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Basic Hydrolysis of Crystal Violet in β-Cyclodextrin/ Surfactant Mixed Systems

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The basic hydrolysis of crystal violet (CV) in mixed systems consisting of β-cyclodextrin (β-CD) and a micelle-forming surfactant, cetyltrimethylammonium chloride (CTACl), has been studied. β-CD was found to catalyze the basic hydrolysis of CV through the interaction of its hydroxyl group, in its deprotonated form, with the carbocation in the complexed substrate. The addition of small amounts of CTACl, with [CTACl] below the critical micelle concentration, to β-CD solutions does not have an effect upon the observed rate constant for the basic hydrolysis of CV. This behavior is different from that observed for the alkaline hydrolysis of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and nitrophenyl acetates in mixed β-CD/cationic surfactant systems. The proposed mechanism allows us to explain the experimental results on the basis of the high percentage of uncomplexed β-CD in equilibrium with the micellar system, the low CV concentration, and the high value for the binding constant of CV by β-CD.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of several glucose units linked by α-1,4 glycoside bonds.[1] These systems possess a toroidal or hollow, truncated cone shape with a nonpolar, hydrophobic interior and two hydrophilic rims formed by the primary and secondary OH groups (narrower and wider rim, respectively). By virtue of their unusual structure, CDs can form inclusion complexes through noncovalent interactions with molecules of specific size, shape, and polarity.[2] The ability of these systems to modulate reactivity depends on their capacity to complex organic substances. Changes in physicochemical properties and reactivities result from such host−guest interactions.[3] The effects that the formation of inclusion complexes have on reactivity vary widely depending on the guest, the CD, and the reaction. In some cases, the reaction rate is greatly reduced, which has led to the use of CDs as stabilizers; but of more interest are the situations in which CDs accelerate reactions. Moreover, the CDs may even participate directly in the reaction.[4]

The addition of a cyclodextrin to a micellar system alters its physicochemical properties because the oligosaccharide complexes with surfactant monomers.[5] Complex formation increases the concentration of surfactant required for micellization.[6] This situation means that the critical micelle concentration of a micellar system in the presence of a cyclodextrin is equivalent to the combined concentrations of surfactant monomers complexed to the CD and of free dissolved monomer in equilibrium with the micellized surfactant. As a result, if the stoichiometry of the complex is 1:1,[7] the critical micelle concentration (cmc) of a micellar system in the presence of a CD (cmc_{app}) will be $cmc_{app} = [surfactant_{monomer}{\cdot}CD] + cmc_{real}$.[8] Our group has developed a kinetic model that accounts for reactivity in mixed surfactant−CD systems.[9] The kinetic model is a combination of the traditional pseudophase model including ion exchange and a competitive binding model for the CD-catalyzed reaction.

In the work described here, we carried out a study of the basic hydrolysis of crystal violet (see Scheme 1) in mixed systems containing β-CDs and cetyltrimethylammonium chloride (CTACl). The hydrolysis of this carbonium ion and its reactivity in general are of high physicochemical interest since it was used, together with similar cations, to establish Ritchie's N_+ nucleophilic

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Scheme 1

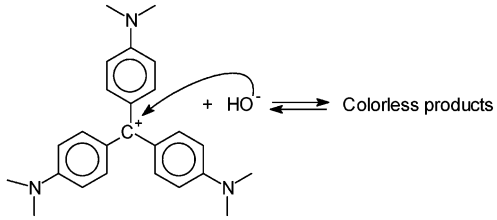

Table 1. ^{1}H NMR Chemical Shifts for β-CD and for the β-CD−CV Complex at 298 K

	δ/ppm			δ/ppm	
proton	β-CD	β-CD−CV complex	proton	β-CD	β-CD−CV complex
H-1	4.90	4.95	H-4	3.41	3.46
H-2	3.49	3.53	H-5	3.56	3.7−3.8
H-3	3.65	3.84	H-6$_{a,b}$	3.71	3.7−3.8

index.[10] In fact, the alkaline fading of stable triarylmethyl carbocations is a reaction with a long chemical tradition. The rate for the process, despite it being a cation/anion combination, is sufficiently slow for a conventional kinetic study. For this reason, the reaction has become a popular one in the undergraduate laboratory.[11] This reaction has also become useful for studying chemical reactivity in organized media. One of the first studies on micellar catalysis and inhibition[12] referred to the alkaline fading of crystal violet (CV), and these reactions have since been used many times for studies in normal micelles,[13] micelles in the presence of additives,[14] reverse micelles or microemulsions,[15] and clusters.[16]

We studied the basic hydrolysis of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide[9a] (MNTS) and nitrophenyl -acetates[8,9b] (NPA) in mixed β-CD/cationic surfactant systems. MNTS complexation by β-CD decreases the rate of alkaline hydrolysis due to the formation of unreactive complexes. The addition of small concentrations of cationic surfactants, that is, TTABr (tetradecyltrimethylammonium bromide), to a β-CD solution results in an increase in the rate constant because TTABr complexation by β-CD expels MNTS in the bulk aqueous medium. Such an increase in the MNTS concentration in the bulk aqueous medium causes an increase in the observed alkaline rate constant due to destruction of the unreactive complex. On studying the basic hydrolysis of nitrophenyl acetates in mixed β-CD/cationic surfactant systems, we observed the opposite behavior. The observed alkaline rate constant decreased on adding small amounts of cationic surfactants to β-CD solutions as a result of surfactant complexation by cyclodextrin. Such surfactant complexation destroys the β-CD/NPA complex and diminishes the catalytic effect of β-CD on NPA cleavage. In the work described here, we studied the alkaline fading of crystal violet in mixed β-CD/cationic surfactant systems. On the basis of the catalytic effect of β-CD on the alkaline hydrolysis of CV, one would expect similar behavior to that observed in the cleavage of nitrophenyl acetates. However, the basic hydrolysis of CV in the presence of β-CD is not altered by the addition of small amounts of hexadecyltrimethylammonium chloride, CTACl. These experimental results, which differ from both the inhibition observed for NPA hydrolysis and the catalysis for MNTS hydrolysis, seem to indicate a third type of behavior.

