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ORIGINAL ARTICLE

Study of host–guest interaction between ß-cyclodextrin and alkyltrimethylammonium bromides in water

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Abstract Cyclodextrins were found to play important roles in self-assembly systems of surfactants. The interactions between host molecule ß-cyclodextrin (CD) and model cationic surfactants, alkyltrimethylammonium bromides with different alkyl chain length: dodecyl-(C_{12}TAB), tetradecyl-(C_{14}TAB) and hexadecyl-(C_{16}TAB) are studied by means of conductivity measurements at 313.2 K. The data obtained indicate that inclusion complexes (CD:S^+) had formed, and apparent critical micelle concentration (CMC*) is equivalent to the combined concentrations of surfactant monomers complexed with the CD and that of a free dissolved monomer in equilibrium with the micellized surfactant without CD. Inclusion complexes were characterized by an equilibrium binding constant K_{11}, which value increases as the length of alkyl chains, and consequently the hydrophobicity, increases. From mathematical model the concentrations of the uncomplexed cyclodextrin, uncomplexed surfactant ion, and inclusion complex in the submicellar, as well as in the micellar range were calculated. The competition between the micellization and complexation processes leads to the existence of a significant concentration of free CD in equilibrium with the micellar aggregates. The percentage of uncomplexed cyclodextrin in equilibrium with the micelles is independent on cyclodextrin concentration for a particular ternary system and is 31, 37, and 34 % for C_{12}TAB/water/ß-CD, C_{14}TAB/water/ß-CD and C_{16}TAB/water/ß-CD, respectively. By using standard Gibbs free energy for micellization and surfactant complexation by CD, we can explain the observed behavior.

Keywords Inclusion complex · Cyclodextrin · Alkyltrimethylammonium bromides · Micelles · Conductivity

Introduction

Cyclodextrins (CDs) are a series of cyclic oligosaccharides formed through α (1–4) ether linkages of glucopyranose units. The practically important, industrially produced CDs are classified as α-, β- and γ-cyclodextrin, whether they have six, seven, or eight glucoside units. Larger CDs also exist, e.g. δ-, ε-cyclodextrin, with nine or ten glucose residues and were isolated from the commercially available CD conversion mixture by chromathography. Schardinger identified cyclodextrins in the early 20th century as products produced by the degradation of starch trough the action of amylase enzyme cyclodextrin glycosyl transferase [1]. β-CD is the most commonly used because of the relative ease of synthesis, low price and the size of its internal cavity. The relatively strong binding of β-CD molecules in the crystal state and intramolecular hydrogen bond within the β-CD ring prevent their hydrogen bond formation with surrounding water molecules, expressed in the low solubility in water [2–4]. The chair conformation of the glucopyranose units provides that cyclodextrins are shaped as a hollow, truncated cone rather than a perfect cylinder. External surfaces are hydrophilic due to the primary and the secondary hydroxyl groups, located on the narrow and wide rims of the truncated cone, while the inner walls of CD are slightly hydrophobic, forms by the carbon backbones of glucopyranose monomers [5, 6].

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Surfactants are among the most versatile chemicals available. The important properties of surfactant compounds follow from their particular structure: a non-polar hydrophobic part, generally a hydrocarbon chain and a polar hydrophilic head group. In the cationic surfactants, the polar head is charged positively and is accompanied by a counter ion. In polar solvents, this dual character of the amphiphile leads to a self-association or micellization [9, 11]. The hydrophobic part of the aggregate forms the core of the micelle, while the polar head groups are located at the micelle-water interface in contact with and hydrated by water molecules [8]. Nuclear magnetic resonance shows that the hydrocarbon tails are mobile, but slightly more restricted than in the bulk. Micelles are important in industry and biology on account of their solubilizing function in their hydrocarbon interior [7]. Cationic surfactants are also important as corrosion inhibitors, and in the food industry [10].

The main feature of cyclodextrin is to form inclusion complexes with guest molecules such as surfactants. Mixtures of cylodextrin-surfactant offer the possibility of studying the association process because properties of micellar solutions can be modulated by systematic variations of the surfactant structure, important in the fundamental and practical applications [14]. The thermodynamic quantities for CD/surfactant complexation are a consequence of the weighted contributions from release of the enthalpy-rich water molecules from the cavity, van der Waals interactions, and hydrophobic interactions, as well as hydrogen bonds, electrostatic interactions, and release of conformational strain [12]. The cyclodextrin/surfactant host/guest compounds leads to an increase in the critical micelle concentration and also in the solubility of surfactants, as the formed inclusion complexes are hydrophilic they lose ability to aggregate into micelles via hydrophobic interaction and the micelles are destroyed [13]. The formation of an inclusion compound enables the beneficial modification of guest molecular properties helpful in a number of applications related to chemical synthesis and catalysis, pharmaceutical chemistry, analytical chemistry, food industry etc. [15–17].

