 18C6 is associated to the micellar phase as compared to DTABr or TTAN₃. In fact, the distribution constant of 18C6 in HDS micelles K_D should be around 7 times larger than that measured with DTABr or TTAN₃ in order to fit the experimental results. Nevertheless, it is usually assumed that the hydrophobic environment of TTAN₃, DTABr, and HDS are similar, and binding constants of 18C6 to these micellar systems should be of the same order as is the case of other substrates.^{5,25}

These considerations lead us to think that 18C6 binds to HDS due to both hydrophobic and electrostatic effects (i.e., that 18C6 complexes H_3O^+ at the micellar surface). A similar case was found by Stilbs where the binding constant of 18C6 was about 30 times larger in SDS than DTABr.² Therefore, there should be a larger amount of micellized 18C6 in HDS due to counterion complexation giving rise to a greater dilution of the reagents in the micelle and decreasing the observed rate constant k_0 . Hydronium complexation by 18C6 in the micellar phase would not be surprising because the micellar interface provides a microenvironment with different solvent properties.³⁵ In this way, De Lisi et al.³⁶ considered the possibility of Na^+ complexation by 18C6 in SDS micelles both in water and micellar phases, obtaining a value for complexation constant of sodium by 18C6 in the micellar phase of SDS around 300 M^{-1} , which is about 50 times larger than its value in water. This behavior can be related to the effect of solvents on the complexation constants of metal ions by crown ethers (i.e., DMSO, MeCN, or MeOH^{30,37,38} and solvent mixtures³⁹). For example, Na^+ complexation constants by 18C6 in water and methanol are very different (6.6 M^{-1} vs $2.26 \times 10^4 \text{ M}^{-1}$, respectively⁴⁰), and studies in methanol–water mixtures^{41,42} showed almost a linear behavior between the logarithm of the complexation constant and the percentage of aqueous methanol.⁴¹ With respect to the hydronium ion, the H_3O^+ complexation constant by 18C6 in MeCN was estimated as $2.5 \times 10^6 \text{ M}^{-1}$,⁴³ whereas in H_2O it is about 0.4 M^{-1} ,²¹ as it has been indicated above. In media with different MeCN:H₂O ratios, a progressive change in the H_3O^+ complexation constant would be expected, similar to that found with Na^+ in MeOH:H₂O mixtures.^{41,42}

Hence, we studied the effect of 18C6 on the acid hydrolysis of MNTS for different MeCN:H₂O ratios (Table 1). The higher MeCN:H₂O volume ratio used in the present study (Table 1) was 75:25 because there is evidence of mechanistic changes for larger organic solvent ratios.⁴⁴ For all MeCN:H₂O ratios studied, k_0 was found not to be dependent on crown ether concentration as shown in Table 1 (note that in one case we used a crown ether concentration about 40 times larger than proton concentration). Table 1 also shows that the bimolecular rate constant for the acid hydrolysis of MNTS slightly decreases as the percentage of MeCN in the mixture increases. Taking into account that k_2^m is typically 5–10 times slower than k_w , a fact usually attributed to the lower polarity of the Stern layer (similar to that of a medium of 25:75 or 50:50 (v/v) MeCN:

SCHEME 2: 18C6 Distribution between Water and HDS Micelles



H_2O), we expect that H_3O^+ complexation constant by 18C6 is much larger in media of high organic solvent ratios and also in micellar media than in pure water. However, in spite of the expected higher complexation constant, no effect of [18C6] upon the rate constant of MNTS decomposition was observed (see Table 1), which indicates that in the solvent mixtures used in these experiments the reactivity of free and complexed H_3O^+ are similar.

Taking the previous data and discussions into account we should consider the system described in Scheme 2, where $K_D = 1.1 \text{ M}^{-1}$ is the binding constant of uncomplexed 18C6 to micellar phase, and K_C^m is the hydronium complexation constant by 18C6 in the micellar phase. In the same way, we consider that the effect of micellized complexed H_3O^+ ($18\text{C6} \cdot \text{H}_3\text{O}_m^+$) on k_0 is only due to the increase in the molar volume of reaction in the micellar phase. We ignore complexation of H_3O^+ in water due to the low constant measured and to the low concentrations of both 18C6 and H_3O^+ .