Experimental Section

The surfactant (CTACl) and β-CD were supplied with the highest available purity by Sigma and used as received. The purity of the surfactant was verified by determining its critical micelle concentration as described elsewhere.[9] CD solutions were made up bearing in mind that commercial β-CD has an H_2O content of 8 mol/mol.

Cyclodextrin was deprotonated under the alkaline conditions used ([NaOH] > 0.1 M) as it has a pK_a value of 12.2.[17] All hydroxyl ion concentrations quoted in this work were obtained by subtracting the CD concentration from that of NaOH. The reaction kinetics was studied using an Applied Photophysics MX18 stopped-flow spectrophotometer. All experiments were carried out at 25.0 ± 0.1 °C. The concentration of dye (ca. 10^{-5} M) was always much lower than that of NaOH. The absorbance/time data for all kinetic experiments were fitted by first-order integrated equations, and the values of the pseudo-first-order rate constants (k_{obs}) were reproducible within 3%.

The procedure used to prepare the cetyltrimethylammonium hydroxide (CTAOH) solutions was described in a previous paper.[18] The reactive-ion cationic micelles were prepared from solutions of CTACl by ion exchange in Amberlite IRA400 anionic resin. Solutions were used shortly after preparation.

^{1}H NMR experiments were performed using a Bruker AMX 500 MHz spectrometer. The residual HDO peak was used as the internal standard referenced at 4.60 ppm. The instrument was field-locked on the deuterium resonance. To an 8 mM solution of β-CD (dried under a vacuum at 100 °C over phosphorus pentoxide overnight) in D_2O (with a 99.9% degree of deuteration supplied by CIEMAT) was added 1 equiv of CV. This sample was used for 2D-1H rotating-frame Overhauser enhancement spectroscopy (ROESY) experiments.[19] A time of 300 ms was used for the spin-lock pulse, and the HDO residual peak was suppressed by irradiation throughout the experiment.

Results and Discussion

A. Characterization of the Inclusion Complex. In an attempt to understand the kinetic behavior of alkaline fading of CV in the presence of β-CD, it is necessary to understand the nature of the inclusion complex. Experiments were carried out using ^{1}H NMR spectroscopy to compare the chemical shifts of β-CD and the β-CD−CV complex (Figure 1 and Table 1). These studies confirmed the formation of the inclusion complex and showed interactions between the aromatic ring of CV and H(3) and H(5) corresponding to the β-CD internal cavity.This situation was confirmed by the ROESY spectrum of CV with β-CD in aqueous solution at 298 K (Figure 2). ROESY experiments show interactions between the methyl groups of the guest and protons H(3) and H(5) of the CD. Analysis

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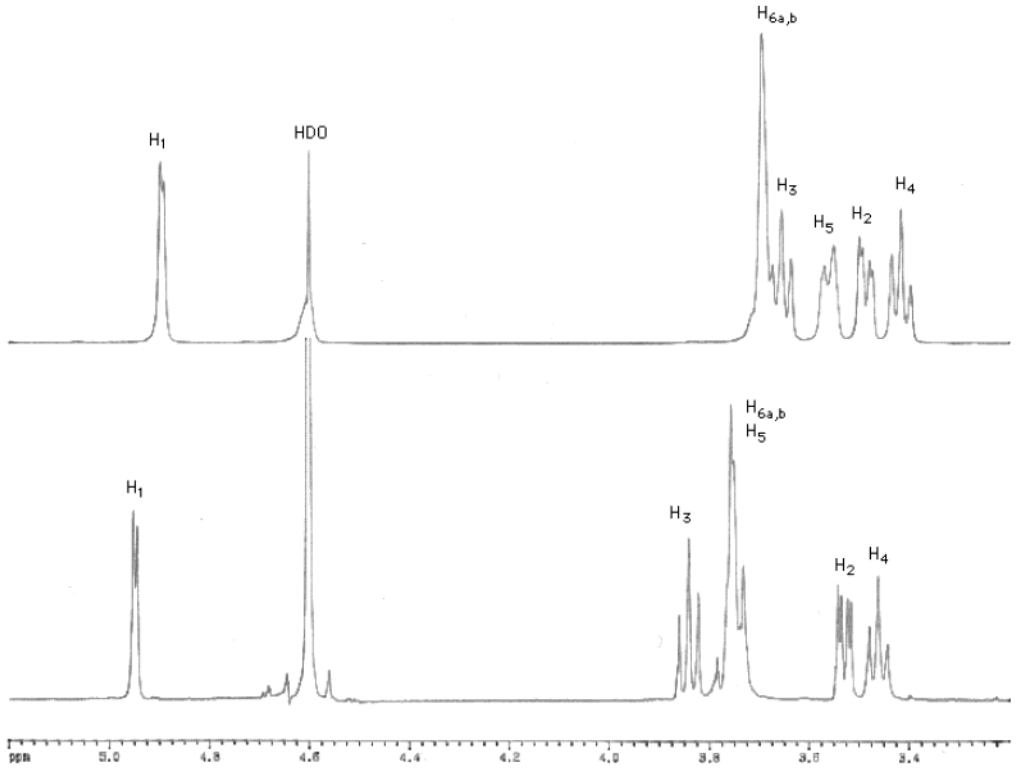
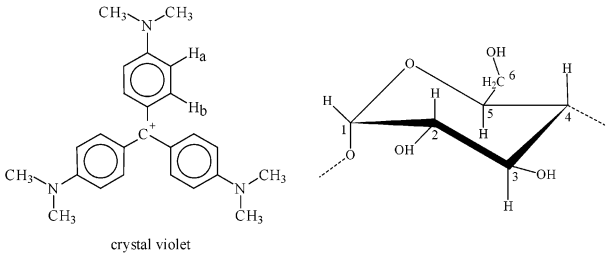