Surfactant inclusion complexes have been characterized by a wide variety of experimental techniques. Garcia-Rio et al. analyzed the interaction between tetradecyltrimethylammonium bromide and tetradecyltrimethylammonium hydroxide with ß-CD. In this papers where present the kinetic evidences of the presence of CD in equilibrium with micellized surfactant [18–20]. By determining the kinetics of the acid hydrolysis Fernández et al. analyzed the interaction between lauryltrimethylammonium bromide, tetradecyltrimethylammonium bromide and cetyltrimethylammonium chloride with ß-CD. Cyclodextrin has no effect on existing micelles but raises the critical micelle concentration [21]. Surface-tension measurements of cetyltrimethylammonium bromide in the presence of ß-CD indicate that neither the surfactant-CD complexes nor CD itself are surface active [22]. ß-CD forms with tetradecyltrimethylammonium bromide only the 1:1 complex as studied by a surfactant-selective electrode [23]. The inclusion complexation of ß-CD with dodecyltrimethylammonium bromide was investigated by isothermal titration microcalorimetry, a direct method for determination of the reaction enthalpy [24]. The complexation processes of CnTAB (n = 10, 12, 14) with ß-CD were shown to be enthalpy and entropy favored [25]. The binding constant and the free surfactant concentration have been obtained by a conductometric study of the interaction of beta-cyclodextrin with dodecyltrimethylammonium bromide in water solution [26]. There has been also other literatures studied the alkyltrimethylammonium bromides and ß-cyclodextrin by speed of sound [27], fluorescence [28], and NMR [14].

In this work, a systematic study of the complexation of model ionic surfactants, hexadecyltrimethylammonium bromide (C_{16}TAB), tetradecyltrimethylammonuim bromide (C_{14}TAB) and *n*-dodecyltrimethylammonium bromide (C_{12}TAB), with ß-cyclodextrin has been carried out. The association process has been analyzed using conductometry to observe the changes in the micellar properties and to understand the interaction mechanisms. Results are interpreted in terms of formation of a 1:1 CD-surfactant complex to determine binding constants. To the best of our knowledge, this report provides the new evidence of equilibrium concentrations of all species in the solutions at premicellar and postmicellar region. Considering the possible applications of the cyclodextrin-surfactant mixed systems, these results may be important from theoretical and practical view.

Experimental

Materials

The hexadecyltrimethylammonium bromide (C_{16}TAB), tetradecyltrimethylammonium bromide (C_{14}TAB) and *n*-dodecyltrimethylammonium bromide (C_{12}TAB) were purchased from Merck and used as received. ß-cyclodextrin (ß-CD) was obtained from Sigma-Aldrich and used as supplied. All solutions were prepared in ultra-pure water (resistivity 18.2 MΩ·cm at 298.2 K).

Conductivity measurements

Electrical conductivity data were collected with WTW 3210 Conductivity Meter by using a TetraCon 325

electrode. The conductivity measurements were made at 313.2 K for surfactant/water/ß-cyclodextrin ternary system, as a function of total surfactant concentration for different constant values of ß-CD concentrations. Glass bottles with solutions of different concentrations were placed into thermostatted bath (Lauda Alpha A6 thermostat) for maintaining the temperature within ±0.1 K. The conductivity meter was calibrated with KCl solutions of different concentrations and known conductivity (0.1, 0.05, 0.02, 0.01, 0.005, 0.001, 0.0005 and 0.00001 M). The solutions were prepared by weight using analytical balance (Mettler AE 100, an accuracy of $\pm 1 \cdot 10^{-4}$ g).

Results and discussion

Conductivity behavior

Figure 1 shows the variation of the conductivity κ as a function of $[C_{16}TAB]_t$ for aqueous solutions of hexadecyltrimethylammonium bromide in the presence of different constant ß-CD concentrations. Similar plots were obtained for the ternary system $C_{12}TAB$/water/ß-CD as a function of $[C_{12}TAB]_t$ at various constant $[ß\text{-}CD]_t$ (Fig. 2) and the ternary system $C_{14}TAB$/water/ß-CD as a function of $[C_{14}TAB]_t$ at various constant $[ß\text{-}CD]_t$ (Fig. 3).