A simple mass balance of 18C6 according to Scheme 2,

$$[18\text{C6}]_t = [18\text{C6}]_w + [18\text{C6}]_m + [18\text{C6} \cdot \text{H}_3\text{O}^+]_m \quad (5)$$

and the corresponding balance of the micellar charge,

$$\beta[\text{D}_n] = [\text{H}^+]_m + [18\text{C6} \cdot \text{H}_3\text{O}^+]_m \quad (6)$$

allows us to finally obtain

$$\begin{aligned}
 & [18\text{C6}]_m^2 + \\
 & [18\text{C6}]_m \frac{1 + K_D[\text{D}_n](1 + K_C^m\beta[\text{D}_n] - K_C^m[18\text{C6}]_t)}{K_C^m(1 + K_D[\text{D}_n])} - \\
 & \frac{K_D[\text{D}_n][18\text{C6}]_t}{K_C^m(1 + K_D[\text{D}_n])} = 0 \quad (7)
 \end{aligned}$$

Taking into account the definition of K_C^m (see Scheme 2) and using eq 6, it is possible to obtain $[18\text{C6} \cdot \text{H}_3\text{O}^+]_m$:

$$[18\text{C6} \cdot \text{H}_3\text{O}^+]_m = \frac{K_C^m\beta[\text{D}_n][18\text{C6}]_m}{1 + K_C^m[18\text{C6}]_m} \quad (8)$$

To obtain the K_C^m value that better fits the experimental results, we used an iterative method in which from a starting value for K_C^m is possible to calculate $[18\text{C6}]_m$ and then

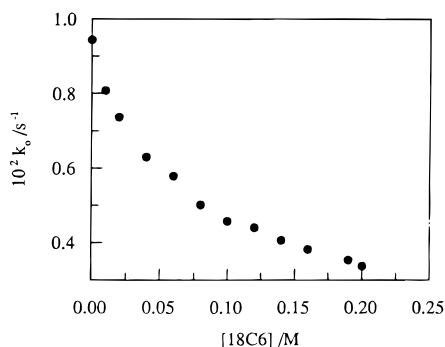


Figure 6. Influence of 18C6 concentration, [18C6], on the rate of MNTS decomposition in HDS micelles. [HDS] = 1.67×10^{-2} M, [HCl] = 4.91×10^{-2} M.

$[18C6 \cdot H_3O^+]_m$ from eqs 7 and 8, respectively. With these values of micellized crown ether concentration and from eq 2, it is possible to calculate V_r for each pair of values k_o vs $[D_n]$: [18C6]. (Note that eq 2 was developed to interpret the results with TTAN₃, but in the present case $[18C6]_m$ in eq 2 is now the sum of both the free and complexed forms obtained from eq 7 and 8, respectively). In this work we have assumed the same molar volume for 18C6 and $18C6 \cdot H_3O^+$ (V_{18C6} and $V_{18C6 \cdot H_3O^+}$) which, although it is not strictly true, may be considered within the limits of the fitting errors (by example, volumes of 18C6 and $18C6 \cdot Na^+$ are 0.223 and 0.235 M⁻¹, respectively²⁹). Now, using V_r and the other parameters (k_w , K_S , and b) we can estimate k_2^m for each experimental point, k_o :

$$k_2^m = \frac{V_r[k_o(1 + K_S[D_n]) + k_w(\beta[D_n] - [H_3O^+]_l)]}{K_S\beta[D_n]} \quad (9)$$

Convergence was achieved for the K_C^m value which shows the minimum deviation of all k_2^m values calculated from eq 9 for both sets of experimental data of Figures 4 and 5.

With this fitting procedure we obtained for the 1:1 ratio a value of $K_C^m = 100 \pm 30$ M⁻¹ (Figure 4) and for the 1:4 ratio a value of $K_C^m = 80 \pm 20$ M⁻¹ (Figure 5). K_C^m is similar (within the error limits) for both series (1:1) and (1:4) and is considerably larger than that obtained in aqueous media. This result is expected taking into account the solvent properties of the micellar interface and is comparable to the larger complexation constants for other cations as is the case of Na⁺ at the micellar interface.³⁶

