Investigation of Micellar Media Containing β-Cyclodextrins by Means of Reaction Kinetics: Basic Hydrolysis of *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide

L. García-Río and J. R. Leis*

Departamento de Química Física, Facultad de Química, Universidad de Santiago, 15706 Santiago, Spain

J. C. Mejuto and J. Pérez-Juste

Departamento de Química Física y Química Orgánica, Facultad de Ciencias, Universidad de Vigo, Vigo, Spain

Received: March 6, 1997; In Final Form: June 30, 1997[⊗]

The kinetics of the basic hydrolysis of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide were studied in media containing sodium dodecyl sulfate (SDS) or tetradecyltrimethylammonium bromide (TTABr) micelles and β-cyclodextrin (CD). Under the experimental conditions, [NaOH] = 0.17 M, all CD will have been deprotonated; thus, binding constants apply to the CD anion. The results have been interpreted in terms of a pseudophase model that takes into account the formation of both CD−surfactant and CD−substrate complexes and also, for TTABr systems, the exchange of Br^- and OH^- ions between the micellar and aqueous pseudophases. The presence of CD has no effect on existing SDS or TTABr micelles but raises the cmc: complexation of surfactant by cyclodextrin makes the cmc dependent on CD concentration because the cmc is now the sum of the concentrations of free and complexed surfactant when micelles begin to form; increasing [CD] reduces the former quantity but increases the latter to a greater extent. At surfactant concentrations above the cmc, competition between the micellization and complexation processes leads to the existence of a significant concentration of free cyclodextrin.

Introduction

Cyclodextrins are cyclic oligomers of α-D-glucose linked by α-(1→4) bonds. Natural cyclodextrins are classified as α-, β-, or γ-cyclodextrin according to whether they have six, seven or eight glucose units respectively.[1] Their importance stems from their ability to form inclusion complexes, which derives from the gross geometrical form of their molecules being a truncated hollow cone that is able to accommodate small organic molecules of suitable size, shape, and polarity. A commonly used rule of thumb is that α-, β-, and γ-cyclodextrin snugly accommodate benzene, naphthalene, and anthracene respectively.[2]

Because of their ability to form inclusion complexes, cyclodextrins can influence the rate and/or selectivity of certain chemical reactions,[3] either by simply sequestering one of the reagents or, in some cases, because a deprotonated cyclodextrin hydroxyl group catalyzes the rearrangement of a guest molecule.[1a] Catalytic processes of this latter kind have been regarded as a model of enzyme action.

The kinetic effects of cyclodextrins have led to intense research on their complexation properties. Initially, most of the substrates used were aromatic dyes and other molecules with strong chromophores,[1a,b] but in recent years there have been numerous studies of complexation of surfactants, whose chain length and head groups can be varied systematically. The CD−surfactant complexation are due to the ability of the CD to screen the hydrophobic groups of surfactant molecules from contact with the aqueous medium forming inclusion complexes in which the surfactants hydrophobic chain is inserted in the CD cavity. In the case of common water-soluble ionic surfactants, the magnitude of the interaction between cyclodextrin and the hydrocarbon chain of the surfactant molecule increases with chain length.[4] The techniques most often used to investigate complexation of surfactants have been based on measurements of conductivity,[5] fluorescence,[6] surface tension,[7] and ultrasound;[8] unfortunately, the equilibrium constants reported for cyclodextrin−surfactant complexation depend greatly on the technique used to obtain them. The value of conductimetric methods for this purpose has been questioned.[7b,9]

In spite of the numerous studies on cyclodextrin−surfactant complexation, and although it is recognized that the addition of cyclodextrin to aqueous surfactant solutions greatly affects the physicochemical properties of the latter,[10] there has been little research either on how cyclodextrins affect the properties of the micelles that are formed at sufficiently high surfactant concentrations or on how the presence of micelles affects the behavior of cyclodextrins. It seems generally to have been assumed that micelles are only formed once all the cyclodextrin present has been rendered inactive by complexation with surfactant monomers. The lack of experimental investigation of this assumption is all the more surprising given that micelles, like cyclodextrins, can influence reaction rates;[11] in principle, their presence could augment or counteract the rate-controlling effects of cyclodextrins, depending on the reaction in question.

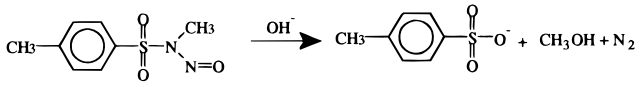
Micellar effects on bimolecular reaction rates are due mainly to the increase or decrease of reactant concentration in the micellar pseudophase,[1c] and the changes in the reaction rate with surfactant concentration often can be explained quantitatively in these terms.[11] Generally it is easier to evaluate the partition of hydrophobic reactants between the aqueous and micellar pseudophases. In the case of hydrophilic ions it is generally assumed that counterions compete to get the ionic positions on the micellar surface. The fraction (β) that is neutralized by counterions is approximately constant.[12] This general approximation has been applied satisfactorily to determine rate and equilibrium constants in micellar systems.[13]

In the work described in this article we studied the influence of β-cyclodextrin on the behavior of aqueous systems containing either sodium dodecyl sulfate (SDS) or tetradecyltrimethylam-

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

S1089-5647(97)00862-6 CCC: $14.00

SCHEME 1



monium bromide (TTABr) by determining the kinetics, in these media, of the basic hydrolysis of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS), a molecule whose geometry and polarity suggested the possibility of its forming an inclusion complex with β-cyclodextrin and whose basic hydrolysis occurs by nucleophilic attack by hydroxyl ions on the MNTS SO_2 group (Scheme 1).[14] This reaction has been studied previously[15] in the presence of SDS or TTABr micelles.