The change in the slope of the conductivity (Figs. 1, 2, 3) is assigned to the apparent critical micelle concentration (CMC*) in the presence of ß-cyclodextrin. From the break point, the CMC* is evaluated by fitting the premicellar and postmicellar region into linear regression analysis giving the coefficient of determination $R^2 = 0.9990$ to 0.9999. The CMC* of $C_{16}TAB$ ($C_{14}TAB$ or $C_{12}TAB$) increases with ß-CD concentration because the addition of cyclodextrin to the surfactant solution results in the inclusion of the surfactant apolar tail into the cyclodextrin cavity. Only when the cyclodextrin is in the complexed form does the addition of more surfactant result in the formation of micelles [29]. Table 1 reports the values of CMC* obtained at all the studied surfactants and ß-cyclodextrin concentrations, along with literature reports in Table 2.

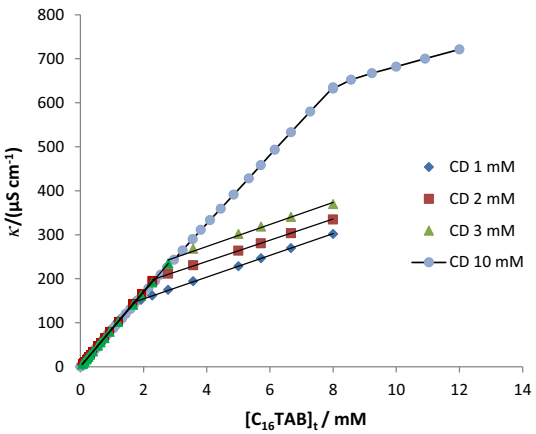

Fig. 1 Conductivity plots for $C_{16}TAB$/water/ß-CD ternary system at 313.2 K for different constant concentrations of ß-CD

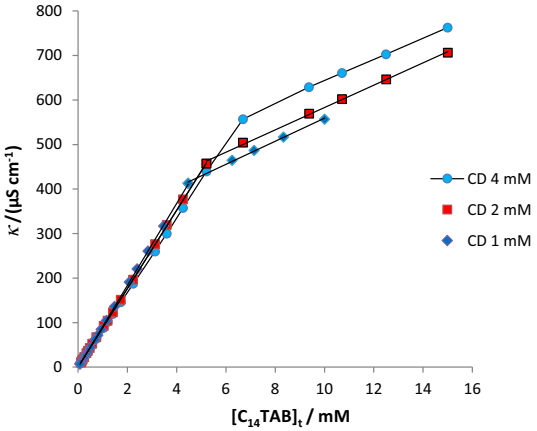

Fig. 2 Conductivity plots for $C_{14}TAB$/water/ß-CD ternary system at 313.2 K for different constant concentrations of ß-CD

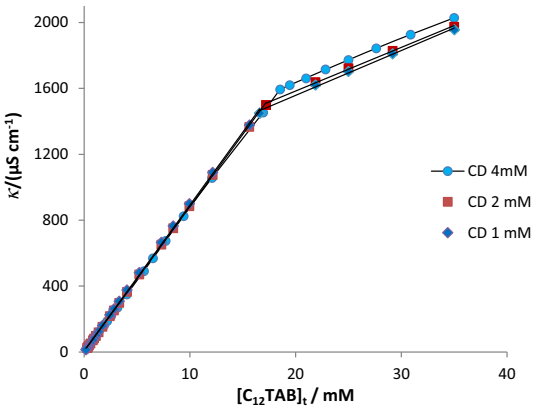

Fig. 3 Conductivity plots for $C_{12}TAB$/water/ß-CD ternary system at 313.2 K for different constant concentrations of ß-CD

Table 1 Values of apparent critical micelle concentration (CMC*) for $C_{12}TAB$, $C_{14}TAB$ and $C_{16}TAB$ at 313.2 K in the presence of different constant concentrations of ß-CD

$[ß\text{-}CD]_t$/mM	$C_{12}TAB$ CMC*/mM	$C_{14}TAB$ CMC*/mM	$C_{16}TAB$ CMC*/mM
0.0	15.7	4.21	1.05
1.0	16.6	4.68	1.70
2.0	17.2	5.3	2.31
3.0	/	/	2.90
4.0	18.5	6.7	/
10.0	/	/	7.6

The uncertainty in the measurements is: CMC* ± 2 %

Table 2 Literature values of apparent critical micelle concentration (CMC*) for C_{12}TAB, C_{14}TAB and C_{16}TAB at different temperatures using different methods, in the presence of constant concentrations of ß-CD