This analysis has also shown that the above calculated values of k_2^m for the 1:1 ratio (2.60×10^{-3} M⁻¹ s⁻¹) and the 1:4 ratio (1.85×10^{-3} M⁻¹ s⁻¹) were smaller than in experiments without crown ether (3.78×10^{-3} M⁻¹ s⁻¹). In order to check this decrease in k_2^m , further experiments were carried out working at different HDS:18C6 ratios (see Figure 6). Interpretation of data of Figure 6 on the basis of Scheme 2 using $K_D = 1.1$ M⁻¹ and $K_C^m = 90$ M⁻¹ (mean value of the ones calculated above) allows us to calculate $[18C6]_m$, $[18C6 \cdot H_3O^+]_m$ and k_2^m from eqs 7, 8, and 9, respectively (see Table 2). From k_2^m data shown in Table 2, it is possible to conclude that the bimolecular reaction rate constant k_2^m for acid hydrolysis of MNTS in HDS micelles is feeling (or responding) to the change in composition of the Stern layer. As more crown ether is incorporated in the micellar phase a further decrease in k_2^m was observed; in other words, the incorporation of $18C6 \cdot H_3O^+$ to the micelle produces two effects: on one hand the previously commented increase of the volume of the Stern layer and on the other changes in k_2^m . This effect on k_2^m was not detected for TTAN₃ (very good fittings with constant k_2^m for ratios TTAN₃:18C6 ranging from 1:0.5 to 1:11 were observed) although similar amounts of $[18C6]_m$

TABLE 2: Concentration of Micellized 18C6 in HDS and TTAN₃ Micelles at Different Ether:Surfactant Ratios and Estimation of the Bimolecular Rate Constant of MNTS Decomposition in HDS Micelles^a

[18C6]: [HDS]	$10^3[18C6]_m/M$	$10^3[18C6 \cdotH_3O^+]_m/M$	$10^3 k_2^m/M^{-1} s^{-1}$	[18C6]: [TTAN ₃]	$10^3[18C6]_m/M$
0.6	0.157	0.133	2.62	0.5	0.112
1.2	0.314	0.263	2.44	2.0	0.626
2.4	0.628	0.511	2.18	4.0	1.06
3.6	0.943	0.747	2.09	6.4	1.76
4.8	1.26	0.971	1.88	7.9	2.04
6.0	1.57	1.19	1.77	11.3	3.19
7.2	1.89	1.39	1.77		
8.4	2.20	1.58	1.68		
9.6	2.52	1.77	1.62		
11.4	2.99	2.03	1.56		
12.0	3.15	2.11	1.50		

^a [HDS] = 1.67×10^{-2} M, and [TTAN₃] = 1.60×10^{-2} M. Data were obtained from experimental results of Figures 1 and 6 for TTAN₃ and HDS, respectively.

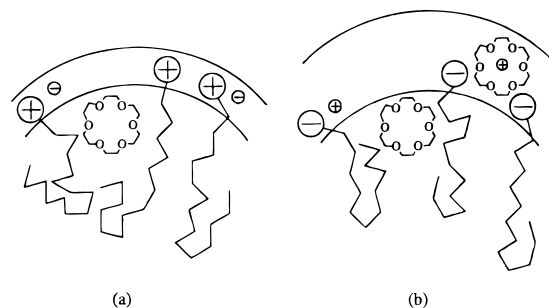


Figure 7. Schematic representation of 18C6 location in micelles of (a) TTAN₃ and (b) HDS. (Not to scale).

are present in both TTAN₃ and HDS (see Table 2). The fact that k_2^m appears to change only in the case of HDS led us to think that the micellized complexed crown ether ($18C6 \cdot H_3O^+$) must be the responsible for the effect on k_2^m in HDS micelles, whereas the uncomplexed crown ether ($18C6_m$) does not produce any significant effect on the micellar rate constant. All this leads us to conclude that there are two possible sites for the location of the micellized crown ether.

Site 1. Uncomplexed crown ether ($18C6_m$) is preferentially solubilized in a more hydrophobic region of the micelle acting as a spacer of the surfactant monomers, increasing the micellar radius and hence the volume of the reaction region, but not significantly affecting the Stern layer composition (see Figure 7). In this case the reactivity is only affected by dilution of the micellar phase, the crown ether behaving like typical additives as alcohols.⁵

Site 2. Complexed crown ether ($18C6 \cdot H_3O^+$) will be located in the Stern layer acting as a counterion (see Figure 7). Since this is the reaction zone the effect of crown ether is double: (a) it increases the volume of micelles diluting the reagents, and (b) it is responsible for changes in the bimolecular reaction constant in the micellar phase (k_2^m) due to modifications in the microenvironment of reagents in the Stern layer.

