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The formation of host-guest complexes between surfactants and cyclodextrins

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Abstract

Cyclodextrins are able to act as host molecules in supramolecular chemistry with applications ranging from pharmaceutics to detergency. Among guest molecules surfactants play an important role with both fundamental and practical applications. The formation of cyclodextrin/surfactant host-guest compounds leads to an increase in the critical micelle concentration and in the solubility of surfactants. The possibility of changing the balance between several intermolecular forces, and thus allowing the study of, e.g., dehydration and steric hindrance effects upon association, makes surfactants ideal guest molecules for fundamental studies. Therefore, these systems allow for obtaining a deep insight into the host-guest association mechanism. In this paper, we review the influence on the thermodynamic properties of *CD*-surfactant association by highlighting the effect of different surfactant architectures (single tail, double-tailed, gemini and bolaform), with special emphasis on cationic surfactants. This is complemented with an assessment of the most common analytical techniques used to follow the association process. The applied methods for computation of the association stoichiometry and stability constants are also reviewed and discussed; this is an important point since there are significant discrepancies and scattered data for similar systems in the literature.

In general, the surfactant-cyclodextrin association is treated without reference to the kinetics of the process. However, there are several examples where the kinetics of the process can be investigated, in particular those where volumes of the CD cavity and surfactant (either the tail or in special cases the head group) are similar in magnitude. This will also be critically reviewed.

Contents of paper:

1. An introduction to cyclodextrins and surfactants

Cyclodextrins (*CD*s) are a series of cyclic oligosaccharides formed through α(1-4) ether linkages of glucopyranose units [1,2]. The most commonly used *CD*s are the α-, β- and γ- cyclodextrins, having six, seven and eight glucoside unities, respectively. Among them, β-*CD* is the most commonly used, due to relative ease of synthesis, low price and also to the size of its internal cavity into which a large number of guest molecules will fit. However, β-*CD* has a major drawback: the low solubility in water when compared with α- and γ-*CD*s. This is often discussed in terms of the relatively strong binding of β-*CD* molecules in the crystal state [3] and intramolecular hydrogen bond within the β-*CD* ring, preventing their hydrogen bond formation with surrounding water molecules [4,5]. *CD*s have the shape of a truncated cone with internal cavities ranging from 5 to 8 Å. The C-H bonds on the ring point inward producing a hydrophobic cavity. The nonbonding electron pairs of the glycosidic oxygen bridges are directed toward the inside of the cavity, producing a high electron density and lending it some Lewis base character. The primary and the secondary hydroxyl groups are located on the narrow and wide rims, respectively, of the truncated cone [6]. As a result of this spatial arrangement of the functional groups in the cyclodextrin molecules, the cavity shows a relatively hydrophobic character while the external surfaces are hydrophilic.

Although the synthesis of cyclodextrins was initially reported in 1891 by Villiers [7], it was only after the works of Schardinger [8], in the first decade of the 20th century, and of Szejtli, in the 1970s [9], that these molecules become popular among the scientific community. The number of publications dealing with various aspects of cyclodextrins have increased ca. 40 % in the last decade (2002-2012) when compared with the previous decade (*Web of Science*®, accessed at 20.12.2012). Such attractiveness is justified by the ability of cyclodextrins' cavity to include a large range of guest molecules, such as drugs [10-17], surfactants [18-22], dyes [23-28], polymers [29-31] and inorganic salts [32-37], while the hydrophilic exterior renders *CD*s water soluble [38].

Cyclodextrin host-guest complexes may impart beneficial modifications of the properties of guest molecules such as solubility enhancement [39-41], stabilization of labile guests [42-44], physical isolation of incompatible compounds and control of volatility and sublimation [45-47]. These properties, complemented with their non-toxicity toward humans, make these molecules highly suitable for a large range of

applications [48], including food technology [49,50], pharmaceutical and biomedicals [5,29,51-55], cosmetics [56,57], textile [58-62], analytical chemistry [63-65], chemical synthesis and catalysis [66-72], waste water and soil treatment [73-79], and corrosion coatings [80-82].

Cyclodextrins are also important in the context of the control of thickening of hydrophobically modified polymers, e.g., ethyl(hydroxyl ethyl) cellulose and modified poly(ethylene glycol) in water, by decoupling hydrophobic-hydrophobic intermolecular interactions [83-85].

Recently, Lindman et al. have shown that β- [86], 2-hydroxypropyl-β- [87], and α-cyclodextrins [88] can be efficiently used for decompaction of DNA-cationic surfactant complexes [89], on account of the high strength of the specific surfactant-cyclodextrin interactions, when compared with surfactant-DNA interactions. Similar studies were then carried out with *CD*-DNA-lipid systems [90,91]. The formation of inclusion compounds between *CD* and lipids allows one to control lipids self-assembly and, consequently, the DNA compaction/decompaction process.

The formation of the host-guest supramolecular complexes involving an amphiphilic compound and a cyclodextrin is driven by non-covalent interactions, including van der Waals, hydrophobic, electrostatic and charge transfer interactions, metal coordination, hydrogen bonding and steric effects [92,93]. The formation of these host-guest complexes allows one, by tunning the amphiphilicity of guest molecules, to control the assembly and disassembly of the supramolecular structure [93]. In aqueous solutions, the inclusion of the (dehydrated) guest into the non-polar cavity of the *CD* is accompanied by the release of water from the *CD* cavity. The latter process is strongly dependent on the interactions between water-water and water-cyclodextrin occurring inside the cyclodextrin cavity [94-96], and it also depends on other factors, including the size of both the cyclodextrin cavity and guest as well as the structure (geometry) of guest molecules [97,98].

Another factor that may influence the formation of host-guest compounds is the self-aggregation of *CD* in water [99-101]. It is however unclear how large fraction of the *CD* that takes part in the aggregation. Some papers report mass contributions of aggregates in α-, β- or γ-*CD* aqueous solution of 0.001 %, 0.0011 % and 0.02 % for initial concentrations of 12, 10 and 12 mM, respectively [102,103]. These low fractions of aggregated *CD* could explain why there are no evidences of aggregates as seen by ^{1}H NMR self-diffusion [104] or intermolecular diffusion, since these methods monitor the

entire *CD* population [105-107]. If *CD* aggregation occurs, the evaluation of the binding constants in cyclodextrin-containing supramolecular structures becomes rather complicated.

Although much of the discussion on the host-guest association is based on the interactions between the guest and cyclodextrin cavity, the role of the hydrophilic part of cyclodextrin cannot be neglected [108]. For example, interactions between gemini surfactants and β-cyclodextrin appears to be affected by the hydrophilic part of the cyclodextrin [19]; on the other hand, the hydration shell of the highly soluble calcium lactate decreases in the presence of cyclodextrins [109], suggesting that *CD* has a structure-making effect on water [4].