[ß-CD]$_t$/mM	CMC*/mM	*T*/K	Obs.
C_{12}TAB			
0.0	10.7	298.15	(1) [14]
0.0	10.0	298.15	(2) [34]
0.0[a]	15.0[a]	298.15	(4) [39]
10.0	19.0	298.15	(2) [34]
10.078[a]	22.3[a]	298.15	(4) [39]
11.0	21.0	298.15	(1) [14]
C_{14}TAB			
0.0	2.22	298.15	(1) [14]
0.0	1.20	298.15	(2) [34]
0.0	1.20	298.15	(2) [19]
0.0[a]	3.80[a]	298.15	(4) [39]
0.0	3.80	303.15	(3) [41]
0.0	3.60	303.15	(6) [41]
0.0	3.30	298.15	(3) [42]
1.3	4.2	298.15	(3) [42]
2.5	3.0	298.15	(2) [19]
3.0	5.4	298.15	(1) [14]
3.206[a]	5.79[a]	298.15	(4) [39]
3.4	5.2	298.15	(3) [42]
4.0	6.2	303.15	(3) [41]
4.0	6.0	303.15	(6) [41]
5.0	6.5	298.15	(3) [42]
5.05	5.2	298.15	(2) [19]
8.0	9.2	303.15	(3) [41]
10.0	10.0	298.15	(2) [34]
10.3	10.0	298.15	(2) [19]
C_{16}TAB			
0.0	0.91	300.15	(3) [38]
0.0[a]	0.92[a]	298.15	(4) [39]
0.0	0.851	298.15	(5) [40]
0.0	1.0	303.15	(3) [41]
0.0	0.95	303.15	(6) [41]
0.0	0.908	298.15	(3) [43]
0.0	0.95	298.15	(3) [44]
0.35	1.13	298.15	(5) [40]
0.5	1.33	298.15	(3) [43]
0.75	1.45	298.15	(5) [40]
0.9	1.55	298.15	(3) [44]
1.0	1.5	300.15	(3) [38]
1.0	1.41	298.15	(3) [43]
1.5	2.1	298.15	(5) [40]
2.20	2.70	298.15	(3) [44]
2.241[a]	2.63[a]	298.15	(4) [39]
3.0	3.3	300.15	(3) [38]
4.0	3.6	303.15	(3) [41]
4.0	3.7	303.15	(6) [41]
4.40	4.32	298.15	(3) [44]
5.0	4.8	300.15	(3) [38]
5.0	2.84	298.15	(3) [43]
8.0	6.7	303.15	(3) [41]

(1) NMR diffusometry; (2) kinetic methods; (3) electrical conductivity; (4) speed of sound; (5) cyclic voltammetry; (6) surface tension

[a] (mmol kg^{-1})

All the curves in Fig. 1 (as also in Figs. 2, 3) present the same slopes in the postmicellar region, independently on concentrations of ß-cyclodextrin. This feature implies that the micelles are the same and thus the cyclodextrin does not participate in them [30]. The addition of cyclodextrin only delays the process of micellization as evident from the conductivity curves for ternary systems.

The degree of ionization of micelles (α) has been estimated from the ratio of the slopes of the two intersecting lines below and above CMC*. The average values of micelle dissociation degree in the presence of ß-CD for C_{12}TAB, C_{14}TAB, and C_{16}TAB were similar to that of the respective surfactants in water at 313.2 K. It can be deduced that CD species neither participate in micelle nor affect the micellar parameters [30].

Binding constants for the inclusion complexes of ß-CD with surfactant

To see the effect of ß-CD on the micellization process, we have carried out conductivity experiments to evaluate the CMC* values of alkyltrimethylammonium bromides at different concentrations of ß-CD. Figure 4 shows the relationship between the apparent critical micelle

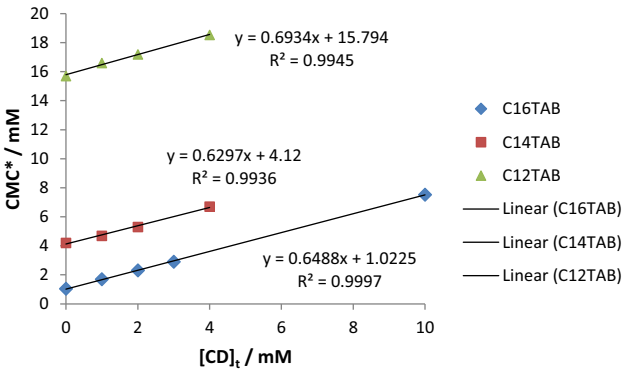

Fig. 4 Dependence of apparent critical micelle concentrations (CMC*) of C_{12}TAB, C_{14}TAB and C_{16}TAB on ß-CD concentration (T = 313.2 K)