Figure 1. ^{1}H NMR spectra of β-CD (upper spectrum) and CV with β-CD (lower spectrum) in D_2O at 298 K. Proton assignments are shown in Scheme 2.

Scheme 2



of the NMR spectrum shows interactions between H_b of the CV and H(3) and H(5) of the β-CD as well as interactions between H_a and H(6) and H(5) of the host system. The existence of these interactions suggests that one guest molecule is introduced into one cyclodextrin molecule through its wide opening and one complete phenyl group is accommodated within its interior. These observations are in accordance with previous data reported in the literature[20] where NMR results are supported by theoretical calculations. This study also show evidence that the stoichiometry of the complex is 1:1.

It must be assumed that the structure of CV will determine the way in which it is included within the β-CD cavity and also the efficiency of CD catalysis. Molecular mechanics calculations were carried out to obtain the dimensions and optimal geometry of CV using the MM2 technique, and the results were compared with the host molecule cavity.[1] The energy-minimized structures are shown in Scheme 3.

B. Influence of CD on the Alkaline Fading of CV. The alkaline fading of CV in the presence of β-CD has been studied. The hydrolysis of CV was carried out by varying the [CD] in the range 0−0.013 M. Figure 3 reveals a catalytic effect of CD on this reaction. The catalysis is consistent with the possibility of nucleophilic attack by an ionized hydroxyl group of CD on the CV^+ associated with the CD. This behavior is similar to that reported in the literature (i.e., cleavage of aryl esters in the presence of CD).[21] For a substrate that undergoes an uncatalyzed reaction in a given medium and a catalyzed reaction through a 1:1 substrate/CD complex, the expected variation of the observed rate constant with CD concentration is given by eq 1.[22] This equation can be easily obtained from Scheme 4.

$$k_{obs} = \frac{k_w[HO^-] + k_{CD}K_{CV}^{CD}[CD]}{1 + K_{CV}^{CD}[CD]} \qquad (1)$$

where the rate constant k_w refers to the bulk water and k_{CD} is the catalytic rate constant of CD. K_{CV}^{CD} corresponds to the binding constant of CV to the CD: $K_{CV}^{CD} = [CV{-}CD]/[CD][CV]$ (see Scheme 4).

The K_{CV}^{CD}, k_w, and k_{CD} values obtained by fitting the data in Figure 3 to eq 1 are given in Table 2. The obtained values of k_w are in accordance with the corresponding rate constant obtained from separate experiments in pure water and are also consistent with literature values.[10b]

C. Potential Inhibitors. In an effort to shed light on the host−guest interaction process, we studied the effect of the addition of CTACl to the reaction medium. Typical results obtained for $[OH^-] = 0.1$ M with a constant ratio of [CTACl]/[β-CD] ([CTACl]/[β-CD] = 0, [CTACl]/[β-CD] = 0.5, and [CTACl]/[β-CD] = 1) and [CD] = (0−0.013) M are plotted in Figure 4. In all cases, [CTACl] was kept below the cmc_{app} value. Addition to the reaction mixture

