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Cucurbit[7]uril: Surfactant Host–Guest Complexes in Equilibrium with Micellar Aggregates

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In order to compare the formation of host–guest complexes between β-cyclodextrin (β-CD) or cucurbit[7]uril (CB7) and cationic surfactants we studied the hydrolysis of 4-methoxybenzenesulfonyl chloride (MBSC). The selected surfactants allowed the length of the hydrocarbon chain to be varied between 6 and 18 carbon atoms. Contrary to the expected behaviour, the values of the binding constants between CB7 and surfactants are independent of the alkyl chain length of the surfactant. In the case of β-CD, however, a clear dependence of the binding constant on the hydrophobic character of the surfactant was observed. The values obtained with CB7 are significantly higher than those obtained with β-CD and these differences are explained to be a consequence of electrostatic interactions of the surfactants with the portals of CB7. It was found that a small percentage of uncomplexed CB7 was in equilibrium with the cationic micelles and this percentage increased on increasing the hydrophobic character of the surfactant.

1. Introduction

Studies of host–guest interactions often provide fundamental insights into supramolecular chemistry.[1,2] Cyclodextrins (CDs)[3,4] and cucurbiturils (CB*n*)[5–7] are both important host molecules that have been extensively studied and characterized in condensed media. Cyclodextrins are cyclic oligosaccharides composed of glucose units. The best characterized forms are α-, β- and γ-CD and these consist of six, seven and eight D-glucose units, respectively. The CD structure provides an external hydrophilic region, where primary and secondary OH groups are located, as well as a relatively hydrophobic cavity. Therefore, CD hosts can form inclusion complexes with guest molecules of appropriate size, shape and polarity.[3] In contrast to the host–guest chemistry of α-, β- and γ-CDs, which has developed steadily over the past century, the supramolecular chemistry of cucurbit[6]uril, CB6, only began to develop in the 1980s and 1990s as a result of the pioneering work of Mock,[8] Buschmann and co-workers[9] and Kim and co-workers.[10,11] Interest in the CB*n* family has increased dramatically in the new millennium following the preparation of four new CB*n* homologues (CB5, CB7, CB8 and CB10.CB5) by the research groups of Kim and Day.[7,12,13] Cucurbiturils are pumpkin-shaped cavities composed of *n* glycoril units linked by a pair of methylene groups.[6,7,10,11] The two identical carbonyl-fringed portals have a considerable negative charge density, which facilitates the binding of metal ions and cationic organic compounds, while the inner cavities are relatively hydrophobic and can host neutral molecules that fit within.[14–21] The cavity sizes of CB7 and CB8 are comparable to those of β- and γ-CD, respectively, and they exhibit extraordinary host–guest properties[5,6,10,11,22–25] that are distinctly different from those of the cyclodextrins.

Despite extensive studies on the host–guest chemistry of CB*n*, little attention has been paid to the interaction of CB*n* with amphiphilic molecules that contain a long alkyl chain. In the literature there are a few previous studies on the complexation of cationic[26,27] or nonionic[28] surfactants with CB*n*, but none of these studies covers the postmicellar region. Mixed cyclodextrin–surfactant systems have been widely studied due to their numerous applications in commercial formulations[29,30] and the capacity of cyclodextrins to modulate the physicochemical properties of micellar solutions. These systems offer the possibility to systematically study the association process, because the properties of micellar solutions can be modulated in a controlled manner by varying the surfactant structure. As a consequence of the binding process some properties of the target molecules can change dramatically [e.g. the critical micelle concentration (cmc)]. The presence of CDs in solutions of amphiphiles that form micelles or other types of self-assembled aggregates introduces a new equilibrium into the medium and this may lead to the dissolution of the self-assembled aggregates.[31,32] Inclusion complexes have been characterized by a wide variety of techniques such as conductance,[33,34] speed of sound,[35,36] NMR,[33] fluorescence,[37] surfactant selective electrode,[38,39] surface tension[40] and kinetic methods[41–43] among others.

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Herein we present a systematic study of mixed systems of trimethylalkylammonium surfactants [$(CH_3)_3N^+C_nTA$, C_nTA^+, $n=6$–18] and CB7. In studying these systems we used the hydrolysis of 4-methoxybenzenesulfonyl chloride (MBSC) as a chemical probe. MBSC is a molecule the geometry and polarity of which are suitable for complex formation with CB7. Published work on the solvolysis of MBSC shows that the reaction is highly susceptible to changes in the polarity of the medium.[44–46]

Experimental Section

The surfactants and MBSC were supplied by Aldrich in the highest available purity and were used without further purification. Cucurbit[7]uril was synthesized as described in our previous paper.[47] Solutions of MBSC were prepared in acetonitrile due to the low solubility of this compound in water. The fraction of acetonitrile in the reaction mixtures was always 1% (v/v). Surfactant–CB7 systems were prepared by mixing appropriate volumes of stock aqueous solutions of CB7 and the surfactant. Kinetic runs were initiated by injection of a stock solution of MBSC into the mixed system in a 1 cm cuvette.

The reaction kinetics were monitored by UV-Vis at 270 nm (the absorption maximum of MBSC) in a Cary UV-Vis spectrophotometer thermostated at 25.0 ± 0.1 °C. In all cases the MBSC concentration was 1.0×10^{-4} M. The absorbance-time data for all kinetic experiments were fitted to a first-order integrated equation, and the values of the pseudo-first-order rate constants, k_{obs}, were reproducible to within 3%. The critical micelle concentration (cmc) of the mixed systems was obtained kinetically and in the case of $C_{18}TACl$ by calorimetric measurements. The binding constants for the inclusion complex of C_nTA^+ with CB7 were determined by isothermal titration calorimetry using a VP-ITC instrument from MicroCal. The binding constant calculations were performed with Origin 7.0, which is part of the MicroCal VP-ITC software suite.