concentrations and the concentrations of CDs. As shown in the Fig. 4, the CMC* values of C_{12}TAB, C_{14}TAB and C_{16}TAB are linearly correlated with the ß-CD concentrations which indicate that more surfactant monomers form inclusion complexes with cyclodextrin and lead to a delay in the micelle formation. The intercepts of these lines are consistent with the critical micelle concentration (CMC) of pure alkyltrimethylammonium bromides in water.

From these data we are able to evaluate constant of formation the inclusion complex between CD and surfactant (binding constant). In the evaluation we assumed that: ß-CD does not associate in water, and there is no interaction between ß-CD and counter ion (Br^-), and each complex contain only one surfactant ion [31, 32].

Our starting point is the equilibrium between uncomplexed ß-cyclodextrin (CD), uncomplexed surfactant ion (S^+), and inclusion complex ($CD:S^+$) in the submicellar concentration as shown in Eq. (1):

$$CD + S^+ \rightleftharpoons CD : S^+ \tag{1}$$

An equilibrium constant for the 1:1 inclusion complex, K_{11}, is defined as

$$K_{11} = [CD : S^+] / ([CD][S^+]) \tag{2}$$

and

$$[CD : S^+] = K_{11}[CD][S^+] \tag{3}$$

Here, [CD], $[S^+]$ and $[CD:S^+]$ represent the equilibrium concentrations of the unbound cyclodextrin, unbound surfactant and formed inclusion complex, respectively.The mass conservation law equations for Eq. (1) could be written for the total cyclodextrin concentration and surfactant total concentration as shown in Eqs. (4) and (7), where $[CD]_t$ and $[S]_t$ are the total cyclodextrin and surfactant concentrations, respectively. Combining the equilibrium and the mass balance leads to the following expressions [30, 33]:

$$[CD]_t = [CD] + [CD : S^+] \tag{4}$$

$$[CD]_t = [CD] + K_{11}[CD][S^+] \tag{5}$$

$$[CD] = [CD]_t / (1 + K_{11}[S^+]) \tag{6}$$

$$[S]_t = [S^+] + [CD : S^+] \tag{7}$$

By substituting Eq. (3) into Eq. (7), we get

$$[S]_t = [S^+] + K_{11}[CD][S^+] \tag{8}$$

and by substituting Eq. (6) into Eq. (8), we get

$$[S]_t = [S^+] + K_{11}[CD]_t[S^+] / (1 + K_{11}[S^+]) \tag{9}$$

From Eq. (9), it is found that for a 1:1 inclusion complex, $[S]_t$ varies linearly with $[CD]_t$, which we also observe in Fig. 4. This leads to binding constants of CD with C_{12}TAB, C_{14}TAB and C_{16}TAB of 143, 413 and 1807 M^{-1}, respectively. The binding constant value increases as the length of alkyl chains, and consequently the hydrophobicity, increases. This phenomenon may attribute to the hydrophobic interactions (London dispersion forces) between the CD cavity and the hydrocarbon chain. The strength of these interactions is approximately proportional to the reciprocal of the distance between two components raised to the sixth power, and to the polarizability of the molecules. Elongated molecules tend to be more easily polarized because the valence electrons are less firmly held by nuclei. In fact, the strength of CD-hydrocarbon chain interactions increases for the common water- soluble ionic surfactants as the length of alkyl chains increases [34, 35].

An increase in the hydrophobicity of the surfactant gives rise to an increase in its affinity to complex with the CD but simultaneously implies in its tendency to micellize [36]. The standard Gibbs energy of micellization (ΔG^0_{mic}) of surfactant can be considered as a measurement of its tendency to autoassociation. In our previous work [37], the ΔG^0_{mic} was evaluated from the experimental CMC values, using the following equation:

$$\Delta G^0_{mic} = (2 - \alpha)RT \ln X_{CMC} \tag{10}$$

where the R is the gas constant, T is the temperature, and X_{CMC} stands for the CMC in the mole fraction unit.Moreover, from the binding constant of the alkyltrimethylammonium bromides to the cavity of ß-cyclodextrin we can evaluate the standard Gibbs energy, ΔG^0, of complexation:

$$\Delta G^0 = -RT \ln K \tag{11}$$

where K is binding constant K_{11} in mole fraction unit. The data are shown in Fig. 5, also with a ΔG^0_{mic} for alkyltrimethylammonium bromides [37]. The negative Gibbs energy of complexation indicates that the formation