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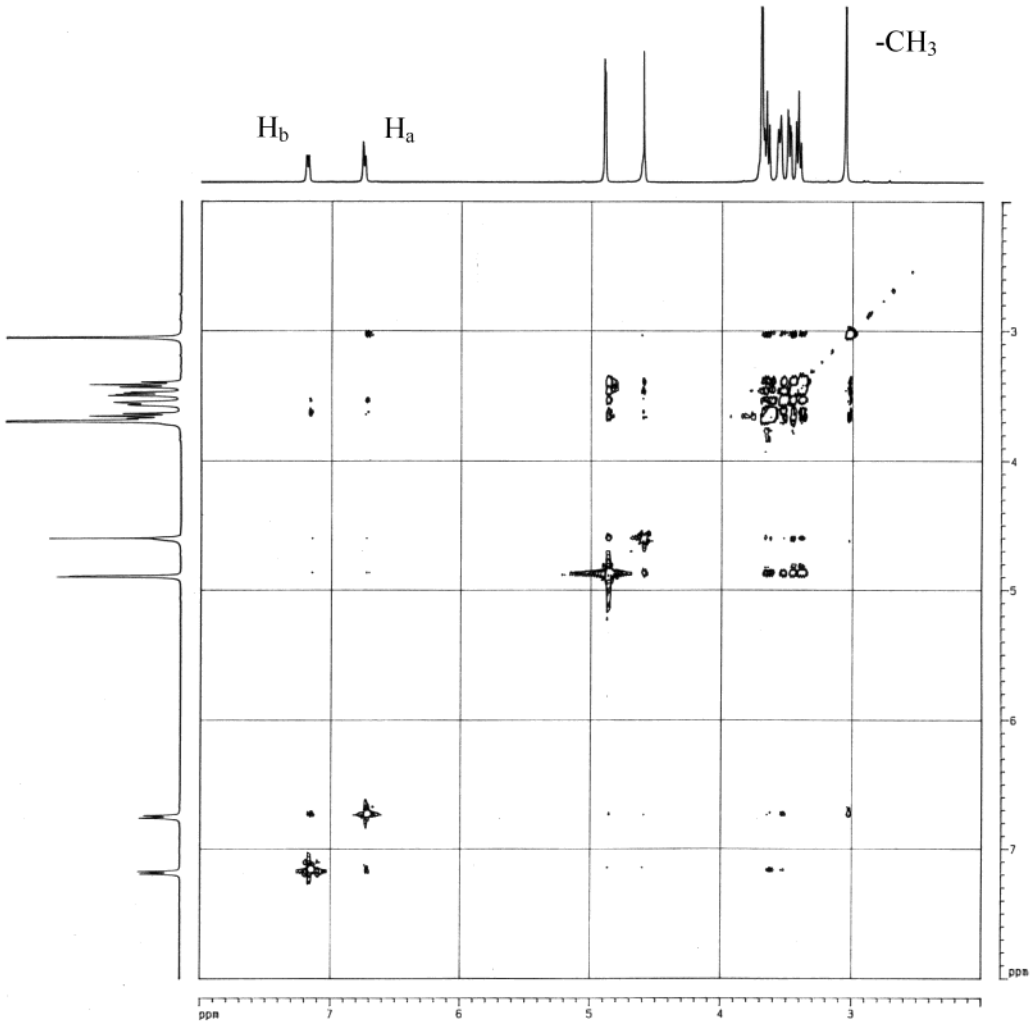
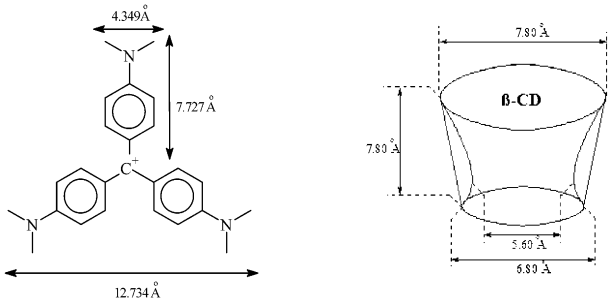


Figure 2. ^{1}H NMR spectra (ROESY) of CV with β-CD in D_2O at 298 K. Proton assignments are shown in Scheme 2.

Scheme 3



of an inert species, that is, a potential inhibitor (PI), that forms a complex with CD[8,9] reduces the concentration of free CD, and consequently, a smaller amount of CD−CV complex will be formed. Under these conditions, one might expect a decrease in the catalytic effect of CD on the alkaline fading.

Surprisingly, the addition of PI does not have any effect on k_{obs} (see Figure 4). In this case, it is clear that there are no differences between the k_{obs} values obtained in the absence of PI and in the presence of [CTACl]/[CD] = 0.5 and [CTACl]/[CD] = 1. These results agree with the fact that a large amount of free CD coexists with the PI−CD complex.[9] The influence of the surfactant chain length on the free CD concentration in equilibrium with the micellar system has recently been analyzed by our research group.[8b,c] The results of those studies did not support the

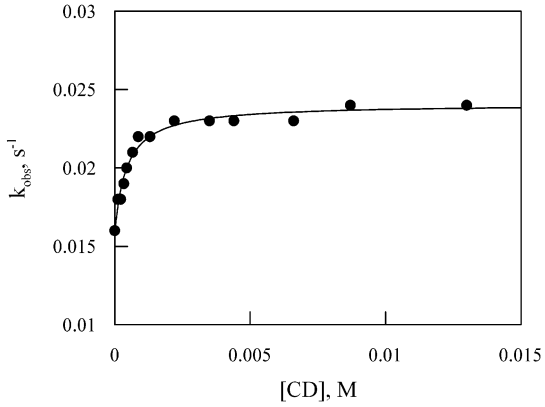


Figure 3. Influence of β-CD concentration on k_{obs} for the basic hydrolysis of crystal violet. [NaOH] = 0.10 M. The solid curve represents the fit of eq 1 to the experimental results (parameter values in Table 2).

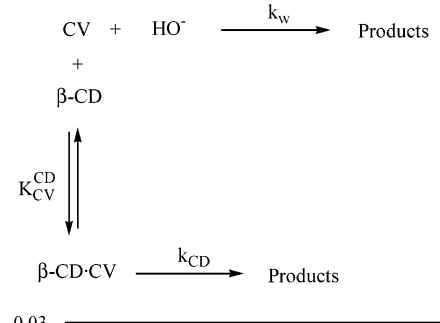
widely accepted ideas on mixed surfactant−CD systems based on the assumption that the micellization process only begins once the complexation capacity of the CD has been saturated. This assumption is not correct because such a situation would lead to the absence of uncomplexed CD in equilibrium with the micellar systems. The percentage of free CD present in equilibrium with CTACl was evaluated to be ~30%.[8c] In accordance with this result and bearing in mind the large value of K_{CV}^{CD} and the fact that [CV] ≪ $[CD]_f$, under our experimental conditions it