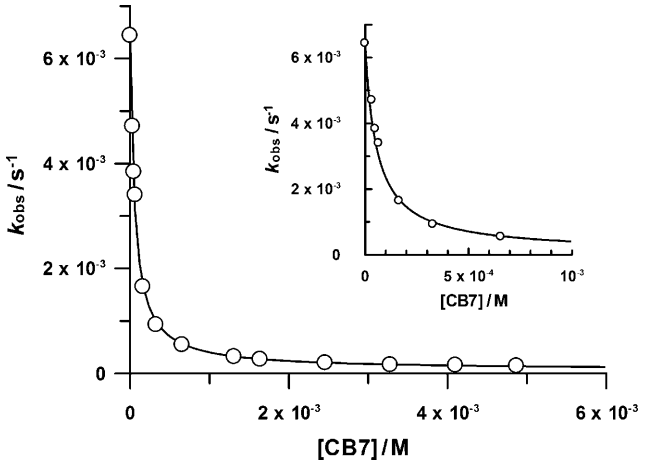
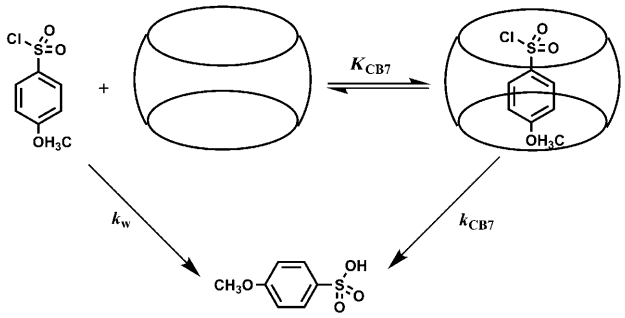


Figure 1. Influence of CB7 on the pseudo-first-order rate constant, k_{obs}, for the hydrolysis of MBSC at 25 °C.



Scheme 1.

$$k_{obs}=\frac{k_w+k_{CB7}K_{CB7}[CB7]}{1+K_{CB7}[CB7]} \quad (1)$$

2. Results and Discussion

The aim of the work described here was to study the differences in the formation of host–guest complexes between cationic surfactants and β-cyclodextrin or cucurbit[7]uril. In order to study these systems the hydrolysis of MBSC was used as a chemical probe. The geometry and polarity of this compound are suitable for complex formation with β-CB or CB7.

2.1. Solvolysis of MBSC in the Presence of CB7

The influence of CB7 on the rate constant for solvolysis of MBSC was studied. The influence of the CB7 concentration on the observed rate constant is shown in Figure 1 and it can be seen that the addition of CB7 to the reaction medium inhibits the hydrolysis of MBSC. The observed inhibition is attributed to the formation of an inclusion complex (MBSC–CB7) between MBSC and CB7, as shown in Scheme 1.

The kinetic scheme considers that the solvolytic reaction takes place in two well-differentiated environments: water, k_w, and the CB7 cavity, k_{CB7}. The following rate equation can be obtained from Scheme 1 [Eq. (1)]:

where K_{CB7} is the equilibrium binding constant of the substrate to CB7, k_{CB7} is the rate constant for the reaction in the cavity of CB7 and k_w is the rate constant for hydrolysis in the aqueous medium. Equation (1) gave an excellent fit to the experimental data (Figure 1) from which the parameters $k_w=(6.44\pm0.01)\times10^{-3}\ s^{-1}$, $K_{CB7}=(1.8\pm0.1)\times10^4\ M^{-1}$ and $k_{CB7}=(6.2\pm0.1)\times10^{-5}\ s^{-1}$ were obtained. The k_{CB7} value is clearly lower than the value obtained in bulk water but is similar to that obtained in 90% ethanol, $k_{90\%EtOH}=5.99\times10^{-5}\ s^{-1}$.[45] This behaviour is compatible with that previously found for the solvolysis of substituted benzoyl chlorides in the cavity of CB7.[47]

2.2. Solvolysis of MBSC in the Presence of Cationic Micelles

The influence of surfactant concentration on the solvolytic rate constant was studied over a wide range of surfactant concentrations that included the region before the cmc, where the molecules of the surfactants are like monomers dispersed in the solution, and the region after the cmc, where the surfactant molecules are associated to form micelles. The effect of the surfactant concentration, $C_{18}TACl$ as an example, on the pseudo-first-order rate constant, k_{obs}, for the hydrolysis of

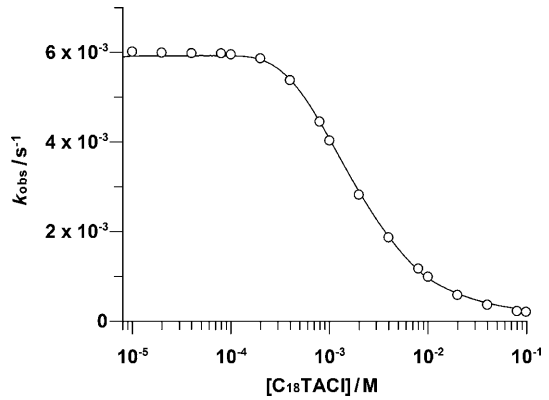
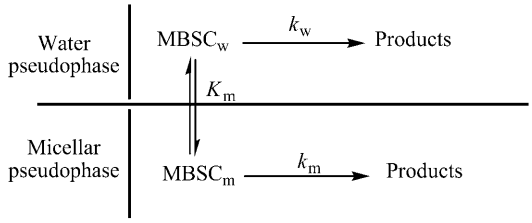


Figure 2. Influence of C_{18}TACl concentration on the pseudo-first-order rate constant, k_{obs}, for the hydrolysis of MBSC at 25 °C.