Surfactants are of particular interest as guest molecules due to the balance of several intermolecular forces: the hydrophobic effect which tends to protect the tail from the aqueous environment, the requirement of dehydration of tails and head groups during complex formation, as well as effects due to steric hindrances. Surfactants also allow for carrying out systematic studies on the association (binding) process, by changing the surfactant structure and thus achieving a necessary balance between hydrophilic and hydrophobic contributions. This generally leads to changes in the physicochemical properties of surfactants, such as, e.g., the critical micelle concentration, of crucial importance for commercial formulations [110,111], from detergents and cleaners to cosmetics including detergency and personal care products [112,113].

The effect of *CD*s in micelle-containing amphiphilic solutions or in surfactant muticomponent systems (e.g., cationic/anionic surfactant-cyclodextrin mixed systems [114-118]), normally characterized by multiple competitive equilibria, is outside the scope of the present review; however, several interesting and significant works in this area have recently been published [21,119,120].

In this review we will focus on several aspects related to surfactant-cyclodextrin host-guest association including fundamentals, drawbacks and advantages of techniques commonly used to obtain insights on the structural and bulk solutions changes resulting from host-guest association mechanism, and corresponding methods for binding quantification, as well as to carry out a critical assessment on different systems involving surfactants and natural cyclodextrins.

2. Techniques for measuring association between cyclodextrins and surfactants

Mixed cyclodextrin-surfactant systems have been studied from the point of view of fundamental issues but also on account of their role in practical applications. Host-guest interactions lead to measurable changes in physical-chemistry properties of the corresponding systems and thus, depending on the techniques used, structural and thermodynamic information on the binding process can be obtained. According to Mwakibete *et al.* [121], and recently reviewed by Brocos *et al.* [122], the available experimental techniques can be subdivided into two categories, labeled as I and II. Methods from group I, which includes electrical conductivity and isothermal titration calorimetry (ITC), take advantage of the existence of any physically observable properties that are proportional in some way to the extent of binding, while those from group II (e.g., ^{1}H NMR spectroscopy) rely on direct measurements of the free and bound ligand in a solution containing a known amount of the cyclodextrin and surfactant. They also claim that only techniques belonging to group II, with the exception of ITC [122], are able to produce reliable and accurate binding constants. Such a division must be carefully considered for several reasons. One of them is the number of experimental data points used for the computation of binding constants. It is often found that, even for Group II techniques different initial conditions can lead to different binding constants [123-125].

Here we present a critical assessment on the most common techniques used to follow cyclodextrin-surfactant association by giving a resume of their background and drawbacks.

NMR has been used to determine association constants through the use of chemical shift changes [126,127], which is limited to substrates that induce a significant chemical shift on cyclodextrin upon complexation (or vice versa) and on the absence of host and guest overlapping resonances. Changes in relaxation times have also been measured [128,129], but the interpretation of the data is model dependent and less straightforward than data from self-diffusion measurements, which are conceptually easier and often nowadays experimentally easy to obtain. NMR diffusometry has been used to study inclusion complexes between cyclodextrin and different substrates [130-133]. The self-diffusion measurements are in principle applicable to any systems as long as the free and complexed guests (please note that on account of the rapid exchange on the NMR time scale, average diffusion coefficients for both the guest and for the *CD* are obtained) are soluble to an extent that allows for a good signal-to-noise ratio. The method relies on the fact that the self-diffusion coefficients of the uncomplexed guest are smaller than

the self-diffusion of the host−guest complex (recall that the self-diffusion scales with inverse size). Clearly, the method works better when the guest and host differ significantly in size. The change in self-diffusion coefficient of the *CD* upon complexation is often small since the complex is often of the same size as the *CD* molecule, and the information from the *CD* self-diffusion is rather limited. On the other hand, the change of the self-diffusion of the surfactant is often large, and it is here that the main informations about the complexation and binding constant are conveyed [134].

Electrical conductivity is a simple routine technique, leading to quick and reliable data that provide information on the structure of ionic solutions, including solvated ionic radii, solvation enthalpy and the degree of counter ion dissociation [135-137]. In the case of ionic surfactant-based solutions, electrical conductivity has been successfully used for determination of critical micelle concentration and degree of counter ion dissociation of micelles [138-140], or in the case of multicomponent systems, such as polymer-surfactant or multivalent salt-surfactant, polymer saturation points [141] and critical aggregation concentrations (see, e.g., [142]). That is, even in systems where the interpretation becomes rather complicated as a consequence of multiple contributions for the overall ionic conductance, electrical conductivity measurements may discriminate between structural or configurational changes as a consequence of counter-ions release (or charge neutralization followed by structural re-arrangements) or by significant changes in the size of ionic species. An example of the latter includes the formation of host-guest supramolecular structures [125,143,144] involving ionic surfactants and cyclodextrins. The application of this technique is limited to non-associated surfactants and to systems with relatively high binding constants. Furthermore, the application of models for quantification of binding constants relies on a number of assumptions, such as the neglect of the variation of dissociation degree as a function of concentration and ion pair formation.

Calorimetry is a useful and accurate technique that allows the direct determination of thermodynamic properties (binding constant, binding stoichiometry, enthalpy, entropy and heat capacities of complex formation). In fact, isothermal titration calorimetry (ITC) is the most direct method to measure the heat change on formation of a complex at constant temperature [145]. The experiment is performed by titrating a small volume of cyclodextrin (surfactant) with small aliquots of a surfactant (cyclodextrin) solution. After each addition, the heat released or absorbed in the sample cell is measured with respect to a reference cell. As a consequence of the experimental procedure, the heat of

dilution of surfactant or cyclodextrin must be subtracted from the experimental heat measured in order to obtain accurate values of the heat related to the binding process [146].

Figure 1 shows the raw data of an ITC experiment and the corresponding heat released upon addition of dodecane-1,12-bis(trimethylammonium bromide) to a β-cyclodextrin solution [98]. The profile of the thermal power as a function of injection number is of importance since reliable thermodynamic parameters can only be computed if there is a well defined inflection point in the binding curve [147]. This point can be found by tuning host and guest concentrations and/or the temperature [98].

These techniques are commonly used to obtain information concerning the formation of host-guest surfactant-cyclodextrin complexes; however, there is a number of other techniques used to get static and dynamic information about these interactions, which will be described below.

The speed of sound in a liquid solution depends on the perturbation of medium particles to the ultrasound waves, and can be related to the size and shape of molecules [148]. From this principle, several surfactant-cyclodextrin systems, including decyltrimethylammonium bromide-, SDS- and dodecyltrimethylammonium bromide-β-*CD* [149-151] have been studied. Later, speed of sound measurements has been coupled to density measurements [152-155] allowing the calculation of thermodynamic properties, such as molar apparent and partial volumes and adiabatic compressibilities, which are sensitive to the degree and nature of the solute hydration, and thus information about the nature of the complex, the stoichiometry, and the effect that the *CD* has on the surfactant micellization can be obtained.