Experimental Section

SDS, TTABr, and β-cyclodextrin (CD) were Sigma products of the highest available purity and were used without further purification. MNTS was purchased from Merck. Because of its poor solubility in water, aqueous solutions of MNTS were prepared by adding to water a small quantity of a solution of MNTS in acetonitrile; the final acetonitrile concentration in the reaction medium was 3% (v/v).

All CD will have been deprotonated under the basic conditions used in this work (pK_a^{CD}=12.2[1a]); all [OH^-] values quoted in what follows are the result of subtracting CD concentration from the concentration of NaOH used to basify the medium.

Reaction kinetics were recorded by measuring absorbance due to MNTS at 250 nm in a Kontron Uvikon 930 or Milton Roy Spectronic 3000 diode array spectrophotometer with a cell holder thermostated at (25.0 ± 0.1) °C. The MNTS concentration was always 5.0×10^{-4} M and [OH^-] > 0.1 M, and first-order pseudoconstants k_0 were obtained by the integration method, fitting the experimental absorbance−time data with equations of the form

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_0 t \qquad (1)$$

where A_0, A_t, and A_∞ are the absorbances at times 0, t, and infinity respectively. In all cases, good agreement between observed and optimized values of A_∞ confirmed that under these conditions the reaction was of first order with respect to MNTS. All experiments were repeated at least three times, and the corresponding values of k_0 were always within 3% of each other.

Results and Discussion

Basic Hydrolysis of MNTS in the Presence of β-Cyclodextrin. The presence of CD inhibits the basic hydrolysis of MNTS (Figure 1). The observed inhibition of the reaction by CD is attributed to the formation of an inclusion complex (MNTS−CD) between MNTS and CD: since the negative charge on the dissociated CD will repel OH^- ions, complexed MNTS will be unreactive (there was no evidence of reaction between MNTS and the dissociated CD hydroxyl group).

The above considerations, formalized in Scheme 2, imply that k_0 is given by the expression

$$k_0 = \frac{k_w[HO^-]}{(1 + K_{MNTS}[CD])} \qquad (2)$$

The good fit between eq 2 and the experimental results (Figure 1) and the agreement between the resulting estimate of $k_w = (7.99 \pm 0.09) \times 10^{-2}$ M^{-1} s^{-1} and those obtained in water without CD[14,15] corroborate the validity of Scheme 2. The resulting estimate of 226 ± 9 M^{-1} for K_{MNTS}, the equilibrium

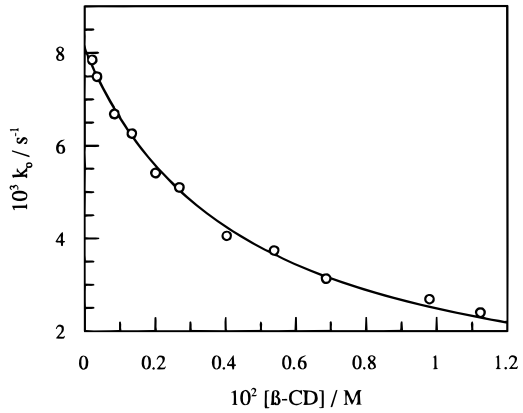


Figure 1. Influence of [CD] on k_0, the first-order pseudoconstant for basic hydrolysis of MNTS. [OH^-] = 0.17 M.

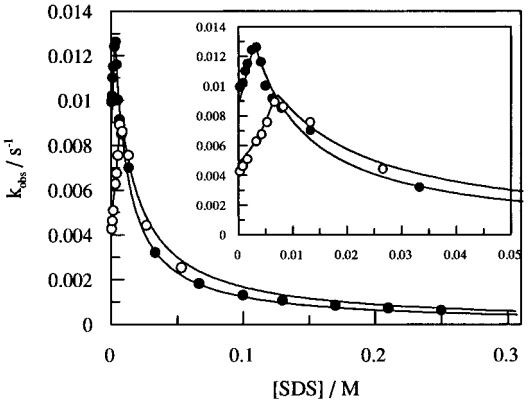
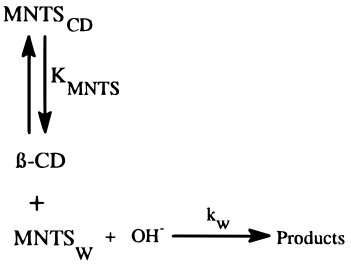


Figure 2. Influence of [SDS] on k_0, the first-order pseudoconstant for basic hydrolysis of MNTS, in the presence of CD concentrations of 2.25×10^{-3} M (●) and 9.00×10^{-3} M (○). Curves are the results of fitting eq 8 to the experimental data as described in the text.