MBSC is shown in Figure 2. As can be seen, the observed rate constant remains practically unchanged on increasing the surfactant concentration up to the cmc. At concentrations above the cmc a clear decrease in k_{obs} can be seen. At this point the surfactant forms micellar aggregates and the substrate is incorporated into the micelles, a situation that explains why the rate of the solvolytic reaction is lower than that in bulk water.

The cmc values were also determined by calorimetric measurements (as an example, the determination for C_{18}TACl is represented in Figure 3). As can be seen (Figure 3c), the minimum in the first derivative of the integrated heat corresponds to the C_{18}TACl cmc value of cmc $\approx 3\times10^{-4}$ M and this is identical to the value obtained kinetically, cmc $= 3.02\times10^{-4}$ M.

The micellar pseudophase formalism was applied to obtain a quantitative interpretation of the experimental results for the solvolysis of MBSC. Two well-differentiated environments were considered: water and a micellar pseudophase between which MBSC is distributed (Scheme 2).



Scheme 2.

By considering simultaneous reactions in both bulk water and the micellar pseudophase, the following expression can be obtained for k_{obs} [Eq. (2)]:

$$k_{obs} = \frac{k_w + k_m K_m [Dn]}{1 + K_m [Dn]} \quad (2)$$

where K_m is the distribution constant of MBSC between the water and the micellar pseudophases, [Dn] is the concentration of micellized surfactant ([Dn] = [Surfactant]$_T$−cmc) and k_m is the rate constant in the micellar pseudophase. The critical micelle concentration values are required to fit the experimental results to Equation (2) and these values can be obtained kinetically as the minimal surfactant concentration necessary to observe an appreciable change in k_{obs}. Fitting the experimental results to Equation (2) allowed us to obtain the parameters listed in Table 1.

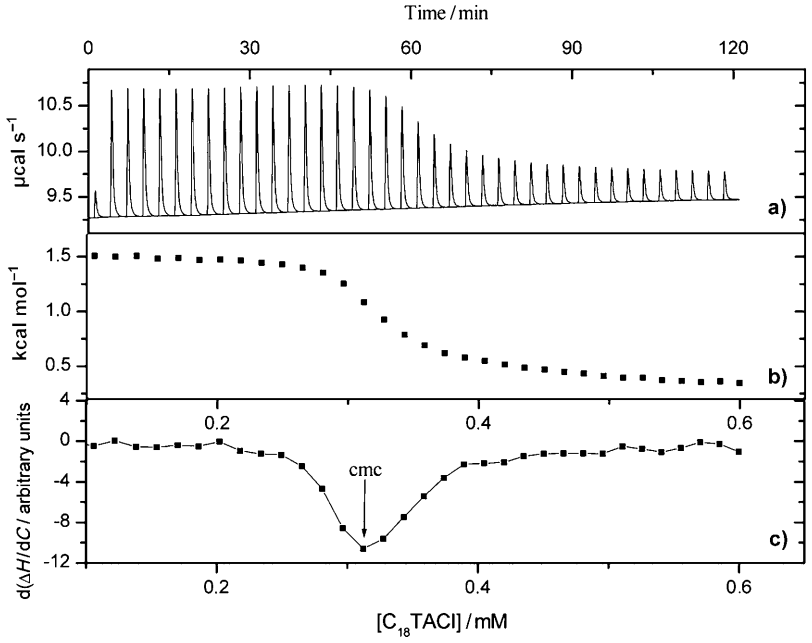


Figure 3. Titration of 158 μL of C_{18}TACl micelles (6 mM) into 1.459 mL of water in 40 steps at 25 °C. a) Calorimetric traces (heat flow against time). b) Enthalpy process versus [C_{18}TACl] in the cell. c) First derivative of curve b calculated numerically from interpolated values.

2.3. Solvolysis of MBSC in the Presence of CB7–Surfactant Mixed Systems

The effect of cationic micelles on the solvolysis of MBSC containing CB7 was assessed by carrying out experiments at a constant CB7 concentration (7×10^{-4} M) and varying the surfactant concentration from values clearly lower than the cmc to values beyond the micellization point. As an example, the results obtained for C_{12}TABr and C_{18}TACl in the presence of CB7 are shown in Figure 4.

2.3.1. Qualitative Explanation

It can be observed from Figure 4 that the value of the rate constant, k_{obs}, extrapolated to zero surfactant concentration is in

Table 1. Critical micelle concentrations obtained experimentally and the parameters of Equation (2) for the hydrolysis of MBSC in the presence of surfactant.

Surfactant	cmc [M]	k_m [s^{-1}]	K_m [M^{-1}]
C_{10}TABr	6.04×10^{-2}	$(8.7\pm0.1)\times10^{-5}$	92 ± 9
C_{12}TABr	1.09×10^{-2}	$(1.4\pm0.3)\times10^{-4}$	273 ± 24
C_{14}TABr	3.00×10^{-3}	$(1.3\pm0.7)\times10^{-4}$	292 ± 17
C_{16}TACl	1.00×10^{-3}	$(1.0\pm0.9)\times10^{-4}$	471 ± 27
C_{18}TACl	3.02×10^{-4}	$(1.6\pm0.4)\times10^{-4}$	678 ± 25

agreement with the values obtained in the absence of surfactant (Figure 1). When the CB7 concentration was kept constant, the value of k_{obs} increased to a maximum as the concentration of surfactant increased. This change is due to the competitive formation of an inclusion complex between CB7 and the surfactant. The formation of this complex displaces MBSC toward the aqueous medium where the rate constant is higher. The competitive formation of the CB7–surfactant inclusion complex occurs until the concentration of surfactant monomers reaches the value at which the micellization process begins. When the micelles are formed an inhibitory effect is observed because MBSC is incorporated into the micelles. Therefore, the minimal surfactant concentration necessary to observe an appreciable change in the maximum of k_{obs} is attributed to the micellization point.