Conclusions

The reactivity of MNTS with two different ionic species (N_3^- and H_3O^+) was studied in order to investigate the effect of 18C6 in the micellar phases of TTAN₃ and HDS. Cationic micelles of TTAN₃ bind crown ether due to hydrophobic effects yielding inhibition of MNTS decomposition due to the dilution of reagents in the Stern layer. This effect is similar to that described for association of alcohols⁵ to SDS and HDS micelles, and following a parallel reasoning the binding constant of 18C6

K_D was calculated. The inhibition of the acid decomposition of MNTS due to crown ether addition to anionic HDS micelles is much larger than that in TTAN₃. Results using HDS were interpreted by considering complexation of micellar counterions (hydronium ions) by 18C6 as it has been reported for the Na⁺ complexation at the interface of SDS micelles.³⁶ The H₃O⁺ complexation constant obtained by 18C6 in the micellar phase K_C^m ca. 90 M⁻¹ was considerably larger than that measured in water (0.4 M⁻¹).²¹ The larger H₃O⁺ complexation constant by 18C6 at the water-micelle interface shows the different properties of this micellar region acting like a solvent. The crown ether binds to HDS micelles both by hydrophobic (as free crown) and electrostatic (as 18C6·H₃O⁺) effects, acting in the latter case as a micellar counterion. On the other hand, the fit of the results obtained for HDS shows a different behavior when compared to those of TTAN₃ because the bimolecular rate constant in the micellar phase of HDS is modified as the proportion of 18C6 bound to the micelle increases. In this way, the comparison of both micellar systems (TTAN₃ and HDS) indicates that the free crown ether is located in a deeper region of the micelles, while complexed crown ether is located in the Stern layer. As a result, the composition of the Stern layer is modified, therefore introducing changes in the bimolecular reaction rate constant in the micellar phase k_2^m . The study of MNTS reactivity with H₃O⁺ in MeCN:H₂O mixtures (a similar medium to the one existing at the micellar interface) clearly shows that, in all cases, the bimolecular rate constant of acid hydrolysis of MNTS was independent of the crown ether concentration. This fact suggests that in the working conditions, both free and complexed micellized H₃O⁺ react with a similar rate constant.

Acknowledgment. We are most grateful for financial support from the Dirección General de Investigación Científica y Técnica of Spain (project PB93-0524). S. Amado thanks the Vicerrectorado de Investigación da Universidade de Santiago de Compostela for a Predoctoral Grant.