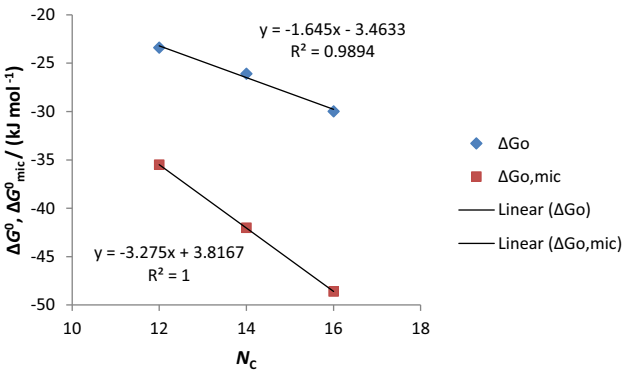

Fig. 5 ΔG^0 for the complexation of alkyltrimethylammonium bromides with ß-CD and ΔG^0_{mic} for the micellization of alkyltrimethylammonium bromides at 313.2 K as a function of the number of C atoms in alkyl chain (N_C) of surfactants

of inclusion complexes is thermodynamically spontaneous, as well as is spontaneous micellization process. But for alkyltrimethylammonium bromides micellization is more favorable than cyclodextrin complexation: $-\Delta G^0_{mic} > -\Delta G^0$.The role of matching between host and guest is further demonstrated by examining the unit increment, $d(\Delta G^0)/dN_C = -1.6$ kJ mol^{-1}, for the complexation of alkyltrimethylammonium bromides with ß-cyclodextrin in water (Fig. 5). It is of interest to compare that the carbon atom contribution to the Gibbs energy of micellization being $d(\Delta G^0_{mic})/dN_c = -3.3$ kJ mol^{-1}. The linear dependence of ΔG^0 on the alkyl chain length can be attributed to the degree of inclusion of the surfactant chain within the ß-CD cavity. As some methylene groups are not included within the ß-CD interior and extend outside, ΔG^0 decreases less than ΔG^0_{mic}.

A mathematical model for calculation of equilibrium concentrations occurring in a surfactant/water/ß-CD system

Let's consider what happens when ß-CD dissolves in a surfactant micellar solution. The simple process of dissolving ß-CD in aqueous micellar solution therefore can involve two simultaneous equilibria and we must consider each of these reactions if we want to predict what will be happen under a particular set of experimental conditions. The first is equilibrium as shown in Eq. (1) and the second one is the micellization equilibria Eq. (12):

$$CD + S^+ \rightleftharpoons CD : S^+ \tag{1}$$

$$S^+ + (p/n)\, C^- \rightleftharpoons (1/n)(S_n^+ C_p^-)^{z+} \tag{12}$$

where S^+ and C^- represent surfactant ion and counter ion, respectively, $z = (n-p)$ is the effective charge of the micelle, and p is the number of counter ions associated with the micelle. In accordance with the pseudo-phase separation model, it is assumed that the monomer concentration of the surfactant after micellization is always equal to its concentration at the CMC.

The effect of adding cyclodextrin to a micellar solution we can predict by applying Le Chatelier's principle: according to Eqs. (1) and (12), incorporating of surfactant monomers into the CD cavity leads to a decrease in the amount of "free" S^+ ion, which tied up as CD:S$^+$ complex ions. As a result, adding ß-CD cause more micelles to dissolve to attain equilibrium concentration of S^+ that is equal to CMC.

On the other hand, at surfactant concentrations lower than the micellization point, complexation equilibrium between the surfactant and the cyclodextrin is established and the decrease of "free" surfactant monomers available in solution making that a higher total concentrations of surfactant are needed to form micelles, consistent with the results obtained by conductivity methods.

It is necessary to obtain the concentration of complexed monomers ([CD:S$^+$]) for each surfactant concentration. Taken into account that 1:1 complex CD:S$^+$ is formed, the mass balances for the total concentration of cyclodextrin and surfactant were combined with the binding constant to give the

$$[CD : S^+]^2 - \left([CD]_t + [S]_t + (1/K_{11})\right)[CD : S^+] + [CD]_t[S]_t = 0 \tag{13}$$

A quadratic formula was used to solve this second degree equation for [CD:S$^+$] at different [S]$_t$ and [CD]$_t$. There are two possible roots, but only the one has physical reality. The concentration of uncomplexed cyclodextrin ([CD]) is then calculated from Eq. (4) and uncomplexed surfactant ([S$^+$]) from Eq. (7). The values obtained for the C_{14}TAB/water/ß-CD ternary system are reported in Table 3, for the C_{16}TAB/water/ß-CD is shown in Fig. 6, and for the C_{12}TAB/water/ß-CD in Fig. 7.