As can be seen in Figure 4, as the alkyl chain length of the surfactant decreases one can observe a limiting value at which k_{obs} is independent of the surfactant concentration. This is because the cmc increases as the alkyl chain length decreases.

2.3.2. Binding Constants of C_nTA^+ to CB7 and Comparison with β-CD

The binding constants between CB7 and each surfactant, K_s, were studied by calorimetric measurements. As an example, the results obtained in the case of C_{10}TABr are shown in Figure 5. The binding isotherm data were fitted to a theoretical curve "one set of sites" supplied by MicroCal, with K, ΔH and ΔS as adjustable parameters. The values of the binding constants of C_nTA^+ to CB7 are listed in Table 2.

It can be seen from Figure 6 that there is a relationship between K_s and the chain length of the surfactants in the complexation by β-CD. The hydrophobic character of the surfactants increases on increasing the alkyl chain length and thus, the affinity to bind with β-CD also increases. Contrary to the expected behaviour, in the case of CB7 the values of the binding constants between CB7 and surfactants, K_s, are essentially independent of the increasing length of the hydrocarbon chain of the surfactant. As an example, the K_s value for C_{14}TABr and CB7 of $K_s=(2.6\pm0.9)\times10^6\,M^{-1}$ is significantly higher than that for β-CD,[43] $K_s=(49.5\pm0.5)\times10^3\,M^{-1}$, and this difference can be explained by electrostatic effects. Electrostatic effects can play a crucial role in molecular recognition events in both aqueous and organic solutions.[48] The electrostatic potential at the portal and within the cavity of CB7 is significantly more

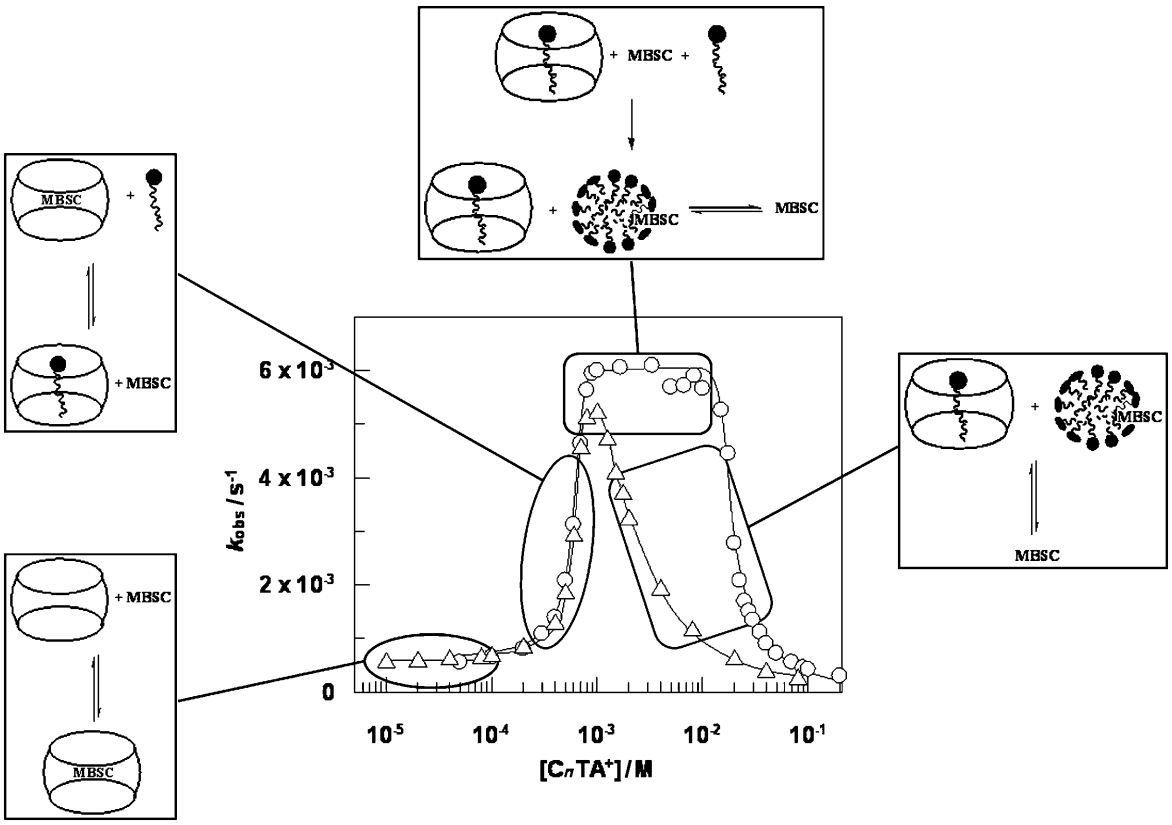


Figure 4. Influence of surfactant concentration on the observed rate constant for the solvolysis of MBSC in the presence of CB7. C_{18}TACl (△) and C_{12}TABr (○).