Ultrasonic relaxation technique is based on the application of ultrasound to a given solution, with a frequency ranging from 20 kHz to several GHz, and subsequently measuring the molecular structural relaxation. The relaxation is sensitive to molecular volume changes [156] and, therefore, may convey information on the stability constants of host-guest complexes [157]. Furthermore, the use of a large frequency range allows one to follow processes with relaxation times in the range from 20 ps to 20 μs [158-160] and thus the kinetics of *CD*-surfactant association can be investigated [157]. Aicart et al. studied the effect of surfactant unimer-micelle exchange for decyltrimethylammonium bromide (DTAB) [161] or sodium perfluorooctanoate [162] micelles in the presence of β-*CD*/surfactant complexes; they found that in both cases the unimer-micelle exchange

is unaffected by the presence of β-*CD* or β-*CD*:surfactant complexes. However, Haller and Kaatze, showed that the dynamics of unimer-micelle exchange, in a sugar-based surfactant (octylglucopyranoside) [20] or DTAB [155], can be quantified in the presence of α-*CD*.

Potentiometric techniques, especially those involving surfactant selective electrodes [163], have also been used to study the stability of cyclodextrin-surfactants complexes. The drawbacks of this technique derive from properties of the selective electrode itself, since the response of these electrodes is dependent on the presence of interfering species and also the need of a Nernstian-like behaviour (i.e., a linear relationship of the measured EMF as a function of the logarithmic concentration) for the quantification of free surfactant in solutions. This is normally achieved by adding an electrolyte (e.g., NaBr) to maintain a constant ionic strength [164]. The study of the complexation between alkyltrimethylammonium acetates and β-*CD* has been reported by Jezequel et al. by using a surfactant concentration range between 0.01 and 0.1 mM [165]. Other studies using potentiometric techniques to investigate the surfactant-cyclodextrin host-guest formation can be found [123,124,166-171].

The use of spectrophotometric techniques to follow and quantify the complexation between *CD* and a surfactant depends on the use of a UV, visible or fluorescent sensitive probe [172-180]. In order to obtain thermodynamic parameters with a satisfactory accuracy it is necessary to choose a probe that exhibits a large absorbance or emission intensity that changes upon the addition of a small amount of *CD* to a surfactant solution; this implies that the association constant of *CD*:probe cannot be too low [181,182]. Another important issue that must be taken into consideration is the balance between association constants of *CD*:probe and *CD*:surfactant, since two competitive equilibria are occurring, the differences of association constants should be high enough to allow for the incorporation of surfactant in the *CD* cavity. These techniques have also been applied to study complexation between cyclodextrins and fluorophoric surfactants [183,184].

The formation of host-guest complexes influences the kinetics of different reactions [28]. When the reaction rate decreases due to the presence of *CD*s, these can be used as stabilisers; however, of more interest are the situations in which *CD*s accelerate reactions or may even participate directly in guest hydrolysis [185,186]. Following this principle, the kinetic analysis of competing reactions involving surfactants,

cyclodextrins and a third species allows one to obtain information about the complexed and uncomplexed concentration of cyclodextrins and thus to calculate the corresponding binding constants [187-191]. Garcia-Rio and coworkers have developed models that allow the computation of stability constants for *CD-S* host-guest association by measuring the rate constants of solvolysis of chemical probes, such as, crystal violet [28], 4-methoxybenzenesulfonil chloride [192], benzoyl chlorides [193], *N*-nitrososulfonamide [194] and *m*-nitrophenyl acetate [195].

Surface tension has also been used to follow the effect of cyclodextrins on the aggregation and interfacial properties of surfactants [22,196-198] as well as the effect of different additives (*e.g.* NaBr) on the critical micelle concentration (*cmc*) of surfactants (*e.g.*, TTAB and CTAB) in *CD*-surfactant-containing solutions [199]. There are several cases, where surface tension measurements have been used to assess the stoichiometry and stability constants of host-guest complexes [116,200-207].

There are other techniques for studying surfactant-cyclodextrin complexation. For example, polypyridyl ruthenium(II) and cobalt(III) complexes were chosen as electroactive probes to study surfactant-cyclodextrin (CD) complexation by means of cyclic voltammetry [208]. Alami *et al.* [197] were the first ones to use small-angle neutron scattering to obtain information on the structure of complexes formed between a non-ionic hetero-gemini surfactant and a series of cyclodextrins. Also, intermolecular diffusion coefficients have been measured to characterize the mass transport of SDS in aqueous solutions with and without the presence of β-*CD* [209].

3. Assessment of the methods for computation of binding constants

A quantitative analysis of the host-guest association is a key issue for a complete assessment on the supramolecular compound properties. However, the estimation of binding constants is a difficult task and very often, binding constant for the same system are reported in literature differing by one, or several, orders of magnitude [122,125,144].

As discussed in the previous section the binding process can be quantitatively followed by changes in the magnitude of any physical property that is proportional to the extent of binding and/or rely on direct measurements of free or bound cyclodextrin or guest molecule.

An important point that must be addressed prior to the calculation of binding constants is the binding stoichiometry. The method of continuous variation or Job's method [210,211] has been used to determine the stoichiometry of the *CD*:surfactant host-guest supramolecular association. The method is based on the analysis of a measurable physical parameter (*Y*), e.g. ^{1}H NMR chemical shifts or UV-visible maximum absorbances, proportional to the complex formation, for a series of *CD*:*S* mixtures, in which the total concentration of the two species is kept constant, and the mole fractions of each component (x_i, with i=*S* or *CD*) vary from 0 to 1. This analysis is based on the assumption that the quantity $\Delta Y \bullet [CD]$ (or $\Delta Y \bullet [S]$), where $\Delta Y = Y(\text{mixture}) - Y(\text{free})$, is proportional to the complex concentration [212] and its maximum, as a function of x_{CD} (or x_S), corresponds to the stoichiometry of the *CD*:*S* association.

An evaluation of the stoichiometric ratio between a guest molecule and the *CD* (host) can also be given by plotting changes in some physical property, ΔY, of the mixed *CD*/*S* solution as a function of cyclodextrin concentration, by keeping constant the surfactant concentration (or vice-versa). At low *CD* concentrations, a linear change of the physical property with increasing *CD* concentration is expected. Upon further addition of *CD* a rather smoothly changing slope of the curve appears until a plateau is reached at high concentrations of *CD*. The intersection of a straight line, obtained by fitting the initial decrease of ΔY as a function of [*CD*], and the constant value of ΔY (reached for an excess of cyclodextrin or surfactant) can been used to give an estimation of *CD:S* stoichiometry [213]. However, such a procedure is dependent on the magnitude of the association constant, and for low *K* values only gives a rough stoichiometric ratio of the *CD:S* association, since it is experimentally difficult to obtain two well defined linear regions (Figure 2-A); again, this can be overcome by plotting the resulting Job's plot (see Figure 2-B).