SCHEME 2

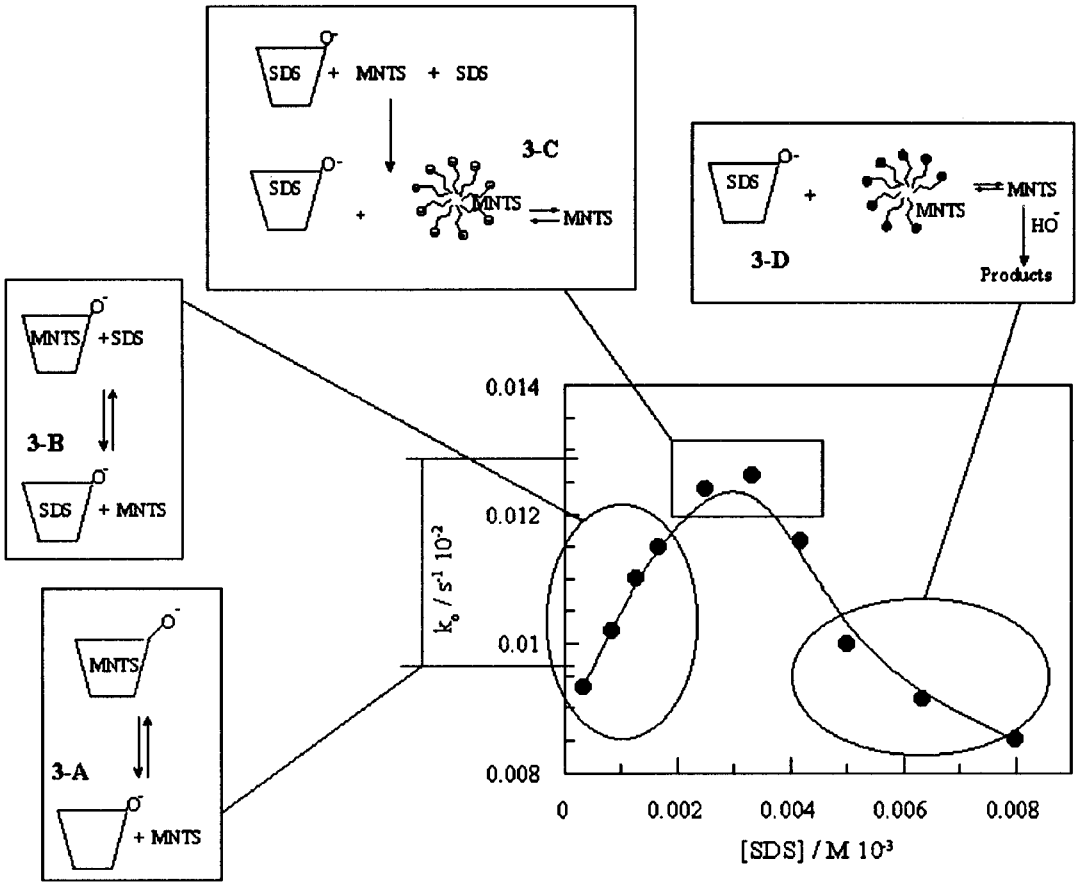


constant for formation of MNTS−CD complexes, will be used in what follows.

Basic Hydrolysis of MNTS in β-Cyclodextrin/SDS Mixtures. In the absence of cyclodextrin, micelles of the anionic surfactant SDS inhibit the basic hydrolysis of MNTS because attacking OH^- ions cannot approach MNTS borne by the negatively charged micelles.[15] In this work, the influence of SDS concentration on k_0 in the presence of CD was determined by varying [SDS] between the premicellization value of 3.33×10^{-4} M and the postmicellization value of 0.25 M in series of experiments in which CD concentration was fixed at 1.35×10^{-3}, 2.25×10^{-3}, 4.50×10^{-3}, or 9.00×10^{-3} M. In each series (Figure 2 shows the results of two of them), k_0 increased with [SDS] until reaching a peak, after which it fell as it does in the absence of cyclodextrin. Increasing CD concentration decreased the peak value of k_0 and increased the SDS concentration at which it occurred.

Substrate complexation in surfactant−CD mixed systems seems to depend strongly upon substrate size.[16] Therefore,

SCHEME 3



pyrene and naphthalene complexation with β-CD in the presence of surfactants shows different behavior. Pyrene size is excessive to totally accommodate itself in the β-CD cavity. In this way, its association constant is considerably smaller than naphthalene's (44 and 850 M^{-1} respectively). Surfactant−CD complexation excludes water molecules originally in the CD cavity that become more hydrophobic. This hydrophobicity increase due to surfactant complexation must be responsible for the increase of pyrene complexation constant with CD in presence of surfactant. Naphthalene shows an opposite behavior: i.e. the complexation constant with CD decreases steeply in the presence of surfactant. Naphthalene size allows us to predict that it will be totally incorporated to the CD cavity. Then surfactant complexation with CD causes an unfavorable situation for the inclusion of naphthalene in its cavity as was reported by Hashimoto and Thomas.[16]

In our case MNTS size makes likely its accommodation inside the CD cavity, and so surfactant presence will show an effect on MNTS complexation qualitatively similar to that of naphthalene.

According to these ideas the experimental behavior observed can be explained qualitatively considering the different complexation/micellization simultaneous processes. The pseudo first order rate constant (k_0) extrapolated to zero concentration of surfactant is significantly lower than that observed in pure water (see Scheme 3A). This behavior is due to the association between MNTS and CD. This association decreases the reactive MNTS concentration present in aqueous medium. Thus k_0 values for each CD concentration correspond to the values obtained in the previous section for experiments in the absence of SDS.

For small SDS concentrations (before the micellization), SDS addition to the reaction medium produces complexation of SDS monomers with CD (SDS-CD), with displacement of MNTS to the aqueous medium (see Scheme 3B), thereby increasing reactive [MNTS] and hence k_0 until the concentration of uncomplexed SDS (SDS_{mon}) is high enough for SDS micelles to form.

In view of the well-known behavior of surfactants in the absence of other additives, it may be assumed that [SDS_{mon}] remains constant when total SDS concentration is increased beyond the point at which micelles begin to form. In view of that, free cyclodextrin concentration ([CD_f]) and [SDS-CD] will therefore also have been constant above the micellization point under the experimental conditions used in this work, because the MNTS concentration was much too low for MNTS-CD to constitute a CD reservoir comparable with the variation in [SDS]. Once the micellization process starts, a competition between two phenomena is established: SDS-CD complexation with the corresponding MNTS expulsion to aqueous media that increases k_0 and, on the other hand, MNTS association to the micelles. As it is an anionic micelle, simple electrostatic considerations let us exclude the presence of HO^- at the micellar surface. The effect of MNTS association to the micelle is reflected as a decrease in concentration of reactive MNTS (MNTS concentration in aqueous medium) and consequently slower reaction rate (see Scheme 3C).