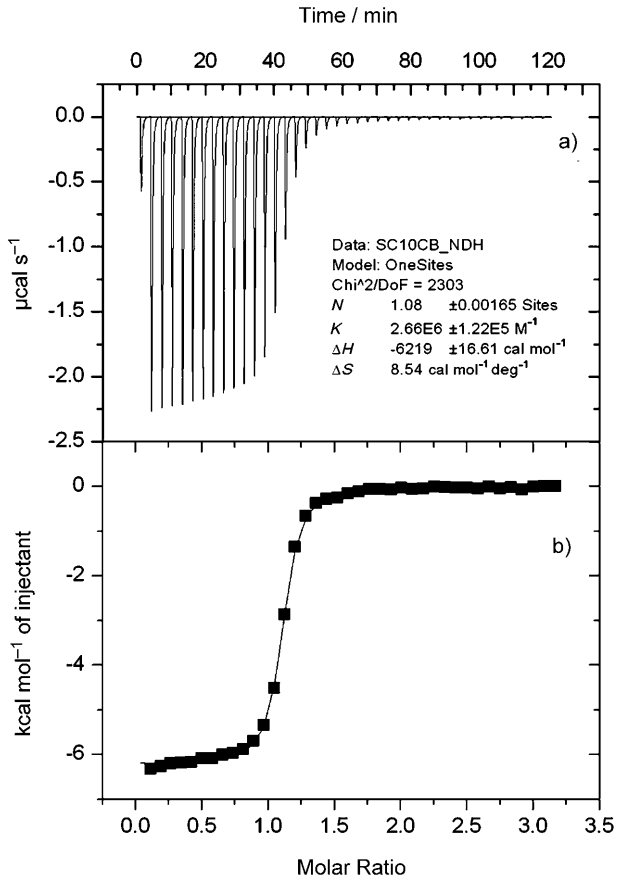


Figure 5. Titration of 158 μL of C_{10}TABr (2.5 mM) into 1.459 mL of CB7 (0.09 mM) in 40 steps at 25 °C. a) Calorimetric traces (heat flow against time). b) Binding isotherms (obtained by integrating the peaks of the upper curve) versus molar ratio.

negative than that for β-CD. This difference in electrostatic potential has significant consequences for their recognition behaviour: CB7 exhibits a pronounced preference to interact with cationic guests whereas β-CD prefers to bind to neutral or anionic guests.[6]

CB7 has two identical carbonyl-fringed portals that have a considerable negative charge density which facilitates the binding of cationic organic compounds, whereas the inner cavities are relatively hydrophobic and can host neutral molecules that fit within. The ammonium group of the guest is located just outside the portal, while the hydrocarbon chain is inside the CB7 cavity.

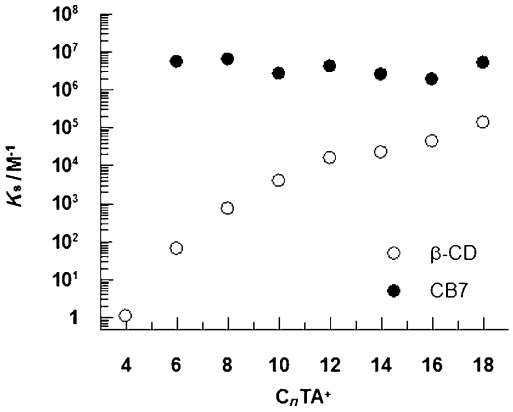


Figure 6. Values of the binding constants for each surfactant obtained by calorimetric measurements.

2.3.3. Influence of the Presence of CB7 on the Critical Micelle Concentration

In the presence of CB7 the maximum in the curve k_{obs} versus [Surfactant] is displaced to higher surfactant concentrations. This effect is due to complexation of the surfactant monomers with CB7 and the consequent effect on the cmc. For example, in the case of C_{18}TACl the addition of CB7, $[CB7] = 7\times10^{-4}$ M, produces an increase in the cmc from 3.02×10^{-4} M in the absence of CB7 to 1.14×10^{-3} M in the presence of 7×10^{-4} M of CB7. For this surfactant the cmc values were also determined by calorimetric measurements (Figures 3, 7). As can be seen, in the absence of CB7 (Figure 3c) the minimum of the curve corresponds to the value of the C_{18}TACl cmc, $cmc \approx 3\times10^{-4}$ M, and this value is identical to that obtained kinetically ($cmc = 3.02\times10^{-4}$ M). In the presence of CB7 (Figure 7c) the curve shows a maximum and a minimum. The maximum is related to the point at which the complexation capacity of CB7 is saturated and the minimum indicates the minimum concentration of surfactant at which the micellization process begins. In the presence of CB7 calorimetric measurements gave a cmc value of $\approx 1\times10^{-3}$ M and this value is comparable to that obtained kinetically, $cmc = 1.14\times10^{-3}$ M.

2.3.4. Is there any Interaction between CB7 and Cationic Micelles?

In the presence of CB7 at surfactant concentrations higher than the cmc we can consider two types of interaction: CB7 is

Table 2. Compilation of kinetic parameters obtained for the solvolysis of MBSC in CB7–surfactant mixed systems.