In general, the formation of the host-guest supramolecular structure is a reversible process that can be described through the following equation:

$$mCD + nS \underset{\longleftarrow}{\overset{K_{m,n}}{\longrightarrow}} CD_m - S_n \qquad (1)$$

where *m* and *n* are stoichiometry coefficients and $K_{m,n}$ is the binding constant.

The large majority of reported cases involve m=1 and n=1, and m=2 and n=1 (or m=1 and n=2). Here, we focus on these cases. For more complex stoichiometries, the computational treatment of the resulting equations (not shown) is not straightforward as a consequence of multi-collinearity [214]. Multi-collinearity causes larger standard

errors in the quantities calculated and lower statistical significance of the results In limiting cases, several local minima may be obtained by iteration; these correspond to noticeably different combinations of the quantities calculated, and may be the reason why different *K* values are reported for the same host-guest systems.

The stability of the inclusion complexes, *CD-S* and CD_2-*S*, can be described in terms of the association constant, $K_{1,1}$ and $K_{2,1}$:

$$K_{1,1} = [CD-S] / \left([CD]_f [S]_f \right) \quad (2)$$

$$K_{2,1} = [CD_2-S] / \left([CD]_f [CD-S] \right) \quad (3)$$

where $[CD]_f$ and $[S]_f$ are the concentration of uncomplexed (free) species in the system. Conservation of mass gives:

$$[S]_f = [S]_T - [CD-S] - [CD_2-S] \quad (4)$$

and

$$[CD]_f = [CD]_T - [CD-S] - 2[CD_2-S] \quad (5)$$

where $[S]_T$ and $[CD]_T$ are the total concentration of surfactant and cyclodextrin, respectively.

3.1 Modelling CD:S association at pre-micelle concentrations

On the assumption that a 1:1 complex (*CD-S*) is formed, the association constant (Eq. 2) can be re-written as

$$K_{1,1} = \frac{f}{(1-f)([CD]_T - f[S]_T)} \quad (6)$$

where *f* is the fraction of surfactant complexed with cyclodextrin.

If the binding process is monitored by ^{1}H NMR shift data, and assuming that the condition of fast exchange on the NMR time-scale applies, the observed chemical shift for a host molecule is expressed as

$$\delta_{obs} = (1-f)\delta_{CD,f} + f\,\delta_{CD-S} \quad (7)$$

where $\delta_{CD,f}$ and δ_{CD-S}, represent the chemical shift of a given nucleus when free and complexed, respectively.

The chemical shift change of a given nucleus of the cyclodextrin, in the presence and absence of a guest molecule, $\Delta\delta_{obs} = \delta_{obs} - \delta_{CD}$, can be expressed as

$$\Delta\delta_{obs} = \frac{\Delta\delta_{CD-S}}{[CD]_T}[CD-S] \quad (8)$$

which, after some algebraic manipulation and simplification, results in [215,216],

$$\Delta\delta_{obs} = \frac{\Delta\delta_{CD-S}}{2[CD]_T}\left\{\left([S]_T + [CD]_T + \frac{1}{K_{1,1}}\right) - \left(\left([S]_T + [CD]_T + \frac{1}{K_{1,1}}\right)^2 - 4\left([S]_T\,[CD]_T\right)\right)^{1/2}\right\} \quad (9)$$

Eq.(9) is then fitted to the experimental data using a non-linear least-squares algorithm, to obtain the fitting parameters $K_{1,1}$ and $\Delta\delta_{CD-S}$. This and similar approaches for other physical properties have been used with some success for the determination of large stability constants, frequently in conjunction with stoichiometric ratios extracted from Job plots. However, for low values of $[CD]_T$ and $[S]_T$, or/and low values of $K_{n,m}$ the use of these equations may pose some problems, which we illustrate for the simpler 1:1 case. Similar results can be obtained for the 2:1 stoichiometry. When *y* is sufficiently small $x - \sqrt{x^2 - y} \approx y/2x$, and Eq. (9) reduces to

$$\Delta\delta_{obs} = \frac{\Delta\delta_{CD-S}}{W + \left(1/K_{1,1}\right)}[S]_T \quad (10)$$

where $W = [CD]_T + [S]_T$. If *M* is kept constant in the experiments, as is common practice when Job plots are used to obtain stoichiometries, the observed displacement varies linearly with $[S]_T$ or $[CD]_T$, but the fitting parameters are present in the form of a ratio that generates an infinite number of acceptable solutions. Consequently, it is suggested that *W* should be chosen in such a way that its value should be of the same order of magnitude than $K_{1,1}^{-1}$ [217,218].

A different approach for computation of association constants, on the basis of, e.g., chemical shifts of *CD* and/or *S* bound nuclei is based on the assumption that the interaction between *CD* surfactants and *S* leads to a 2:1 complexation, in a two step mechanism. Assuming fast-exchange on the NMR time-scale [219], the observed chemical shift δ_{obs} of *CD* is given by:

$$\delta_{obs} = \frac{[CD]\delta_{CD} + [CD-S]\delta_{CD-S} + 2[CD_2-S]\delta_{CD_2-S}}{[CD] + [CD-S] + 2[CD_2-S]} \quad (11)$$

where δ_{CD}, $\delta_{CD\text{-}S}$ and $\delta_{CD2\text{-}S}$ are the chemical shifts of the free *CD*, 1:1 and 2:1 *CD:S* complexes, with concentrations [*CD*], [*CD*-*S*] and [CD_2-*S*], respectively. As above, Eq.

(11) is based on the assumption that the observed shifts are population weighed averages of the different species present. Taking into account the mass balance and mass action laws, the concentrations of the different species can be given as a function of the free cyclodextrin concentration, [*CD*], through a cubic polynominal equation (for a mathematical background see, for example, ref. [213]):

$$[CD]^3+\left(\frac{1}{K_{2,1}}-[CD]_T+2[S]_T\right)[CD]^2+\left(\frac{1}{K_{1,1}K_{2,1}}-\frac{[CD]_T}{K_{2,1}}+\frac{[S]_T}{K_{2,1}}\right)[CD]-\frac{[CD]_T}{K_{1,1}K_{2,1}}=0 \qquad (12)$$

The free cyclodextrins concentration can be estimated through an analytical solution of the real solution of a third-degree equation, using the Cardin-Tartaglia formulae [220].