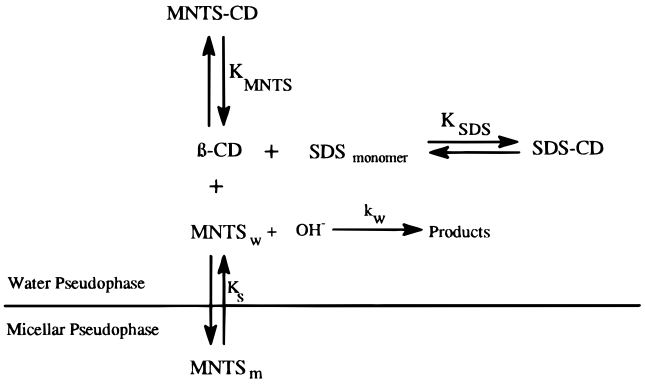
Above the micellization point, all variation in k_0 is due exclusively to increasing association of MNTS with SDS micelles (see Scheme 3D), and we may therefore identify the SDS concentration at which k_0 peaks as the point at which micellization begins and define this value of [SDS] as the [CD]-dependent critical micellization concentration, cmc_{app}. Note that, above the micellization point, just as the conventional cmc of a surfactant solution with no other additives satisfies the equation $[SDS]_T = [D_n] + cmc$ ($[D_n]$ being the micellized surfactant

TABLE 1: Results of Fitting Equation 8 to Experimental Data for the Basic Hydrolysis of MNTS in β-Cyclodextrin/SDS Mixtures[a]

[CD]/M	cmc_{app}/M	$[CD]_f$/M	cmc_{real}/M	K_s/M^{-1}	$k_w/M^{-1}\,s^{-1}$
0[b]			1.00×10^{-3}	108	8.36×10^{-2}
1.35×10^{-3}	1.80×10^{-3}	2.12×10^{-4}	6.62×10^{-4}	88 ± 13	$(7.7 \pm 0.2) \times 10^{-2}$
2.25×10^{-3}	2.46×10^{-3}	3.02×10^{-4}	5.15×10^{-4}	103 ± 6	$(7.89 \pm 0.08) \times 10^{-2}$
4.50×10^{-3}	4.00×10^{-3}	9.47×10^{-4}	4.74×10^{-4}	96 ± 8	$(8.0 \pm 0.1) \times 10^{-2}$
9.00×10^{-3}	7.00×10^{-3}	2.32×10^{-3}	3.20×10^{-4}	78 ± 10	$(8.6 \pm 0.2) \times 10^{-2}$

[a] $K_{SDS} = 8000 \pm 500\ M^{-1}$. $K_{MNTS} = 226\ M^{-1}$. [b] Taken from ref 15a; k_w value was obtained in 12% (v/v) ethanol−water mixtures.

SCHEME 4



concentration), so cmc_{app} satisfies the equation $[SDS]_T = [D_n] + cmc_{app}$; this follows that at the micellization point $cmc_{app} = [SDS] = [SDS\text{-}CD] + [SDS_{mon}]$ and the fact that [SDS-CD] and $[SDS_{mon}]$ are constant when [SDS] is varied above the micellization point (when $[SDS_{mon}] = cmc_{real}$).

The above behavior may be explained on the basis of the pseudophase model shown in Scheme 4, in which distribution of the reagents in the two pseudophases (aqueous and micellar) is considered. The global reaction rate is assumed to be exclusively the reaction at the aqueous pseudophase due to electrostatic considerations (eq 3)

$$r = k_w[HO^-]_w[MNTS]_w \tag{3}$$

According to Scheme 4, total CD concentration can be expressed as

$$[CD]_T = [CD_f] + [MNTS{-}CD] + [SDS{-}CD] \tag{4}$$

and the total surfactant concentration can be expressed as the sum of free SDS monomers, SDS-CD complex, and micellized surfactant.

$$[SDS]_T = [SDS_{mon}] + [SDS{-}CD] + [D_n] \tag{5}$$

In the same way, the total MNTS concentration will be given by the sum of MNTS concentration in the aqueous pseudophase ($[MNTS]_w$), MNTS−CD complex concentration, and MNTS concentration in the micellar pseudophase ($[MNTS]_m$).

$$[MNTS]_T = [MNTS]_w + [MNTS{-}CD] + [MNTS]_m \tag{6}$$

As is usually assumed for the micellar systems, the concentration of micellized surfactant was taken as total surfactant concentration minus cmc_{app}. In the presence of CD, the cmc_{app} will be the concentration of free monomers plus [SDS−CD]. The use of conventional definitions for K_{SDS}, K_s, and K_{MNTS}

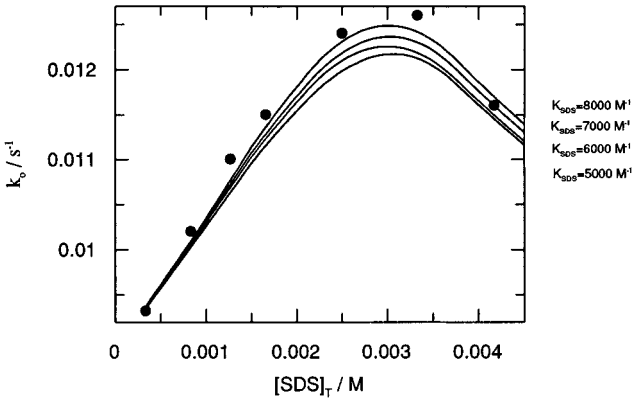


Figure 3. Results of fitting eq 8 to the experimental k_0-[SDS] data for $[CD] = 2.25 \times 10^{-3}$ M using the optimal $cmc_{[CD]}$ and various different tentative values of K_{SDS} (8000, 7000, 6000, and 5000 M^{-1}).