Table 2. Kinetic Parameters for the Basic Hydrolysis of CV in the Presence of CD and CTA Micellar Aggregates

	$k_w/M^{-1}\ s^{-1}$	k_{CD}/s^{-1}	K_{CV}^{CD}/M^{-1}
CDs	$(1.62 \pm 0.01) \times 10^{-1}$	$(2.40 \pm 0.03) \times 10^{-2}$	$(2.75 \pm 0.04) \times 10^{3}$

	[CD]/M	cmc_{app}	$k_w/M^{-1}\ s^{-1}$	k_m/s^{-1}	$k_{2,m}/M^{-1}\ s^{-1}$	K_{CV}^{m}/M^{-1}	K_{Cl}^{OH}
CTAOH		8.21×10^{-5}	1.62×10^{-1}	$(2.12 \pm 0.09) \times 10^{-1}$	2.97×10^{-2}	$(1.01 \pm 0.08) \times 10^{2}$	
CTACl		1.95×10^{-4}	1.62×10^{-1}	$(2.23 \pm 0.04) \times 10^{-1}$	3.12×10^{-2}	$(1.1 \pm 0.2) \times 10^{2}$	11.3
CTACl	3.7×10^{-5}	1.97×10^{-4}	1.62×10^{-1}	$(2.21 \pm 0.02) \times 10^{-1}$	3.10×10^{-2}	$(1.2 \pm 0.1) \times 10^{2}$	11.3
CTACl	1.30×10^{-4}	2.24×10^{-4}	1.62×10^{-1}	$(2.23 \pm 0.03) \times 10^{-1}$	3.12×10^{-2}	$(1.4 \pm 0.5) \times 10^{2}$	11.3
CTACl	3.0×10^{-4}	4.48×10^{-4}	1.62×10^{-1}	$(2.23 \pm 0.01) \times 10^{-1}$	3.12×10^{-2}	$(1.0 \pm 0.1) \times 10^{2}$	11.3
CTACl	2.3×10^{-3}	1.97×10^{-3}	1.62×10^{-1}	$(2.22 \pm 0.04) \times 10^{-1}$	3.11×10^{-2}	$(0.9 \pm 0.2) \times 10^{2}$	11.3
CTACl	5.0×10^{-3}	3.04×10^{-3}	1.62×10^{-1}	$(3.10 \pm 0.07) \times 10^{-1}$	4.34×10^{-2}	$(0.9 \pm 0.2) \times 10^{2}$	11.3
CTACl	1.0×10^{-2}	4.70×10^{-3}	1.62×10^{-1}	$(1.92 \pm 0.09) \times 10^{-1}$	2.69×10^{-2}	$(1.3 \pm 0.4) \times 10^{2}$	11.3

Scheme 4



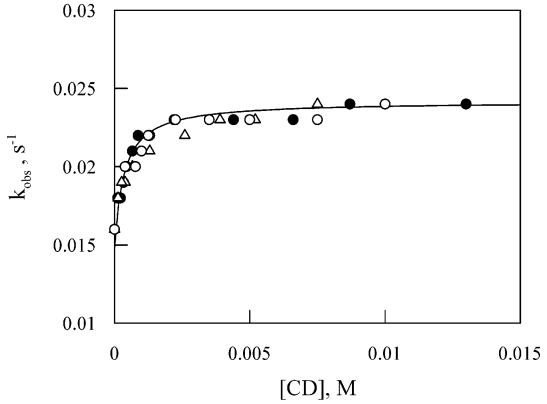


Figure 4. Influence of β-CD concentration on k_{obs} for the basic hydrolysis of crystal violet. [NaOH] = 0.10 M in the presence of CTACl as a potential inhibitor. (●) [CTACl]/[CD] = 0, (○) [CTACl]/[CD] = 0.5, and (△) [CTACl]/[CD] = 1.

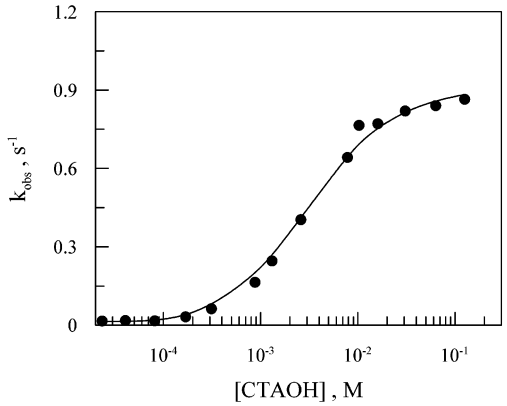
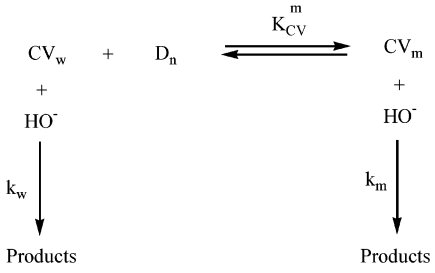


Figure 5. Influence of CTAOH concentration on k_{obs} for the basic hydrolysis of crystal violet. [NaOH] = 0.10 M. The solid curve represents the fit of eq 2 to the experimental results (parameter values in Table 2).