The values in Table 3 indicate that the added surfactant participates in formation of complex with cyclodextrin and thus there is an increase in [CD:S$^+$]. With more increase in surfactant concentration ([S]$_t$), the cyclodextrin free concentration, [CD], decreases and the surfactant free monomer concentration, [S$^+$], increases. As we can see, at the added surfactant concentration of 6.70 mM (experimental determined apparent critical micelle concentration, Table 1), the concentration of free surfactant monomer is increased up to 4.17 mM. The concentration of uncomplexed surfactant monomers in equilibrium with the CD is enough for micellization process to begin, and is equal to the critical micelle concentration of C_{14}TAB in water. After micellization, both the free cyclodextrin ([CD]) and the free monomer concentrations ([S$^+$]) are assumed to remain constant and are the same as those present at CMC*. This assumption is reasonable because the surfactant monomer concentration in equilibrium with the micelles is essentially constant and, therefore, the concentration of the CD:S$^+$ complex is constant. All the newly added surfactant molecules go into micelles and the concentration of micellized monomers, $[S]_{mic} = [S]_t - [S^+] - [CD : S^+]$), is increased.

Figure 6 depicts the representative equilibrium concentrations in C_{16}TAB/water/ß-CD ternary system. The obtained results showed also that micellization process in the presence of [CD]$_t$ = 10 mM begin at the experimental determined CMC* = 7.6 mM, where the concentration of free surfactant monomers is [S$^+$] = CMC = 1.05 mM. At surfactant concentrations above the CMC*, competition between the micellization and complexation processes leads to the existence of a constant concentration of free cyclodextrin, [CD] = 3.45 mM, in equilibrium with the

Table 3 Equilibrium concentration of different species occurring in a C_{14}TAB/water/ß-CD ternary system at 313.2 K as a function of total concentration ($[S]_t$) of C_{14}TAB and constant total concentration of ß-cyclodextrin, $[CD]_t = 4$ mM

$[S]_t$/mM	$[S^+]$/mM	[CD]/mM	$[CD:S^+]$/mM	$[S]_{mic}$/mM	$[CD]/[CD]_t$
0.0	0.0	4.0	0.0	0.0	1.0
0.50	0.198	3.698	0.302	0.0	0.924
1.00	0.415	3.415	0.585	0.0	0.854
1.50	0.652	3.152	0.848	0.0	0.788
2.00	0.909	2.909	1.091	0.0	0.727
2.50	1.185	2.685	1.315	0.0	0.671
3.00	1.482	2.482	1.518	0.0	0.620
3.50	1.796	2.296	1.704	0.0	0.574
4.00	2.129	2.129	1.871	0.0	0.532
4.50	2.477	1.977	2.023	0.0	0.494
5.00	2.841	1.841	2.159	0.0	0.460
5.50	3.218	1.718	2.282	0.0	0.429
6.00	3.607	1.607	2.393	0.0	0.402
6.70	4.170	1.470	2.530	0.0	0.367
7.50	4.170	1.470	2.530	0.80	0.367
8.00	4.170	1.470	2.530	1.30	0.367
8.50	4.170	1.470	2.530	1.80	0.367
9.00	4.170	1.470	2.530	2.30	0.367
9.50	4.170	1.470	2.530	2.80	0.367
10.0	4.170	1.470	2.530	3.30	0.367

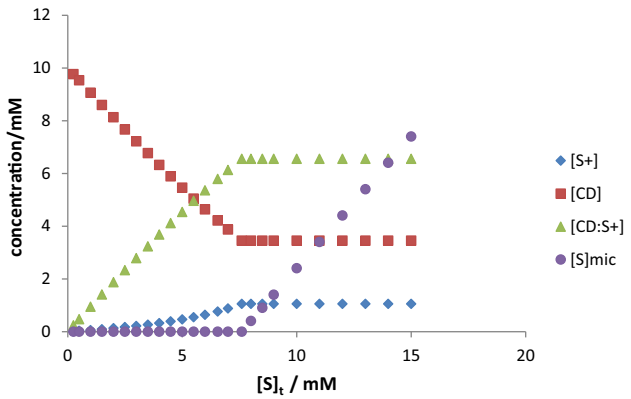

Fig. 6 Dependencies of equilibrium concentrations of different species occurring in C_{16}TAB/water/ß-CD ternary system at 313.2 K upon total surfactant concentration ($[S]_t$), at constant $[CD]_t = 10$ mM