$$K_{SDS} = \frac{[SDS{-}CD]}{[SDS_{mon}][CD_f]} \qquad K_{MNTS} = \frac{[MNTS{-}CD]}{[MNTS]_w[CD_f]}$$

$$K_s = \frac{[MNTS]_m}{[MNTS]_w[D_n]} \tag{7}$$

allows the following expression for the pseudo first order rate constant as a function of the free CD and micellized surfactant concentrations ($[D_n]$):

$$k_0 = \frac{k_w[HO^-]}{1 + K_{MNTS}[CD_f] + K_s[D_n]} \tag{8}$$

The free CD concentration can be obtained as a function of total CD concentration, total surfactant concentration, and total MNTS concentration, from the following third-order equation:

$$\alpha[CD_f]^3 + \beta[CD_f]^2 + \gamma[CD_f] - [CD]_T = 0 \tag{9}$$

where

$$\alpha = K_{SDS}K_{MNTS} \tag{10}$$

$$\beta = \{K_{SDS} + K_{MNTS} + K_{MNTS}K_{SDS}([SDS]_T - [CD]_T + [MNTS]_T)\} \tag{11}$$

$$\gamma = \{1 + K_{SDS}([SDS]_T - [CD]_T) + K_{SDS}([MNTS]_T - [CD]_T)\} \tag{12}$$

The validity of Scheme 4 was tested by fitting eq 8 to the experimental k_0-[SDS] data by means of a two-tier optimization process in which the optimized variables were cmc_{app}, K_{SDS} (published values of which differ widely), and k_w and K_s (comparison of whose optimized values with published values served as a test of the quality of the fit); for K_{MNTS}, the value $226 \pm 9\ M^{-1}$ obtained in the previous section was used. For each of a number of systematically varied pairs (cmc_{app}, K_{SDS}) (cmc_{app} was stepped by 5×10^{-5} M and K_{SDS} by 500 M^{-1}), eq

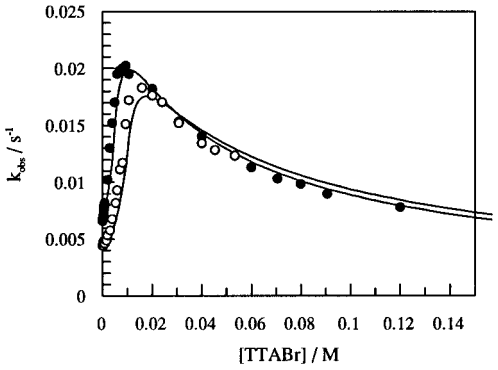


Figure 4. Influence of [TTABr] on k_0, the first-order pseudoconstant for basic hydrolysis of MNTS, in the presence of CD concentrations of 3.60×10^{-3} M (●) and 9.00×10^{-3} M (○). Curves are the results of fitting eq 13 to the experimental data as described in the text.

9 was solved for [SDS] values between 0 and cmc_{app}, and the resulting values of $[CD_f]$ were used to fit eq 8 to the experimental data by standard optimization of k_w and K_s (in all cases, eq 9 had exactly one real root, which as required lay between 0 and [CD]). The (cmc_{app}, K_{SDS}) pair for which optimization of k_w and K_s afforded the least root-mean-square deviation from the experimental data was taken as optimal.

The results are listed in Table 1 and for $[CD] = 2.25 \times 10^{-3}$ and 9.00×10^{-3} M are shown as curves in Figure 2. For $[CD] = 2.25 \times 10^{-3}$ M, Figure 3 compares, for the optimal value of cmc_{app}, the behavior of curves fitted with optimal and suboptimal values of K_{SDS} in the neighborhood of the micellization point; varying cmc_{app} for fixed K_{SDS} shifts the fitted curves horizontally and is accordingly harder to evaluate visually.

The optimized values of k_w and K_s are essentially independent of [CD] and agree satisfactorily with the values obtained in the absence of CD, $k_w = 7.99 \times 10^{-2}$ M^{-1} s^{-1} and $K_s = 108$ M^{-1} respectively.[15d] This supports the model and, in particular, the assumption that the properties of the SDS micelles themselves are not affected by the presence of CD in the medium. The model is further supported by the finding that for all CD concentrations the optimized value of K_{SDS} was the same, 8000 M^{-1}. This value is within the range of published values, but then this range is so very broad (210−25600 M^{-1})[5a,c,d,6a,7b,17] that this is hardly an accreditation. It seems likely that part of the reason for the great variation in published values of K_{SDS} must have been failure to treat the micellization and CD complexation processes as competitive at SDS concentrations above the micellization point; the generally used assumption that CD becomes saturated before micellization starts clearly contradicts the appreciable values of $[CD_f]_{min}$ calculated in this work (Table 1).

The cmc_{app} values obtained for different CD concentrations are in every case inferior to the SDS critical micellar concentration in the absence of CD (8.1×10^{-3} M). In our experiments the presence of a high concentration of HO^- will produce a lower cmc values of SDS as is well-known in the literature.[15] To sum up, the presence[18] of CD, as well as other organic molecules,[19] induces ionic surfactant aggregation beneath the cmc.