Scheme 5



seems that the changes in [CV−CD] are not significant and the absence of inhibition in the presence of PI should therefore be expected. The possibility of a ternary CD−PI−CV complex can be ruled out on the basis of kinetic implications.[3]

D. Influence of CTAX Micelles on the Alkaline Fading of CV. Micellar systems also have the ability to alter chemical reactivity.[23] Reaction rates and equilibria in micellar media are affected by solubilization of reactants, changes in local concentrations due to compartmentalization of reaction media, and changes in physicochemical properties of the medium.[24] The influence of micellar systems on chemical reactivity is usually analyzed in terms of the micellar pseudophase model.[25] 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 occupy the ionic positions on the micelle surface. The micellar charge fraction, β, that is neutralized by counterions remains approximately constant. This general approximation has been applied satisfactorily to determine rate and equilibrium constants in micellar systems.

In this work, we studied the influence of cetyltrimethylammonium micelles on the alkaline fading of CV. To facilitate the kinetic analysis prior to carrying out our reaction in CTACl, the basic hydrolysis of CV was studied in functionalized micelles of CTAOH. In the presence of CTAOH micelles, the rate constant increased with increasing surfactant concentration up to a limiting value (see Figure 5). This catalytic effect was a result of the reactants concentrating in the micellar pseudophase. This behavior can be analyzed in quantitative terms on the basis of the micellar pseudophase model (see Scheme 5), eq 2.

$$k_{obs} = [k_w[HO^-] + cmc\beta(k_w - K_{CV}^{m}k_m) + (k_w - k_w\beta + k_m\beta K_{CV}^{m})[D_n]]/[1 + K_{CV}^{m}[D_n]] \quad (2)$$

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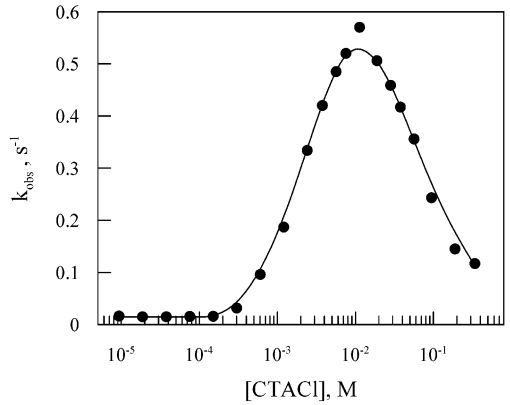


Figure 6. Influence of CTACl concentration on k_{obs} for the basic hydrolysis of crystal violet. [NaOH] = 0.10 M. The solid curve represents the fit of eqs 3 and 4 to the experimental results (parameter values in Table 2).

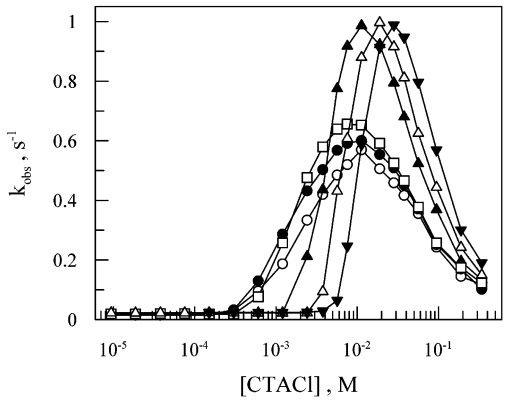


Figure 7. Influence of CTACl concentration on k_{obs} for the basic hydrolysis of crystal violet in the presence of CD. [NaOH] = 0.10 M; (○) [CD] = 0 M, (●) [CD] = 3.7×10^{-5} M, (□) [CD] = 3.0×10^{-4} M, (▲) [CD] = 2.3×10^{-3} M, (△) [CD] = 5.0×10^{-3} M, and (▼) [CD] = 1.0×10^{-2} M.

The experimental results were fitted by means of a nonlinear regression method. A value of $\beta = 0.8$ for the fraction of neutralized micellar charge was used as this is the most frequently employed value for this purpose. The value of k_w was kept constant and was equal to the value previously obtained in pure water. The binding constant of the substrate to the micelles, $K^m_{CV} = (1.01 \pm 0.08) \times 10^2$ M^{-1}, and the rate constant in the micellar pseudophase, $k_m = (2.12 \pm 0.09) \times 10^{-1}$ s^{-1}, are obtained.

On the other hand, the k_m values obtained, s^{-1}, are not strictly comparable with those pertaining to an aqueous medium, k_w (M^{-1} s^{-1}). However, on the assumption that the volume element of the reaction in the micellar phase is equal to the volume of the Stern layer, which is estimated[13c] to be $\bar{V} = 0.14$ dm^3 mol^{-1}, we can obtain a bimolecular reaction rate constant in the micellar phase as $k_{2,m} = k_m \bar{V}$ ($k_{2,m}$ with units M^{-1} s^{-1}). The obtained value, $k_{2,m} = 2.97 \times 10^{-2}$ M^{-1} s^{-1}, is smaller than that obtained in the aqueous medium, $k_w = 1.62 \times 10^{-1}$ M^{-1} s^{-1}. These values imply that the observed catalysis in micellar media is due to the concentration of reactants in the Stern layer, but micelles do not cause an increase in the intrinsic reactivity of the alkaline fading of crystal violet.