The number of experimental data points used to fit Eqs. (11) and (12) affects the computation of stability constants, as it will be discussed. The fitting parameters computed from those equations and using the experimental ^{1}H NMR chemical shifts of H_3 and H_5 β-*CD* nuclei [129], located inside the *CD* cavity, for mixed solutions with different [β-*CD*]/[12-6-12] molar ratios, and keeping [β-*CD*] constant – titration method, are giving in the Table 1. The computed chemical shift fitting parameters show that despite a low imprecision (below 3 %), the fitting convergence has been reached for $\delta^T_{CD}=\delta^T_{CD\text{-}S}$ (no fitting constrains have been applied); the latter result means that the *CD* internal protons (H_3 and H_5) are not affected by the incorporation of the surfactant into the *CD* cavity, which has no physical meaning. Carvalho *et al.* overcome this drawback by increasing the number of points used for the fitting process, by performing a global fit [19,221] of the chemical shifts of the H_3 and H_5 β-*CD* nuclei, obtained from the methods of titration and continuous variation. For the β-*CD*:12-6-12 system we have 2 association constants and a total of 12 shifts (for 3 species in 4 different experiments). Their approach was based on: i) shift values for free *CD* can be obtained from independent experiments and, consequently, these values can be locked in the fit; and ii) the assumption that the variation in the *CD* shift is due to the fact that the gemini threads the *CD*. Furthermore, it was also argued that the shift change should be the same for the 1:1 and for the 2:1 complexes (i.e. $\delta_{CD\text{-}S}=\delta_{CD2\text{-}S}$). With that, the number of fitting parameters has been reduced to 6 (2 binding constants and 1 shift for each proton). Additionally, the number of fitting parameters was further reduced to 4, by noting that the shift for the complexes should indeed be independent of the method. The calculated binding constants and other fitting parameters, by using this approach, are given in Table 1. By increasing the accuracy of the fitted parameters, it was concluded that: a)

the applied model predicts quite similar chemical shifts for the same protons using different sets of results, showing the reliability of the used fitting procedure; and b) $K_{1,1}$ is one order of magnitude higher than $K_{2,1}$, which is characteristic of an anti-cooperative binding mechanism, in agreement with previous findings from a conductometric technique, for identical systems [213].

It is also important to stress that the use of a global fit by using experiments carried out with different initial concentrations of cyclodextrins (or surfactants) gives higher quality in the obtained results.

Finally, it can be expected that the standard deviation of the binding constants increases by increasing the number of fitting parameters [222], and normally increases for increasing values of *K* [134].

Another common approach for simultaneous computation of stoichiometry and association constants of host-guest complexes is given by the modified Benesi-Hildebrand treatment [223] for any physical parameter measurements, although the most used are UV-visible absorbances [224] or emission fluorescence intensities [225,226]. For this reason this approach is rarely used for surfactant-cyclodextrin association processes [227,228]. The relation used is

$$\frac{F_0}{F - F_0} = \frac{1}{A} + \frac{1}{AK_O[CD]^n} \qquad (13)$$

where F_0 and F are the initial fluorescence of the guest in the absence and presence of cyclodextrin, respectively, and A is a constant. The application of Eq. (13) will allow the simultaneous determination of the stoichiometry (n) and the corresponding overall association constant (K_O) for the association process. Hu *et al.* [229] point out that for systems with weak or strong interactions the application of Eq. (13) can lead to misleading fitting parameters; furthermore, there is a necessary but not sufficient condition that must be at hand to ensure accuracy in the fitting procedure, namely that $1/(K_O[CD]) \geq 10$.

3.2 Modelling CD:S association at surfactant concentrations below and above the cmc

In general, the addition of surfactant to a cyclodextrin solution results in three distinct regions (see, for example, Figure 3), which can be described as follows: a) at surfactant concentrations lower than *CD* concentrations, a complexation equilibrium between the

surfactant and the cyclodextrin is established and, consequently only complexes and free excess cyclodextrins exist in solution (region A - Figure 3); b) when the surfactant concentration exceeds the stoichiometric ratio with *CD*s, the concentration of surfactant unimers increases until c) surfactant micellization occurs (region C-Figure 3). The self-aggregation concentration (*cac*) of a surfactant system in the presence of 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 (i.e., for a *m*:*n* (*CD:S*) complexation, $cac=(m/n)[CD]_T+cmc$, where *cmc* is the critical micelle concentration of the surfactant) [134,219,230,231]. It should be stressed that this has been used by different authors [151,172] as an alternative strategy to determine the stoichiometry of the *CD:S* complex.

This complex behavior of three distinct regions depending on the surfactant concentration has been developed to describe self-diffusion coefficients of cyclodextrin and surfactant, in the whole surfactant concentration range. The established procedure to interpret concentration dependent NMR diffusion data in systems where the surfactants are present in two or more distinct states is to make use of a *n*-site exchange model, in which the number and nature of sites are identified and the observed diffusion coefficient is expressed as a population weighed average between the various sites. In the present case assuming a 1:1 complexation, we may identify three different sites: free surfactant, *CD-S* complexes and micellized surfactants. The experimental self-diffusion coefficient of the surfactant, D_S, is then

$$D_S = D_{CD\text{-}S}\,(f_{CD\text{-}S}) + D_{S,f}\,(f_S) + D_{S,M}\,(f_M) \qquad (14)$$

where $D_{CD\text{-}S}$, $D_{S,f}$ and $D_{S,M}$ are the complex, surfactant unimer, and surfactant micelle diffusion coefficients, respectively; f_S, $f_{CD\text{-}S}$ and f_M are the fractions of free, complexed and micellized surfactant, respectively, as given by

$$f_S = ([S]_T - [\text{CD-S}]) / [S]_T \qquad (15)$$

$$f_{CD\text{-}S} = [\text{CD-S}]_{cac} / [S]_T \qquad (16)$$

$$f_M = ([S]_T - cac) / [S]_T \qquad (17)$$

where $[CD\text{-}S]_{cac}$ is the concentration of the complex at the *cac*, which can be assumed as constant at surfactant concentrations higher than the *cac*.

In a similar way, the observed *CD* self-diffusion coefficient, D_{CD}, can be defined through

$$D_{CD} = D_{CD,f}\,(f_{CD}) + D_{CD\text{-}S}\,(1-f_{CD}) \qquad (18)$$

where $D_{CD,f}$ is the self-diffusion coefficient of free (non-complexed) cyclodextrin, and f_{CD} is given by

$$f_{CD} = ([CD]_T - [\text{CD-S}]_{cac}) / [CD]_T \qquad (19)$$

Eqs. (14) and (18) have been successfully applied to the study of association between cyclodextrins and alkyltrimethylammonium bromides [134], and alkyl β-D-glucoside surfactants and cyclodextrins. However, it was found that at surfactant concentrations higher than the *cac*, the model predicts values of D_{CD} that deviate from the experimental data. This was explained as being caused by an obstruction effect between the *CD*-complexes and the surfactant micelles. A simple obstruction model, based on the assumption that the particles interact as hard spheres, gives [232]

$$\frac{D}{D_0} = \left(1 + \frac{\phi}{2}\left(1 + \frac{r}{R}\right)^3\right)^{-1} \qquad (20)$$

where ϕ is the volume fraction of obstructing particles and D/D_0 is the diffusion of the particle of radius r in the presence/absence of obstructing particles of radii R. Equating $1/2(1+r/R)^3$ with a constant k, Eq. (18) can be re-written as

$$D_{CD} = [D_{CD,f}\,(f_{CD}) + D_{CD\text{-}S}\,(1-f_{CD})] / (1+k\,\phi) \qquad (21)$$

The obstruction effect experienced by the surfactants can be neglected since its contribution cannot be separated from the decrease in the surfactant diffusion on account of the micellization process [233].