Basic Hydrolysis of MNTS in β-Cyclodextrin/TTABr Mixtures. In this work, the influence of TTABr concentration on k_0 in the presence of CD was determined by varying [TTABr], usually between the premicellization value of 3.33×10^{-5} M and the postmicellization value of 0.12 M, in a series of experiments in which CD concentration was fixed at 3.60×10^{-3}, 4.99×10^{-3}, 6.75×10^{-3}, or 9.00×10^{-3} M. In each series (Figure 4 shows the results of two of them), k_0 exhibited the same kind of [TTABr] dependence as in the absence of CD,[11a] increasing rapidly with [TTABr] until reaching a peak and falling gradually thereafter.

SCHEME 5

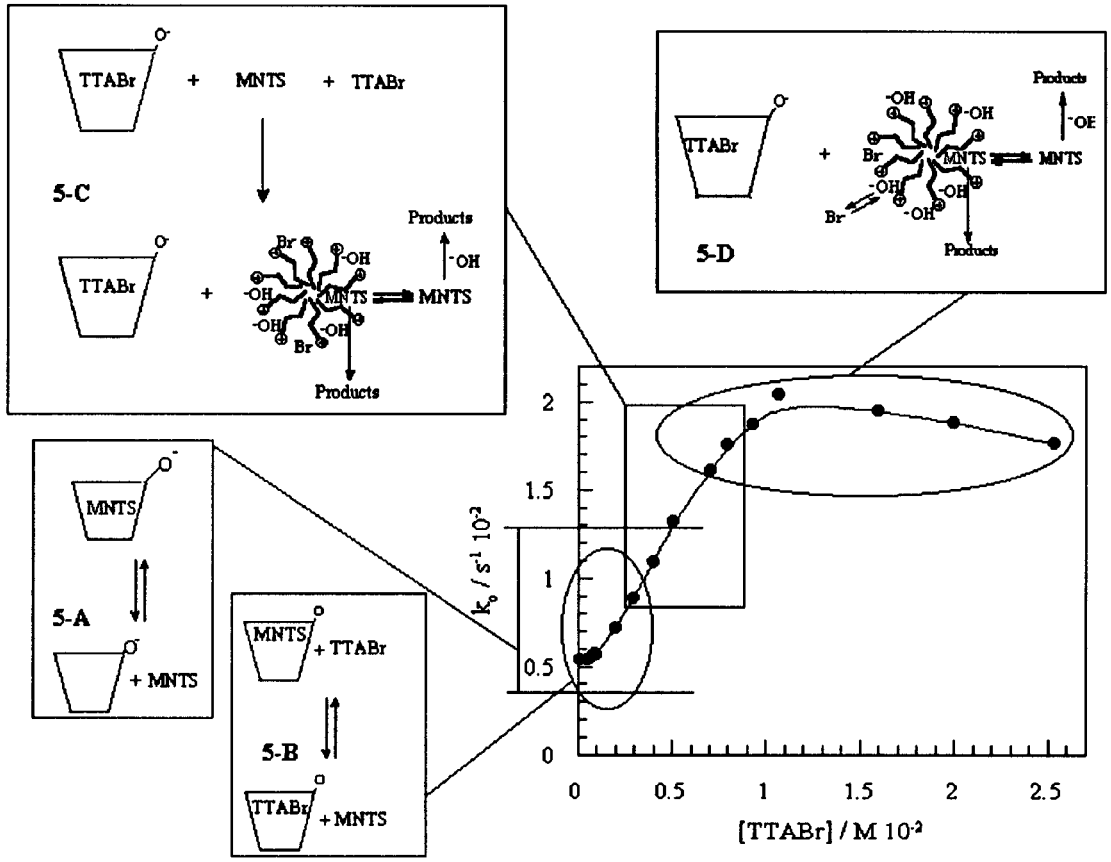
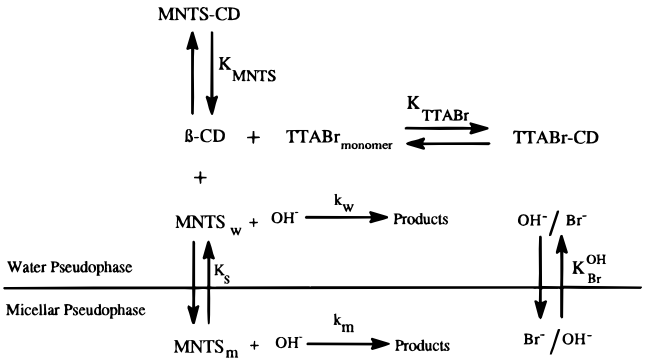


TABLE 2: Results of Fitting Equation 13 to Experimental Data for the Basic Hydrolysis of MNTS in β-Cyclodextrin/TTABr Mixtures[a]

[CD]/M	cmc_{app}/M	$[CD]_f$/M	cmc_{real}/M	K_s/M^{-1}	$k_w/M^{-1}\ s^{-1}$	$k_2^m/M^{-1}\ s^{-1}$
0[b]			1.2×10^{-3}	218	8.36×10^{-2}	1.09×10^{-2}
3.60×10^{-3}	4.00×10^{-3}	1.91×10^{-4}	5.91×10^{-4}	218	7.10×10^{-2}	9.70×10^{-3}
4.99×10^{-3}	5.25×10^{-3}	2.84×10^{-4}	5.44×10^{-4}	218	7.10×10^{-2}	1.03×10^{-2}
6.75×10^{-3}	7.25×10^{-3}	2.76×10^{-4}	7.76×10^{-4}	218	7.50×10^{-2}	1.04×10^{-2}
9.00×10^{-3}	9.50×10^{-3}	3.40×10^{-4}	8.4×10^{-4}	218	8.50×10^{-2}	1.05×10^{-2}

[a] $K_{TTABr} = 30000 \pm 1000\ M^{-1}$. $K_{MNTS} = 226\ M^{-1}$. [b] Taken from ref 15a; k_w value was obtained in 12% (v/v) ethanol−water mixtures.