In the presence of CTACl micelles, the pseudo-first-order rate constant, k_{obs}, increases with increasing surfactant concentration up to a maximum value, beyond which it starts to decrease (see Figure 6). The existence of a maximum can be ascribed to two opposing effects in the micellar pseudophase model (as modified to include ion exchange). The addition of CTACl increases the relative concentrations of the substrate and OH^- ions in the Stern layer, thereby also increasing the reaction rate. As the surfactant concentration is increased, so is the concentration of Cl^- ions added to the medium. Chloride ions (unreactive) compete with OH^- ions in the Stern layer and inhibit the reaction. The relative contributions of these two processes result in the maximum in the experimental k_{obs} versus [CTACl] plot. Application of the micellar pseudophase formalism (Scheme 5) on the assumption of ion exchange yields eq 3 for k_{obs}.

$$k_{obs} = \frac{k_w[HO^-] + (K^m_{CV}k_m - k_w)m_{OH}[D_n]}{1 + K^m_{CV}[D_n]} \qquad (3)$$

where the rate constants k_m and k_w refer to the micellar and aqueous pseudophases, respectively. K^m_{CV} corresponds to the binding constant of CV to the micellar aggregate. β is the fraction of micellar charge that is neutralized by counterions ($\beta = 0.8$). m_{OH} denotes the $[OH^-]_m/[D_n]$ ratio, which was obtained by applying the ion exchange formalism, and satisfies the following equation:

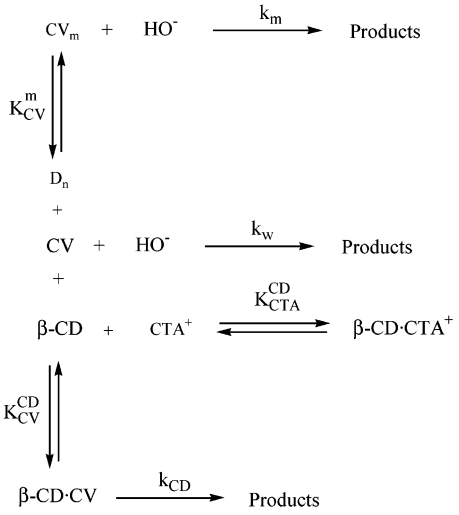
$$m_{OH}^2 + m_{OH}\left[\frac{[OH^-] + K^{OH^-}_{Cl^-}[Cl^-]}{(K^{OH^-}_{Cl^-} - 1)[D_n]} - \beta\right] - \frac{\beta[OH^-]}{(K^{OH^-}_{Cl^-} - 1)[D_n]} = 0 \qquad (4)$$

It is believed that the observed inhibition (Figure 6) is caused by Cl^- ions competing for surface sites, and for this reason, we performed a series of kinetic runs with increasing amounts of NaCl ([NaCl] = 0−0.4 M) and a fixed amount of surfactant ([CTACl] = 4.7×10^{-3} M and [CTACl] = 2.3×10^{-3} M). Inhibition was indeed observed (data not shown) and was in quantitative agreement with the pseudophase ion exchange model [eqs 3 and 4]. The calculations were performed by means of a nonlinear fitting and were carried out using cmc values calculated from the kinetic data. k_w was the experimental value in bulk water, and K^m_{CV} was obtained from fitting of kinetic data for the basic hydrolysis in the presence of CTAOH. In this way, the values of k_m and K^{OH}_{Cl} were found that best reproduce the kinetic data. From these fits, a value of $K^{OH}_{Cl} = 11.3$ was found.

Figure 6 shows the observed behavior and the satisfactory fitting of the experimental data to eqs 3 and 4. As in the previous case, we obtain a bimolecular reaction rate constant in the micellar phase as $k_{2,m} = k_m \bar{V}$ ($\bar{V}$ with units M^{-1} s^{-1}). The obtained value, $k_{2,m} = 3.12 \times 10^{-2}$ M^{-1} s^{-1}, is smaller than that found in an aqueous medium, $k_w = 1.62 \times 10^{-1}$ M^{-1} s^{-1}. This value is similar to the behavior seen for CTAOH (vide supra).

E. Influence of CTACl/CD Mixed Systems on the Alkaline Fading of CV. In the present work, the influence of the CTACl concentration on k_{obs} in the presence of CD was determined by varying [CTACl], usually between the premicellization value of 3×10^{-5} M and the postmicellization value of 0.37 M. A series of experiments were performed in which the CD concentration was fixed at 3.7×10^{-5}, 1.37×10^{-4}, 3.0×10^{-4}, 2.3×10^{-3}, 5.0×10^{-3}, and 1.0×10^{-2} M. In each series (Figure 7), k_{obs} exhibited the same kind of [CTACl] dependence as in the absence of CD, that is, increasing rapidly with [CTACl] until reaching a peak and falling gradually thereafter.

Scheme 6



Experimental results can be explained quantitatively as shown in Scheme 6. The k_{obs} value extrapolated to zero concentration of CTACl increases as the CD concentration increases. This effect is attributed to CV complexation with CD in the absence of surfactant, as proposed previously in section B. An influence of [CTACl] on k_{obs} was not observed for small surfactant concentrations ([CTACl] < cmc_{app}). This behavior is different from that observed in the alkaline hydrolysis of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and nitrophenyl acetates in β-CD/cationic surfactant mixed systems.[8,9] The absence of an influence of [CTACl] on k_{obs} is consistent with the behavior described in section C.