References and Notes

- (1) (a) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1995**, 95, 2529. (b) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, 91, 1721. (c) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, 85, 271. (d) Christensen, J. C.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, 74, 351.
- (2) Stilbs, P. *J. Colloid Interface Sci.* **1982**, 87, 385.
- (3) Stilbs, P. *J. Colloid Interface Sci.* **1983**, 94, 463.
- (4) Vikingstad, E.; Bakken, J. *J. Colloid Interface Sci.* **1980**, 74, 8.
- (5) Bravo, C.; Leis, J. R.; Peña, M. E. *J. Phys. Chem.* **1992**, 96, 1957.
- (6) Stephany, S. M.; Kole, T. M.; Fisch, M. R. *J. Phys. Chem.* **1994**, 98, 11126.
- (7) Luo, H.; Boens, N.; Van der Auweraer, M.; De Schryver, F. C.; Malliaris, A. *J. Phys. Chem.* **1989**, 93, 3244.
- (8) Kumar, S.; Aswal, V. K.; Singh, H. N.; Goyal, P. S.; Ud-Din, K. *Langmuir* **1994**, 10, 4069.
- (9) Caponetti, E.; Causi, S.; De Lisi, R.; Floriano, M. A.; Milioto, S.; Triolo, R. *J. Phys. Chem.* **1992**, 96, 4950.
- (10) Evans, D. F.; Sen, R.; Warr, G. G. *J. Phys. Chem.* **1986**, 90, 5500.
- (11) Evans, D. F.; Evans, J. B.; Sen, R.; Warr, G. G. *J. Phys. Chem.* **1988**, 92, 784.
- (12) Payne, K. A.; Magid, L. J.; Evans, D. F. *Prog. Colloid Polym. Sci.* **1987**, 73, 10.
- (13) Quintela, P. A.; Reno, R. C. S.; Kaifer, A. E. *J. Phys. Chem.* **1987**, 91, 3582.
- (14) Liu, Y. C.; Baglioni, P.; Teixeira, J.; Chen, S. H. *J. Phys. Chem.* **1994**, 98, 10208.
- (15) Baglioni, P.; Kevan, L. *J. Chem. Soc., Faraday Trans. 1* **1988**, 84, 467.
- (16) Baglioni, P.; Rivara-Minten, E.; Kevan, L. *J. Phys. Chem.* **1988**, 92, 4726.
- (17) Caponetti, E.; Chillura Martino, D.; Floriano, M. A.; Triolo, R.; Wignall, G. D. *Langmuir* **1995**, 11, 2464.
- (18) Ginley, M.; Henriksson, U.; Li, P. *J. Phys. Chem.* **1990**, 94, 4644.
- (19) García-Río, L.; Iglesias, E.; Leis, J. R.; Peña, M. E.; Ríos, A. *J. Chem. Soc. Perkin Trans. 2* **1993**, 29.
- (20) Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1838.
- (21) Gaikwad, A. G.; Noguchi, H.; Yoshio, M. *Anal. Sci.* **1987**, 3, 217.
- (22) Bravo, C.; Hervés, P.; Leis, J. R.; Peña, M. E. *J. Phys. Chem.* **1990**, 94, 8816.
- (23) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. *Acc. Chem. Res.* **1991**, 24, 357.
- (24) Romsted, L. S. In *Surfactants In solution*; Vol. 2, K. L. Mittal, B. Lindman, Eds.; Plenum Press, New York, **1984**; Vol. 2, p 1015.
- (25) Amado, S.; García-Río, L.; Leis, J. R.; Ríos, A. *Langmuir* **1997**, 13, 687.
- (26) (a) Athanassakis, V.; Bunton, C. A.; de Buzzaccarini, F. *J. Phys. Chem.* **1982**, 86, 5002. (b) Bunton, C. A.; de Buzzaccarini, F. *J. Phys. Chem.* **1982**, 86, 5010. (c) Otero, C.; Rodenas, E. *J. Phys. Chem.* **1986**, 90, 5771.
- (27) Bunton, C. A.; Romsted, L. S.; Savelli, G. *J. Am. Chem. Soc.* **1979**, 101, 1253.
- (28) Al-Lohedan, H.; Bunton, C. A.; Romsted, L. S. *J. Phys. Chem.* **1981**, 85, 2123.
- (29) Bakshi, M. S.; Crisantino, R.; De Lisi, R.; Milioto, S. *Langmuir* **1994**, 10, 423.
- (30) Lin, J. D.; Popov, A. I. *J. Am. Chem. Soc.* **1981**, 103, 3773.
- (31) García-Río, L.; Leis, J. R.; Peña, M. E.; Iglesias, E. *J. Phys. Chem.* **1992**, 96, 7820.
- (32) (a) Izatt, R. M.; Haymore, B. L.; Christensen, J. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1308. (b) Heo, G. S.; Bartsch, R. A. *J. Org. Chem.* **1982**, 47, 3557. (c) Behr, J. P.; Dumas, P.; Moras, D. *J. Am. Chem. Soc.* **1982**, 104, 4540.
- (33) Gokel, G. W.; Garcia, B. J. *Tetrahedron Lett.* **1977**, 317.
- (34) (a) Liesegang, G. W.; Farrow, M. M.; Arce-Vazquez, F.; Purdie, N.; Eyring, E. M. *J. Am. Chem. Soc.* **1977**, 99, 3240. (b) Izatt, R. M.; Terry, R. E.; Haymore, B. L.; Hansen, L. D.; Dalley, N. K.; Avondet, A. G.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, 98, 7620. (c) de Boer, J. A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1985**, 107, 5347.
- (35) Cordes, E. H. *Pure Appl. Chem.* **1978**, 50, 617.
- (36) Crisantino, R.; De Lisi, R.; Milioto, S.; Pellerito, A. *Langmuir* **1996**, 12, 890.
- (37) Solovev, V. P.; Strakhova, N. N.; Raevsky, O. A.; Rudiger, V.; Schneider, H. J. *J. Org. Chem.* **1996**, 61, 5221.
- (38) Ohtsu, K.; Kawashima, T.; Ozutsumi, K. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 4375.
- (39) (a) Strasser, B. O.; Popov, A. I. *J. Am. Chem. Soc.* **1985**, 107, 7921. (b) Schmidt, E.; Popov, A. I. *J. Am. Chem. Soc.* **1983**, 105, 1873.
- (40) Michaux, G.; Reisse, J. *J. Am. Chem. Soc.* **1982**, 104, 6895.
- (41) Dishong, D. M.; Gokel, G. W. *J. Org. Chem.* **1982**, 47, 147.
- (42) Izatt, R. M.; Terry, R. E.; Nelson, D. P.; Chan, Y.; Eatough, D. J.; Bradshaw, J. S.; Hansen, L. D.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, 98, 7626.
- (43) Kolthoff, Y. M.; Wang, W. J.; Chantooni, Jr., M. K. *Anal. Chem.* **1983**, 55, 1202.
- (44) Bravo, C.; Hervés, P.; Leis, J. R.; Peña, M. E. *J. Chem. Soc., Perkin Trans. 2* **1991**, 2091.