4. Effect of surfactant's chain and headgroup on the association process with cyclodextrins

A large number of studies on host-guest cyclodextrin-surfactant interactions treats salts of alkyltrimethylammonium or alkyl sulfates. Often, dodecyltrimethylammonium bromide (C_{12}TAB), or sodium dodecyl sulfate (SDS), are used as reference systems in the analysis of more complex systems. Recently, a relevant and extensive review treating SDS-cyclodextrin interactions was published [122]. Therefore, we focus this overview on cationic surfactants including a variety of surfactant architectures (monomeric, double-tailed, gemini and bolaform surfactants).

4.1 Cationic single chain surfactants

Tables 2 to 4 show an extensive set of published data on the thermodynamic properties of alkyltrimethylammonium bromide (C_nTAB), and β-, α- and γ-cyclodextrins mixed

solutions, respectively, at different temperatures. It is clear that the binding constants, for a given surfactant, vary considerable with differences typically larger than one order of magnitude. The values obtained depend on the experimental method and/or model used to interpret the data. Nevertheless, an attempt is given below to extract information of the influence of the surfactant chain length, headgroup and counter ion, as well as the effect of cyclodextrin size and functionalization. Effects due to temperature and solvent on the binding are also discussed. Unless stated otherwise, the discussion is based on interactions between surfactants and cyclodextrins at the pre-micelle concentrations.

Starting with the effect of alkyl chain length on the interaction between C_nTAB and β-*CD*, the large majority of *K* values indicate that from hexyl to dodecyltrimethylammonium bromides, 1:1 complexes are formed with increasing binding constants as the surfactant tail length increases. For example, Cabaleiro-Lago *et al*. [134], by using ^{1}H NMR self-diffusion, showed that the experimental data for C_6TAB to C_{14}TAB can be fitted by a 1:1 complexation model, giving *K* values ranging from 66(±2) to 23(±5)×10^3 M^{-1}, respectively. However, the standard free energy of binding ΔG^0_b decrease up to C_{12}TAB and levels off for C_{14}TAB. Taking the inner volume of the β-*CD* cavity as equal to 270 Å^3, and the volume of a methylene group as 27 Å^3, it may be estimated that 8 to 10 -CH_2- groups can be accommodated inside the cavity. The exposure to water of some methylene groups of C_{14}TAB allows the second binding of *CD* although in just a partial way. Such view is consistent with $K_{2,1}<K_{1,1}$ predicting a preferential 1:1 complex [144].

For the case of C_{16}TAB there are experimental evidences for 2:1 complexation, with $K_{1,1}$ of order 10^4 M^{-1} while the second binding constant, $K_{2,1}$ has a value between 100 and 300 M^{-1} [134], indicating a non-cooperative binding mechanism.

Often authors claim the occurrence of stoichiometries other than 1:1, although typically they only report $K_{1,1}$ values which, we believe, is a consequence of the difficulty behind the computation of values for higher stoichiometries.

Based on surfactant/*CD* NMR diffusion data and *cmc* values for alkyltrimethylammonium bromides from C_6TAB up to C_{14}TAB, the free energy of transfer of a methylene group, from the aqueous environment to a micelle (*ca.* −1.7 kJ (mol of -CH_2-)$^{-1}$), is less energetically than the gain resulting from the association of with *CD* (*ca.* −2.3 kJ (mol of -CH_2-)$^{-1}$). This is the reason why the complexation processes with *CD* shift the *cmc* of the surfactant to higher "apparent" *cmc* values

[134,234], in such a way that the onset of micelle formation occurs at a total surfactant concentration equal to the sum of the *cmc* value and the (total) concentration of *CD* (for a 1:1 stoichiometry). Conversely, if one adds *CD* to a micellar system above the *cmc*, the micelles will be broken up, the extent of which will depend on the concentration of *CD* relative to the concentration of micellized surfactant [134,235].

Based on the law of mass action, the relative proportion of the different species in a solution of *CD* and a surfactant can be computed from Eq. (1), with *m*,*n*=1, and the corresponding equation describing the micellization process:

$$NS \xrightleftharpoons{K_{mic}} S_N \tag{22}$$

with the equilibrium constants K_{mic}, given by

$$K_{mic} = \frac{S_N}{S^N} = \frac{S_{mic}}{NS^N} \tag{23}$$

where S_{mic} denotes the concentration of micellized surfactant. We also have the following mass balances:

$$[CD]_T = [CD]_f + [CD-S] \tag{24}$$

$$[S]_T = [S]_f + [S]_{mic} + [CD-S] \tag{25}$$

Given values for the two involved equilibrium constants ($K_{1,1}$ and K_{mic}), these equations can be solved and the concentrations of the various species as a function of the total surfactant concentration can be calculated. $K_{1,1}$ is experimentally obtained and K_{mic} can be calculated from the following equation

$$K_{mic} = \frac{1}{N^2}\left(\frac{1+\frac{1}{N}}{cmc}\right)^{N-1} \tag{26}$$

where the *cmc* is given in M units. Eq. (26) is based on the assumption that *cmc* is the concentration where addition of one surfactant has 50 % probability of ending up in a micelle ((dS_{mic}/dS_T)=(dS/dS_T)=0.5)). For C_{12}TAB with a *cmc* value of 15.34 mM and an aggregation number of 55 [140], we obtain log(K_{mic})=95 and, consequently, the concentrations of various species present can be computed and are presented in Figure 4.

From studies on β-*CD* and hexadecyltrimethylammonium chloride (C_{16}TAC) mixtures [236], it is concluded that neither CD nor its complexes participate in the formation of

the micelles, and the host-guest complexes have negligible effect on the micelles properties after they are formed [237].

From the data in Table 2 we can also conclude that the Gibbs free energy and the enthalpy of binding are both negative. However, there is no consensus on the algebraic contribution of the entropy change (ΔS^0) to the Gibbs free energy of binding. From calorimetric experiments, a positive ΔS^0 is obtained which, combined with the binding exothermicity, characterizes a hydrophobic-controlled interaction.