SCHEME 6



Experimental results can be explained qualitatively as shown in Scheme 5. The k_0 value extrapolated to zero concentration of TTABr decreases when CD concentration increases. This effect is attributed to MNTS complexation with CD in the absence of surfactant as was proposed previously for SDS−CD systems (see Scheme 5A). This complexation will cause a decrease in the free MNTS concentration in the aqueous medium with a following decrease in the reaction rate.

The catalytic effect observed when [TTABr] increases depends on CD concentration. Higher CD concentrations yield bigger catalytic effects. This catalytic process is explained by the means of the existence of two simultaneous processes. First the TTABr monomer complexation with CD expels MNTS from the MNTS−CD complex, transforming it into reactive MNTS (see Scheme 5B). When the TTABr concentration increases, micellization will start, and therefore the catalytic effect of TTABr micelles in basic hydrolysis will be added to the former (see Scheme 5C).

In the presence of TTABr micelles, MNTS will be distributed between the aqueous and micellar pseudophases. In this case, as it is a cationic micelle, HO^- will be present at the micellar surface. The global reaction rate will be the sum of the aqueous and micellar pseudophases rates. The reaction rate will go through a maximum when TTABr concentration is increased. The existence of this maximum is justified on the basis of two effects associated in the pseudophase model with ionic interchange. The addition of TTABr increases the relative concentrations of MNTS and HO^- in the Stern layer (see Scheme 5C), which gives as a result an increase in the reaction rate. When the surfactant concentration goes on increasing, Br^- ions are added to the medium. These are nonreactive counterions. They compete with HO^- ion in the Stern layer inhibiting the reaction (see Scheme 5D). The relative contribution of these two associated factors gives rise to the experimental maximum.

The above behavior may be explained quantitatively in terms of the pseudophase ion exchange model illustrated diagrammatically in Scheme 6, which in addition to processes analogous to those of Scheme 4 includes the micellar phase reaction and an ion exchange equilibrium between OH^- and Br^- ions in the aqueous and micellar pseudophases.

Scheme 6 implies that k_0 is given by

$$k_0 = \frac{k_w[HO^-] + (k_m K_s - k_w) m_{OH}[D_n]}{1 + K_{MNTS}[CD_f] + K_s[D_n]} \qquad (13)$$

where the rate constants, k_m and k_w, refer to the micellar and aqueous pseudophases respectively. They are related to the pseudo first order rate constants, k_m' and k_w', as usual for micellar systems (eq 14).

$$k_w' = k_w[HO^-]_w \qquad k_m' = \frac{k_m[HO^-]_m}{[D_n]}$$

$$m_{OH} = \frac{[HO^-]_m}{[D_n]} \qquad (14)$$

The application of the ionic interchange model allows us to obtain the following expression for m_{OH}

$$m_{OH}^2 - m_{OH}\left[\frac{[HO^-]_T + K_{Br}^{HO}[Br^-]_T}{(K_{Br}^{HO} - 1)[D_n]} - \beta\right] - \left[\frac{\beta[HO^-]_T}{(K_{Br}^{HO} - 1)[D_n]}\right] = 0 \qquad (15)$$

where β is the fraction of micellar charge that is neutralized by counterions. Conductimetric measurements carried out using Hoffmann's method[20] on TTABr/CD and SDS/CD mixtures showed that in all these systems the value of β was very close to its usual value in the absence of CD, $\beta \cong 0.8$.

Equation 13 was fitted to the experimental data in essentially the same way as described in the previous section for eq 8, except that (a) the variables optimized for each (cmc_{app}, K_{TTABr}) pair were k_w and k_m; (b) the value of m_{OH} was obtained for each value of [TTABr] by solving eq 15 with $K_{Br}^{OH} = 23$ (the value obtained in the absence of CD);[15] (c) in view of the earlier finding that CD did not alter the equilibrium constant for association of MNTS with SDS micelles (see previous section), K_s was fixed at the value obtained in the absence of CD, 218 M^{-1}.[15b] The results are listed in Table 2 and, for [CD] = 3.60×10^{-3} and 9.00×10^{-3} M, are plotted as solid curves in Figure 4.

In keeping with the model, the optimized values of K_{TTABr}, k_w, and k_m were essentially the same for all CD concentrations. The values of k_w and k_m were in keeping with those obtained in the absence of CD, and K_{TTABr} was within the range of previously reported values, 9610−44000,[5d,10] although, as in the case of K_{SDS}, this range is so very wide that it affords little support for the value found in this work. As in the case of SDS/CD systems, increasing [CD] increases cmc_{app} and there is always an appreciable concentration of uncomplexed CD, but CD appears to have no influence on the properties of the micelles themselves, once they have formed.

Conclusions

Investigation of the kinetics of the basic hydrolysis of MNTS in aqueous mixtures of cyclodextrin and surfactant has shed

light on the influence of cyclodextrin on the behavior of the surfactant. Cyclodextrin has no effect on the properties of surfactant micelles once these have formed (in particular, it does not alter β, k_m, or K_s, the partition constant governing the distribution of MNTS between the aqueous and micellar pseudophases), but it increases the total surfactant concentration at which micelles begin to form (cmc_{app}) and reduces $[surf_{mon}]_{max}$ (cmc_{real}), the concentration of surfactant that remains in monomer form at total surfactant concentrations greater than cmc_{app}. The increase in cmc_{app} with [CD] is due to complexation of surfactant by cyclodextrin, which reduces the concentration of surfactant that is free to form micelles. The reduction in cmc_{real} is unexplained but agrees with previous reports of the effects of CD[18] and other organic molecules[19] on micellization.