Surfactant	cmc_{app} [M]	k_w [s^{-1}]	k_m [s^{-1}]	K_m [M^{-1}]	k_{CB7} [s^{-1}]	K_{CB7} [M^{-1}]	K_s [M^{-1}]
C_6TABr	–	$(6.44\pm0.01)\times10^{-3}$	–	–	$(7.1\pm0.3)\times10^{-5}$	$(1.6\pm0.3)\times10^{4}$	$(5.5\pm0.5)\times10^{6}$
C_8TABr	–	$(6.44\pm0.01)\times10^{-3}$	–	–	$(6.5\pm0.1)\times10^{-5}$	$(1.8\pm0.1)\times10^{4}$	$(6.4\pm0.4)\times10^{6}$
C_{10}TABr	6.00×10^{-2}	$(6.44\pm0.01)\times10^{-3}$	$(8.0\pm0.3)\times10^{-5}$	88 ± 5	$(9.6\pm0.2)\times10^{-5}$	$(1.8\pm0.1)\times10^{4}$	$(2.7\pm0.1)\times10^{6}$
C_{12}TABr	1.50×10^{-2}	$(6.44\pm0.01)\times10^{-3}$	$(6.8\pm0.8)\times10^{-5}$	230 ± 27	$(1.3\pm0.3)\times10^{-4}$	$(1.8\pm0.3)\times10^{4}$	$(4.2\pm0.3)\times10^{6}$
C_{14}TABr	3.50×10^{-3}	$(6.44\pm0.01)\times10^{-3}$	$(1.4\pm0.5)\times10^{-4}$	349 ± 99	$(9.7\pm0.6)\times10^{-5}$	$(1.8\pm0.1)\times10^{4}$	$(2.6\pm0.9)\times10^{6}$
C_{16}TACl	1.75×10^{-3}	$(6.44\pm0.01)\times10^{-3}$	$(2.8\pm0.1)\times10^{-4}$	561 ± 81	$(6.5\pm0.3)\times10^{-5}$	$(1.8\pm0.1)\times10^{4}$	$(1.9\pm0.2)\times10^{6}$
C_{18}TACl	1.14×10^{-3}	$(6.44\pm0.01)\times10^{-3}$	$(2.9\pm0.6)\times10^{-4}$	861 ± 77	$(9.7\pm0.1)\times10^{-5}$	$(1.6\pm0.2)\times10^{4}$	$(5.2\pm0.4)\times10^{6}$

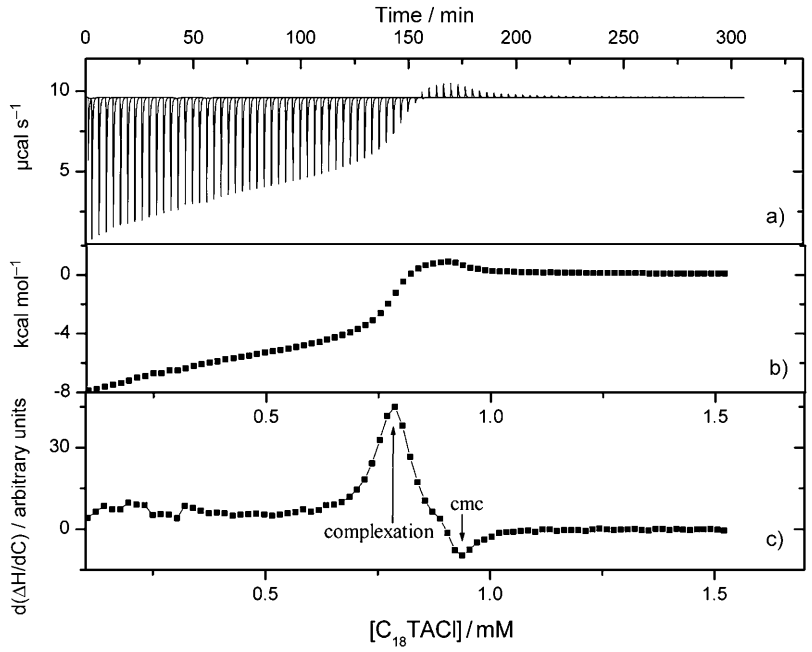


Figure 7. Titration of 275 μL of C_{18}TACl micelles (9 mM) with CB7 (0.7 mM) into 1.459 mL of CB7 (0.7 mM) in 92 steps at 25 °C. a) Calorimetric traces (heat flow against time). b) Enthalpy process versus [C_{18}TACl] in the cell. c) First derivative of curve b calculated numerically from interpolated values.

incorporated into the micelle and/or the host–guest complex micellizes. To address this question, the experimental behaviour in the solvolysis of MBSC should be analyzed at surfactant concentrations beyond the micellization point, in the presence of cationic micelles and also in the CB7–surfactant mixed system.

As an example, the influence of the surfactant concentration in the absence and in the presence of CB7 is shown in Figure 8a,b for the case of C_{12}TABr. If we only focus on the behaviour after the cmc when plotting k_{obs} versus [Dn], it can be seen that the results in the absence and in the presence of CB7 are completely identical. This clearly shows the absence of any kind of interaction between CB7 and the micelle. If an interaction were established, this would change the polarity of the medium and consequently an effect should be observed in the solvolysis of MBSC due to its high sensitivity to the polarity of the medium.

In an effort to confirm this behaviour we performed ^{1}H NMR for the case of $C_{16}TA^+$, paying special attention to the chemical shifts of the $N(CH_3)_3$ group of the surfactant.

From Figure S-7 (see the Supporting Information) we can see that at high concentration of surfactant the experiments in absence and in presence of CB7 converge to the same point. This fact corroborates our interpretation, that is, absence of interaction between CB7 and the micelle. If CB7 were located at the stern layer of the cationic micelles, this would change the observed chemical shifts of the ammonium group.

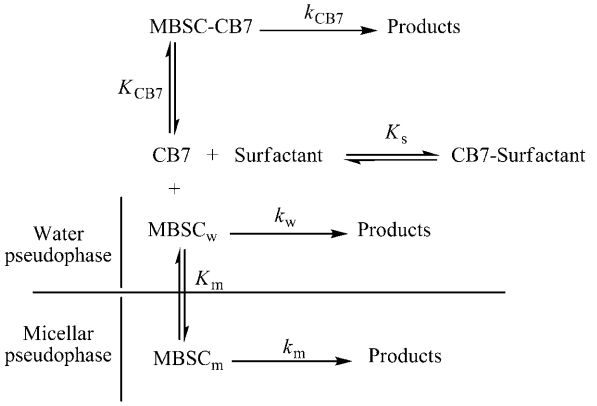
2.3.5. Quantitative Explanation

In an effort to develop a kinetic model we considered the absence of interactions between micelles and CB7 as well as the existence of three simultaneous reaction paths (Scheme 3): the reaction of the free substrate in the aqueous medium, the reaction of the complexed substrate with CB7 and the reaction of the substrate associated with the micelle.