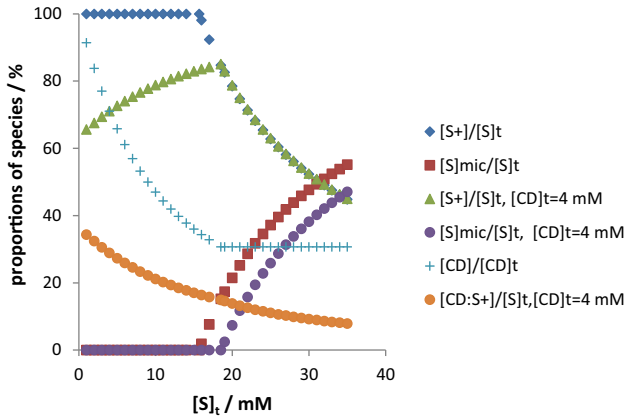

Fig. 7 Dependencies of equilibrium proportions (%) of different species occurring in C_{12}TAB/water/ß-CD ternary system at constant $[CD]_t = 4$ mM and C_{12}TAB/water binary system upon total surfactant concentration, $[S]_t$; $T = 313.2$ K

micellar aggregates. In the coexistence of micellization and complexation equilibriums, surfactant molecules thus exist in free, complexed with CD and micellized states.

Results in Fig. 7 show that the percentage of uncomplexed cyclodextrin decreases to the 30.7 % at $[S]_t = 18.5$ mM (experimental determined CMC*) and is then constant in equilibrium with the micellar system. From this concentration the percentages of free surfactant monomers in a system without and with ß-CD are equal, and indicate the same constant $[S^+] = CMC$ in both systems.

An important aspect of the results obtained in the present study is that the critical micelle concentration in the presence of a cyclodextrin is equivalent to the combined concentrations of surfactant monomers complexed with the ß-CD, and that of a free dissolved monomer in equilibrium with the micellized surfactant: $CMC^* = [CD:S^+] + CMC$. At surfactant concentrations above the CMC*, competition between the micellization and complexation processes leads to the existence of a significant concentration of free CD in equilibrium with the micellar aggregates. The percentage of uncomplexed cyclodextrin in equilibrium with the micelles is independent on cyclodextrin concentration for a particular ternary system and is 31, 37, 34 % for C_{12}TAB/water/ß-CD, C_{14}TAB/water/ß-CD and C_{16}TAB/water/ß-CD, respectively.

By using standard Gibbs free energy for micellization and surfactant complexation by CD, we can explain the observed behavior. An increase in the hydrophobicity of the surfactant gives rise to an increase in its affinity to complex with the CD but simultaneously implies in its tendency to micellize. For alkyltrimethylammonium bromides micellization is more favorable than cyclodextrin complexation: $-\Delta G^0_{mic} > -\Delta G^0$, i.e. the autoaggregation of surfactant monomers is more important than the complexation process in this mixed system. As a consequence a high percentage of uncomplexed cyclodextrin can be observed in equilibrium with the micellar system.

Conclusions

The micelle formation and the formation of CD:S^+ inclusion complexes are governed by the hydrophobic effect. The results obtained in this study have allowed us to confirm that for alkyltrimethylammonium bromides micellization is more favorable than cyclodextrin complexation: $-\Delta G^0_{mic} > -\Delta G^0$, i.e. the autoaggregation of surfactant monomers is more important than the complexation process in this mixed system.

The effect of adding cyclodextrin to a micellar solution we can predict by applying Le Chatelier's principle on two simultaneous equilibria: incorporating of surfactant monomers into the CD cavity leads to a decrease in the amount of "free" S^+ ion, which tied up as CD:S^+ complex ions. As a result, adding ß-CD cause more micelles to dissolve to attain equilibrium concentration of S^+ that is equal to CMC. And as a consequence, a high percentage of uncomplexed cyclodextrin, independent on cyclodextrin concentration can be observed in equilibrium with the micellar system.

From mathematical model the concentrations of the uncomplexed cyclodextrin, uncomplexed surfactant ion (S^+), and inclusion complex (CD:S^+) in the submicellar, as well as in the micellar range were calculated. For a particular ternary system CMC* can be determined on the basis of known CMC and percentage of uncomplexed cyclodextrin in equilibrium with the micelles.

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