The catalytic effect observed when [CTACl] is increased (when [CTACl] is greater than the cmc) is typical for micellar catalysis (see section D), but the maximum rate constant depends on the CD concentration (see Figure 7). This process can be explained in terms of two independent effects present in the media: (a) the catalytic effect of CD and (b) micellar catalysis. In fact, if we compare the observed rate constants at the maximum, k_{max}, and the corresponding value prior to cmc, k_{cmc}, we obtain the following catalytic efficiency: k_{max}/k_{cmc} = 35, 36, 34, 34, 43, 40, and 41 for [β-CD] = 0, 3.7×10^{-5}, 1.37×10^{-4}, 3×10^{-4}, 2.3×10^{-3}, 5.0×10^{-3}, and 1.0×10^{-2} M, respectively. As will be shown, the fact that the catalytic efficiency remains independent of [β-CD] is in good agreement with the absence of interaction between the micelles and cyclodextrins.

Kinetic results in CD/surfactant mixed systems have been explained on the basis of a complexation mechanism that takes into account the surfactant complexation by CD and its self-association to form micelles. Once micelles have been formed, there is no interaction between cyclodextrins and the micellar system. On applying this mechanism (Scheme 6), we have three reaction pathways: basic hydrolysis of CV in bulk water, k_w; hydrolysis of CV complexed by the cyclodextrin, k_{CD}; and hydrolysis of CV bound to the micelle surface, k_m.

This scheme implies that k_{obs} is given by

$$k_{obs} = \frac{k_w[HO^-] + (K_{CV}^m k_m - k_w) m_{OH}[D_n] + k_{CD} K_{CV}^{CD}[CD]_f}{1 + K_{CV}^m[D_n] + K_{CV}^{CD}[CD]_f} \quad (5)$$

where K_{CV}^m and K_{CV}^{CD} correspond to the binding constant of CV to the micellar aggregate and to the cyclodextrins, respectively. The value of m_{OH} was obtained from eq 4.

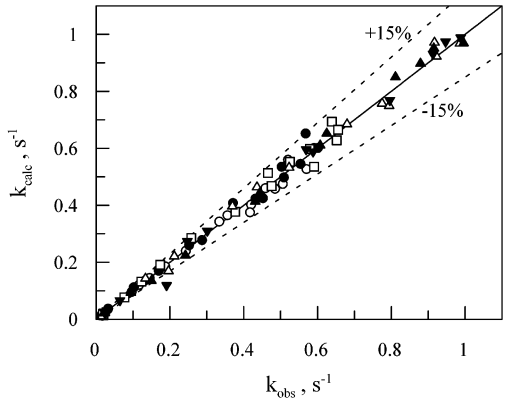


Figure 8. k_{obs} vs k_{calc} for the basic hydrolysis of crystal violet in the presence of CTACl−CD mixtures. [NaOH] = 0.10 M; (○) [CD] = 0 M, (●) [CD] = 3.7×10^{-5} M, (□) [CD] = 3.0×10^{-4} M, (△) [CD] = 2.3×10^{-3} M, (▲) [CD] = 5.0×10^{-3} M, and (▼) [CD] = 1.0×10^{-2} M.

Equation 5 can be simplified by taking into account the results discussed in the previous sections. A knowledge of K_{CV}^{CD}, k_w, and k_{CD} values obtained in section B and the fact that the percentage of free CD present in equilibrium with CTACl was determined to be ~30%[8c] allow us to assume that the belief that $[CD]_t \sim [CD]_f$ does not have any implications on the kinetic model.[27] In all cases, the experimental behavior shows satisfactory agreement with the theoretical values (see Figure 8), thus demonstrating the efficiency of the kinetic model. The values of the different kinetic parameters obtained from this fit also show that these assumptions are satisfactory (see Table 2).

Conclusions

A comparison of the observed rate constants in the presence and in the absence of CD reveals that interaction between the micellar system and cyclodextrin does not take place. The sole effect of CD on the system is the complexation of surfactant monomers, which delays the formation of the micellar system (by increasing cmc_{app}). The competition between the surfactant monomers binding to the cyclodextrin and their self-association (micellization) gives rise to the presence of a substantial concentration of free CD in the reaction medium. This fact is demonstrated by the fact that the cmc_{app}/cmc_{real} (cmc_{real} corresponds to the cmc in the absence of CD) are both greater than unity. This situation is also supported by $cmc_{app} \leq (cmc_{real} + [CD])$. The results obtained in this work provide direct evidence of the presence of an appreciable amount of free CD after micellization starts. As we have stated in previous papers,[8c] this is one of the reasons for the disparity among reported binding constants for surfactant complexation by CD.

The proposed kinetic model, which is an extension of the pseudophase formalism, has been satisfactorily applied to a CD-catalyzed reaction. The model considers two simultaneous pathways in the aqueous medium that

(27) Previous results (ref 8c) show that at least 30% of the cyclodextrin should be uncomplexed in equilibrium with the micellar system. Simple calculations show that a reduction of 70% in the total cyclodextrin concentration has a negligible effect on the observed rate constant for alkaline hydrolysis of crystal violet. If we consider a total cyclodextrin concentration of 1.00×10^{-3} M, the observed rate constant calculated using eq 1 should be $k_{obs} = 2.19 \times 10^{-2}$ s^{-1}. A value of $k_{obs} = 2.00 \times 10^{-2}$ s^{-1} is calculated for [β-CD] = 3.00×10^{-4} M. The difference corresponds to a deviation of 9%.

involve free hydroxyl ions and the substrate−CD complex, respectively. From the data in Table 2, it follows that the presence of CD favors micellization by lowering the cmc: differences between cmc_{app} and (cmc_{real} + [CD]) increase as [CD] increases. This effect is well documented in the literature[28] but has not been fully explained; it is believed to be related to the influence of additives on micellization.[29]

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