This mechanistic scheme allowed us to derive the following equation for the rate constant [Eq. (3)]:

$$k_{obs} = \frac{k_w + k_{CB7}K_{CB7}[CB7]_f + k_mK_m[Dn]}{1 + K_{CB7}[CB7]_f + K_m[Dn]} \quad (3)$$

To solve Equation (3) it is necessary to know the values of cmc_{app}, which were kinetically



Scheme 3.

evaluated as the minimal surfactant concentration where an appreciable change in k_{obs} is observed (see Figure 4) as well as the concentration of uncomplexed CB7, $[CB7]_f$, for each surfactant concentration.

The concentration of uncomplexed CB7 can be obtained by means of a simulation procedure, supposing that the complex formed between the surfactant molecules and CB7 has a stoichiometric ratio of 1:1, as found for the CB7–MBSC complex. The complexation constants for binding of the substrate by CB7 and for surfactant monomers by CB7 are expressed as [Eq. (4)]:

$$K_{CB7} = \frac{[CB7 - MBSC]}{[MBSC]_w[CB7]_f} \qquad K_s = \frac{[CB7 - Surf]}{[Surf]_{mon}[CB7]_f} \quad (4)$$

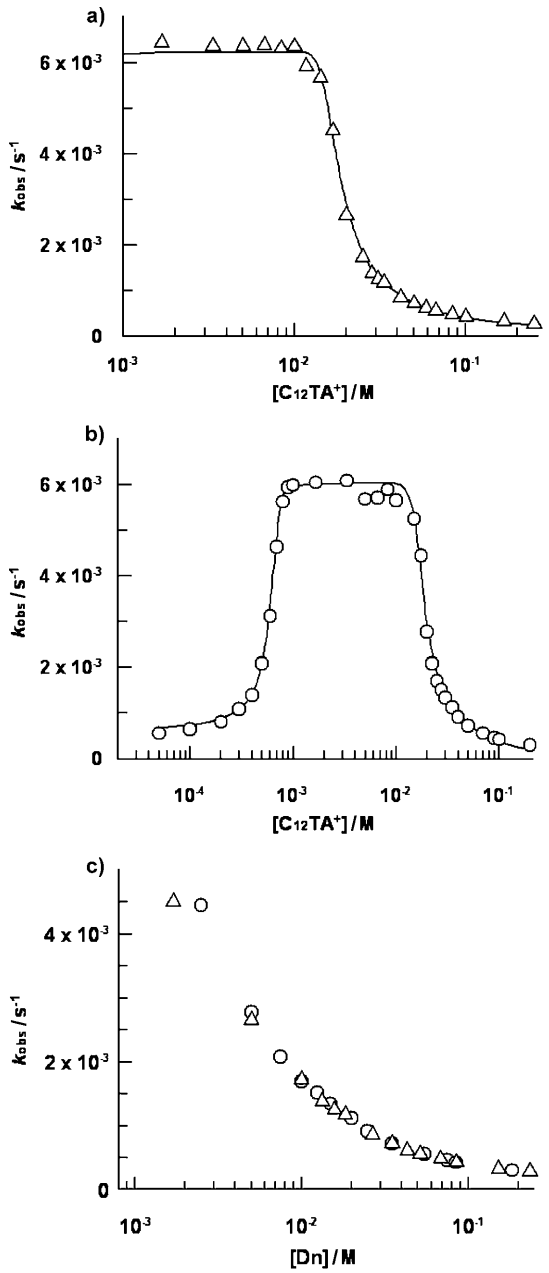


Figure 8. Influence of C_{12}TABr concentration on the observed rate constant for the solvolysis of MBSC: a) in the absence of CB7 (△), b) in the presence of [CB7] = 7×10^{-4} M (○) and c) k_{obs} versus [Dn] in absence (△) and in presence (○) of CB7.

The mass balances for the total concentrations of CB7, surfactant and MBSC for surfactant concentrations below the cmc_{app} are given by Equations (5)–(7):

$$[CB7]_T = [CB7]_f + [CB7-MBSC] + [CB7-Surf] \quad (5)$$

$$[Surf]_T = [Surf]_{mon} + [CB7-Surf] \quad (6)$$

$$[MBSC]_T = [MBSC]_w + [CB7-MBSC] \quad (7)$$

The combination of these equations with the binding constants gives a third order equation for the concentration of uncomplexed CB7 [Eq. (8)]:

$$\alpha[CB7]_f^3 + \beta[CB7]_f^2 + \gamma[CB7]_f + [CB7]_T = 0 \quad (8)$$

where [Eqs. (9)–(11)]:

$$\alpha = K_s K_{CB7} \quad (9)$$

$$\beta = K_s K_{CB7}([MBSC]_T + [Surf]_T + [CB7]_T) + K_s + K_{CB7} \quad (10)$$

$$\gamma = K_{CB7}([MBSC]_T - [CB7]_T) + K_s([Surf]_T - [CB7]_T) + 1 \quad (11)$$

In order to obtain $[CB7]_f$ we need to solve Equations (8)–(11) by using the values K_s and K_{CB7} obtained previously. Solving these equations allowed us to obtain the concentration of uncomplexed CB7 for each surfactant concentration prior to the cmc_{app}. Above the cmc_{app} the concentration of uncomplexed CB7 is assumed to be constant and equal to the value obtained at cmc_{app}. The $[CB7]_f$ and [Dn] values were used to fit the experimental k_{obs} values to Equation (3). As an example, Figure 4 shows the fit of k_{obs} versus [Surfactant] in the presence of a total concentration of CB7 of [CB7] = 7×10^{-4} M on using the concentration of uncomplexed CB7 calculated with Equations (8)–(11). The fitted parameters corresponding to Equation (3) are shown in Table 2.