The effect of alkyl chain length on the association of C_nTAB follows the same trend when the association occurs with α- and γ-*CD*s. However, there are several relevant differences

For α-*CD* host-guest complexes, the binding constants are higher, everything else equal, than those observed for the β-*CD* complex and the entropy change is negative. The former observation can be justified by a higher stability caused by a stronger interaction (due to a smaller diameter of the α-*CD* cavity). In general, by increasing the alkyl chain length both the enthalpy and the entropy tend to decrease (i.e. increasing in absolute value): the release of water molecules from alkyl chains and the *CD* cavity [238], is an entropy increasing process; on the other hand, the formation of the complex itself should cause an entropy decrease since the surfactant tail can sample less conformations. If the two previously mentioned factors have more influence than the hydrophobic interaction, they determine the algebraic value of the entropy change (see section 4.4 for a more detailed discussion), and thus the entropy decrease by increasing the length of the hydrophobic tail.

In the case of γ-*CD* systems, two important observations can be made. The first one is that the *CD* cavity can be threaded by two tails of surfactants, leading to a 1:2 (*CD:S*) complex. Indeed, if the γ-*CD* cavity has an inner diameter of 8.0 Å or more, it should be expected that two independent methylene groups can occupy the cavity The second observation is that, contrary to the previous systems, the second binding indicates a cooperative process; i.e., $K_{1,2}>K_{1,1}$.

The interaction of photosurfactants (ZTAB) based on an azo compound with an ionic head group and an alkyl chain: 2-[4-(4-ethylphenylazo)phenoxy]ethyltrimethyl and 2-[4-(4-butylphenylazo)phenoxy]ethyltrimethyl ammonium bromides (EZTAB and BZTAB, respectively) with α-, β- and γ-*CD*s has been studied by Shirama *et al.* [183,239]. The mechanism of interaction of α- and β-*CD*s with these surfactants is

dependent on their isomer conformations. For surfactants in a trans-conformation, the association with α-*CD* is more stable ($K_{1,1}$=37000 M^{-1} (EZTAB), $K_{1,1}$=50000 M^{-1} (BZTAB)) than with β-*CD* ($K_{1,1}$=6600 M^{-1} (EZTAB), $K_{1,1}$=25000 M^{-1} (BZTAB)) and, for each *CD*, $K_{1,1}$ increases by increasing the alkyl chain length; however, for *cis*- and *trans*-ZTAB no interaction with α-*CD* has been detected, and weaker interactions were found with β-*CD* ($K_{1,1}$=3100 M^{-1} (EZTAB), $K_{1,1}$=13000 M^{-1} (BZTAB)). This has been discussed in terms of the steric hindrance effect caused by the folded molecular structure of the *cis*-ZTAB. The interaction of *trans*-ZTAB with γ-*CD* suggests the formation not only of 1:1 (γ-*CD*:EZTAB:), or 2:2 (γ-*CD*:BZTAB), but also 1:2 complexes, which means that the γ-*CD* is threaded by two ZTAB chains. These studies show that, only interactions with α-*CD* are enthalpy- and entropically-driven. For complexation of ZTAB with β- and γ-*CD* the mechanism is, in general, enthalpy-driven but entropically controlled (i.e. $|T\Delta S^0|>|\Delta H^0|$).

Up to now, we have described and reviewed systems where 1:1 and/or 2:1 (or 1:2) complexes are formed; however, there are some cases involving surfactants where high order stoichiometry complexes can be formed; one example is the case of a cationic surfactant based on 3H-indole: the iodotrimethyl 2-(p-hexylaminophenyl)-3,3-dimethyl-5-carboethoxy-3H-indole ammonium, which at basic pH forms a 3:3 complex with β-*CD* [184].

4.1.1 Counter ion effects

An interesting issue that deserves attention is the effect of counter ion on the *CD-S* association constants. Table 5 shows *K* values for a set of alkyltrimethylammonium chlorides (C_nTAC)-cyclodextrin complexes. Although there is some scatter in the data (see, for example, Table 2) it is possible by taking data from the same source to conclude that the interaction depends little on the counter ion (either Cl^- or Br^-). We note in passing that studies carried out by Junquera *et al.* [240] showed that bromide ions, from C_{12}TAB, also participate in the association process by binding to β-*CD* and to hydroxypropyl-β-cyclodextrin (HP-β-*CD*) with binding constants close to unity: 0.6 (± 0.5) M^{-1} and 1.1 (± 0.9) M^{-1}, respectively.

4.1.2 Effect of β-cyclodextrin derivatives

Results for the interaction of dodecyltrimethylammonium salts with β-*CD* and hydroxypropyl-β-cyclodextrin (HP-β-*CD*), a more water soluble *CD*, is contradictory. While data shown in Table 5 demonstrate that the association constant decreases when β-*CD* is replaced by HP-β-*CD* by ca. one order of magnitude, studies by using electrical conductivity show that $K_{1,1}$ for C_{12}TAB/HP-β-*CD* is just slightly higher (2900 (±750) M^{-1}), than that found for β-*CD* (2400 (±600) M^{-1}). Although the difference appears not to be statistically significant, these results were discussed in terms of a higher solubility of the hydroxypropylated *CD* in water [240].

The interaction between C_{16}TAB and the 2,6-*O*-dimethyl-β-cyclodextrin (DM-β-*CD*) leads to a formation of a 1:1 complex with a more rigid structure than the corresponding host alone; this is contrary to what happens with β-*CD*, confirming that the modified β-*CD* possesses less intramolecular binding sites than does β-*CD* [241]. However, studies using speed of sound [149] show that neither the addition of two methylene groups to the surfactant chain (C_{10}TAB to C_{12}TAB) nor the partial methylation of the glucose rings of β-*CD* leading to DM-β-*CD*, has a marked effect on the stoichiometry of the inclusion complex or influence on the parallel micellization process. This conclusion appoints to similar *K* values for the C_{12}TAB/HP-β-*CD* and C_{12}TAB/β-*CD* association. However, the complexation of C_{14}TAB with an anionic cyclodextrin (*Captisol* - SBE-β-*CD*) leads to a higher *K* value (62 (±1)×10^3) [230] when compared with that obtained for β-*CD* (*K*=49.5 (±0.5)×10^3), clearly suggesting that here the ionic interaction also play a role in the interaction mechanism.

4.1.3 Effect of surfactant headgroup

We now turn to the effect of the surfactant head group. There are several studies where the effect of headgroup polarity on the complexation with *CD*s is evaluated. Studies involving dodecyldimethylethylammonium bromide (Table 5) showed that there is no significant effect on the association with cyclodextrins, when compared with C_{12}TAB.