At total surfactant concentrations higher than cmc_{app}, competition between the micellization and complexation processes results in the presence of an appreciable concentration of uncomplexed cyclodextrin, which is the same for all total surfactant concentrations above cmc_{app}. Traditionally, surfactant−CD complexation constant values have been obtained from changes in cmc_{app} caused by the presence of CD. These methods would be useless due to the existence in the solution of a significant amount of noncomplexed CD. The difference between cmc_{app} and total CD concentration does not show the monomer concentration present in the medium (cmc_{real}). In fact, evidence was reported in the literature about cmc_{app} values lower than the total CD concentration.[21] The results in Tables 1 and 2 show that free monomer concentration in equilibrium (cmc_{real}) depends on CD, in agreement with recent results[18] that report evidence that the presence of CD induces surfactant aggregation under the cmc.

Acknowledgment. Financial support from Xunta de Galicia (project XUGA 20906B93) and from the Dirección General de Investigación Científica y Técnica of Spain (project PB93-0524) is gratefully acknowledged.

References and Notes

(1) (a) Bender, M.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1978. (b) Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 344. (c) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.

(2) (a) Sanemasa, I.; Akamine, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2059. (b) Fujiki, M.; Deguchi, T; Sanemasa, I. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1163. (c) Sanemasa, I.; Takuma, T.; Deguchi, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3102.

(3) Tee, O. S. *Adv. Phys. Org. Chem.* **1994**, *29*, 1.

(4) Jezequel, D.; Mayaffre, A. Letellier, P. *Can. J. Chem.* **1991**, *69*, 1865.

(5) (a) Okubo, T.; Kitano, H.; Ise, N. *J. Phys. Chem.* **1976**, *80*, 2661. (b) Satake, I.; Ikenoue, T.; Takeshita, T.; Hayakawa, K.; Maeda, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2746. (c) Satake, I.; Yoshida, S.; Hayakawa, K.; Maeda, T.; Kusumoto, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3991. (d) Palepu, R.; Reinsborough, V. C. *Can. J. Chem.* **1988**, *66*, 325. (e) Palepu, R.; Reinsborough, V. C. *Can. J. Chem.* **1989**, *67*, 1550.

(6) (a) Park, J. W.; Song, H. J. *J. Phys. Chem.* **1989**, 93, 6454. (b) Park, J. W.; Choi, N. H.; Kim, J. H. *J. Phys. Chem.* **1996**, *100*, 769.

(7) (a) Diaz, A.; Quintela, P. A.; Schuette, J. M.; Kaifer, A. E. *J. Phys. Chem.* **1988**, *92*, 3537. (b) Dharmawardana, U. R.; Christian, S. D.; Tucker, E. E.; Taylor, R. W.; Scamehorn, J. F. *Langmuir* **1993**, *9*, 2258.

(8) (a) Junquera, E.; Aicart, E.; Tardajos, G. *J. Phys. Chem.* **1992**, *96*, 4533. (b) Junquera, E.; Tardajos, G.; Aicart, E. *J. Phys. Chem.* **1993**, *97*, 1243. (c) Junquera, E.; Tardajos, G.; Aicart, E. *Langmuir* **1993**, *9*, 1213.

(9) Hersey, A.; Robinson, B. H.; Kelly, H. C. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1271.

(10) Mwakibete, H.; Cristantino, R.; Bloor, D. M.; Wyn-Jones, W.; Holzwarth, J. F. *Langmuir* **1995**, *11*, 57 and references therein.

(11) (a) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213. (b) Cordes, E. H. *Pure Appl. Chem.* **1978**, *50*, 617.

(12) (a) Romsted, L. S. *Surfactants in Solution*; Lindman, B., Mittal, K. L., Eds.; Plenum Press: New York, 1984; Vol. 2. (b) Romsted, L. S. *J. Phys. Chem.* **1985**, *89*, 5107, 5113.

(13) (a) Bunton, C. A.; Romsted, L. S.; Sepulveda, L. *J. Phys. Chem.* **1980**, *84*, 2611. (b) Al-Lohedan, H.; Bunton, C. A.; Romsted, L. S. *J. Phys. Chem.* **1981**, *85*, 2123 and references therein.

(14) Castro, A.; Leis, J. R.; Peña, M. E. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1861.

(15) (a) Castro, A.; Leis, J. R.; Peña, M. E. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1221. (b) Bravo, C.; Hervés, P.; Leis, J. R.; Peña, M. E. *J. Phys. Chem.* **1990**, *94*, 8816. (c) Bravo, C.; Leis, J. R.; Peña, M. E. *J. Phys. Chem.* **1992**, *96*, 1957. (d) García-Río, L.; Iglesias, E.; Leis, J. R.; Peña, M. E. *J. Phys. Chem.* **1992**, *96*, 7821.

(16) Hashimoto, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 4655.

(17) (a) Wan Yunus, W. M. Z.; Taylor, J.; Bloor, D. M.; Hall, D. G.; Wyn-Jones, E. *J. Phys. Chem.* **1992**, *96*, 8979. (b) Sasaki, K. J.; Cristian, S. D.; Tucker, E. E. *J. Colloid Interface Sci.* **1990**, *134*, 412. (c) Funasaki, N.; Yodo, H.; Hada, S.; Neya, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1323 (and references therein).

(18) Jiang, Y. B.; Wang, X. *J. Appl. Spectrosc.* **1994**, *48*, 1428.

(19) (a) Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, 1987; Vol. 1. (b) Schwuger, M. *Ber. Bunsen.-Ges. Phys. Chem.* **1971**, *75*, 167.

(20) Hoffmann, H.; Ulbricht, W. *Z. Phys. Chem. (Munich)* **1977**, *106*, 107.

(21) Aman, E. S.; Serve, D. *J. Colloid Interface Sci.* **1990**, *138*, 365.