The values obtained for the parameters in simple micellar systems and mixed CB7-micelle systems for the reaction in the micellar pseudophase, k_m and K_m, are shown in Tables 1, 2. The values of these parameters provide valuable information about the micellar aggregate structure. K_m is related to the hydrophobic character of the inner cavity of the micelle, whereas k_m gives information about the polarity of the medium. Thus, if there is some kind of interaction between CB7 and cationic micelles, this will be reflected in the values of K_m and k_m. As can be seen, there is good agreement between the values of k_m and K_m obtained in the presence and absence of CB7, a finding that clearly indicates the validity of the applied model.

2.3.6. Variation of Uncomplexed CB7 Concentration with the Chain Length of the Surfactant

For each surfactant, it is possible to obtain the concentration of uncomplexed CB7 from a calibration curve (Figure 1). On rewriting Equation (1) and using the values of K_{CB7}, k_{CB7} and k_w previously obtained, we can determine the concentration of uncomplexed CB7 [Eq. (12)]:

$$[CB7]_f = \frac{k_w - k_{obs}}{K_{CB7}(k_{obs} - k_{CB7})} \quad (12)$$

The values of $\%CB7_f$ in equilibrium with the micellar system and the maximum values of k_{obs} in the plot of k_{obs} versus the surfactant concentration are shown in Table 3. The maximum values of k_{obs} are lower than the value obtained in bulk water [$k_w = (6.44\pm0.01)\times10^{-3}\ s^{-1}$] and this is due to the presence of uncomplexed CB7 at the micellization point.

The percentage of uncomplexed CB7 increases with the length of the hydrocarbon chain of the surfactant (see

Table 3. Values of $[CB7]_f$ in equilibrium with the micellar system in the presence of different surfactants.

Surfactant	k_{obs} max. [s^{-1}]	% $CB7_f$
C_6TABr	$(6.43\pm0.01)\times10^{-3}$	0.01
C_8TABr	$(6.42\pm0.02)\times10^{-3}$	0.01
$C_{10}TABr$	$(6.39\pm0.01)\times10^{-3}$	0.08
$C_{12}TABr$	$(6.09\pm0.02)\times10^{-3}$	0.46
$C_{14}TABr$	$(5.96\pm0.03)\times10^{-3}$	0.66
$C_{16}TACl$	$(5.706\pm0.003)\times10^{-3}$	1.05
$C_{18}TACl$	$(5.203\pm0.008)\times10^{-3}$	1.95

Figure 9). An increase in the hydrophobicity of the surfactant gives rise to an increase in the percentage of uncomplexed CB7. The increased hydrophobicity due to the nature of the surfactant has no effect on its affinity to complex with CB7, but it does increase its tendency to micellize.

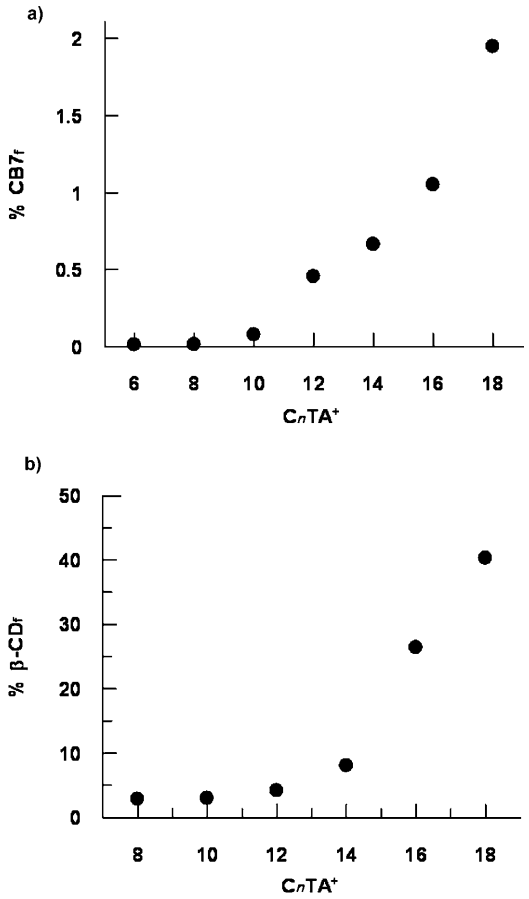


Figure 9. Variation of the percentage of uncomplexed a) CB7 and b) β-CD in equilibrium with the micellar system.

As can be seen in Figure 9, there is a higher percentage of uncomplexed β-CD[49] than CB7 in equilibrium with the micellar system for trimethylalkylammonium surfactants. The percentage of uncomplexed β-CD in the case of $C_{18}TACl$ is approximately 21 times higher than that of CB7. This difference can be explained on the basis of the binding constants between the surfactant and these hosts. As already mentioned, the values of the binding constants with CB7 are significantly higher than those for β-CD, and this is reflected in the percentage of free CB7.

3. Conclusions

The results obtained in this study allow us to conclude that for low surfactant concentrations a CB7–surfactant complex is formed in a competitive model by break down of the CB7–MBSC complex. The competitive formation of the CB7–surfactant complex occurs until the concentration of monomers reaches the value at which the micellization process begins. The values of the binding constants between CB7 and surfactants are essentially independent of the increasing length of the hydrocarbon chain of the surfactant and these values are significantly higher than those obtained with β-CD. A small percentage of uncomplexed CB7 exists in equilibrium with the cationic micelles and this percentage increases with the hydrophobic character of the surfactants.

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