The complexation of alkylpyridinium chlorides (C_nPC) with β-*CD* (Table 6) [242] is characterized by negative enthalpies and the free energy of complexation decreases with increasing alkyl chain length. However, the entropy change increases with increasing alkyl chain length, indicating that desolvation is the major key process in the complexation mechanism. It is also worth noticing that for C_{12}PC the complexation is not entropically favored (i.e., $\Delta S^0<0$). Comparing the effect of pyridinium with those of

trimethylammonium, the former does not contribute to a stronger hydrophobic interaction, since the enthalpy change is less exothermic, which can be attributed to the fact that the positive charge is located between the aromatic ring and the alkyl chain length and thus the charge is less shielded by the *CD*s cavity. On the other hand, the contribution to the entropy change for the complexation is more favorable for, e.g., C_{12}PC than for C_{12}TAB. C_nPBs also show a higher stability with α-*CD* than with β-*CD*, in agreement with the trends for C_nTAB [242].

A comparison between association constants for the complexation between β-*CD* and C_{12}TAB, and lauryl sulfobetaine (LSB), was carried out by Gokturk *et al.* [202]. They have found, by surface tension measurements, that the amphoteric LSB is more strongly bound ($K_{1,1}$=2900 (±300) M^{-1}) to β-*CD* than is the case for C_{12}TAB ($K_{1,1}$=1900 (±400) M^{-1}). This is explained in terms of an additional sulfonate head group that contributes to alterations in the balance of polar-apolar and apolar-apolar interactions. The higher *K* value for LSB indicates that hydrogen bonds can be formed between the sulfonate group and the hydroxyl groups on the rims of the *CD* cavity.

Interactions between α- and β-cyclodextrins and 3-alkoxyl-2-hydroxypropyltrimethylammonium bromides (C_nNBr) were studied by Sun *et al.* (Table 7) [243,244]. They showed that the stoichiometry ratio changes from 1:1 to 2:1 with the increase of methylene groups from 8 to 12. All the complexation processes are shown to be enthalpy driven. For β-*CD* complexes there is a positive contribution from the entropy change (ΔS^0), which in the case of α-*CD* complexes the entropy change is unfavorable, in a similar way to the situation for α-*CD*/C_nTAB and α-*CD*/$C_nMe_6Br_2$ complexes. The absolute value of enthalpy (ΔH^0) increases, while entropy (ΔS^0) decreases, by increasing the number of methylene in the hydrophobic chain. In conclusion, the exchange of trimethylammonium for a pyridinium headgroup, does not significantly change the thermodynamics of the host-guest complexation.

4.1.4 Effect of solvent polarity

The effect of solvent polarity on the interactions between C_{16}TAB and β-*CD* has been investigated, by using different volume fractions (*x*) of water/butanol mixtures. Taking the temperature of 30 ºC as reference, an increase in the volume fraction of butanol (x_{ButOH}) from 0 to a maximum of 4 %, leads to a decrease in $K_{1,1}$ and $K_{2,1}$, resulting in a significant decrease of the free energy of association from −27.64 to −20.05 kJ mol^{-1},

and from −18.87 to −10.50 kJ mol^{-1}, respectively. A thermodynamic analysis shows that in both systems the association is an enthalpy-controlled process; however, in the butanol/water mixture solvent, the entropy change becomes significantly negative, which prevent the complex formation (x_{ButOH} =0 [166], ΔH^0=−23.37 kJ mol^{-1}, $T\Delta S^0$=4.2 kJ mol^{-1}; x_{ButOH}=4 % [245], ΔH^0=−107.08 kJ mol^{-1}, $T\Delta S^0$=−87.03 kJ mol^{-1}). The effect of ethanol/water and N-methylacetamide/water mixed solvents on the complexation of C_{16}TAB/β-*CD* was also studied, and by increasing the fraction of organic solvent, the association constant decreases (K=2000 M^{-1} (EtOH, 1M); K=450 M^{-1} (EtOH, 4 M)) [246]. This may be mainly justified by the stabilization of the surfactant tail by the organic solvent and, consequently, hydrophobic interactions between surfactant and *CD* are weakened. A similar effect was also reported for studies on the effect of iso-propanol/water mixtures on the association/dissociation of β-*CD*/C_{12}TAB complexes.[247] From the latter study, it was also possible to conclude that, in the solvent mixtures, interactions between β-*CD* and the medium are not fundamentally modified by ion inclusion in the hydrophobic cavity. Even so, it is worth noticing that the complexation of an ion-pair is characterized by an higher K when compared with a non-associated ionic surfactant [248].

4.2 Double-tailed surfactants

Double tailed quaternary ammonium salts, di-*n*-alkyl-dimethylammonium, have been investigated for their surface and solution behavior [249] with particular emphasis on their possible applications as biocides [250], phase transfer catalysts and in the context of ionic liquids [251]. It is expected that these surfactants can form different types of complexes with *CD*s, than the corresponding single chain surfactants, since they have two binding sites. Binding constants for the complexation of *N*,*N*-didecyldimethylammonium bromide (DDAB) with *CD*s (Table 8), reported by Funasaki and Neya [169], show that DDAB forms 1:1 and 2:1 complexes with α- and β-*CD*, while γ-*CD* form 1:1 complexes The magnitude of $K_{1,1}$ changes in the order of β-*CD* ≥ α-*CD* > γ-*CD*, and for $K_{2,1}$ the interaction with α-*CD* is more stable than with β-*CD*. These authors concluded that the first and second binding constants, $K_{1,1(dc)}$ and $K_{2,1(dc)}$, for a given alkyl chain length, are comparable with the stability constants for the single chain surfactants, $K_{1,1(sc)}$ and $K_{2,1(sc)}$, when using the following relationships: $K_{1,1(sc)}=K_{1,1(dc)}/2$ and $K_{2,1(sc)}=2\ K_{2,1(dc)}$. The analysis of data for γ-*CD*-DDAB indicates

that there is no second binding of a γ-*CD* to DDAB because both tails of DDAB are incorporated in the γ-*CD* cavity [252]. Also, the effect of alkyl chain length on the interaction with α-*CD* was studied by comparing DDAB with *N,N*-dioctyldimethylammonium bromide (DOAB). For both surfactants, the two alkyl chains are able to interact with α-*CD* forming a 2:1 complex; however, for the DOAB the second binding is clearly cooperative, while for DDAB: $K_{1,1}>K_{2,1}$; this finding suggests that by increasing the alkyl chain length the steric hindrance caused by the first association interfere with the second binding.

More recently, a study involving the complexation between *N,N*-didecyldimethylammonium chloride (DDAC) and a set of natural and substituted *CD*s was published [249]. By using ^{1}H NMR spectroscopy and molecular dynamic studies it was concluded that β-*CD*, and its derivatives, can be threaded by two independent surfactant tails, making the enthalpy change of this process for β-*CD* more exothermic (ΔH = −26 kcal mol^{-1}) than the formation of a 1:1 complex, but just involving one surfactant tail (ΔH = −20 kcal mol^{-1}). These enthalpy results were computed based on PM3/COSMO calculation (RHF, MOPAC2009^{TM}).

4.3 Gemini surfactants

Gemini (*G*) surfactants are made up of two amphiphilic moieties connected at the level of the head group [253-256]. Compared with conventional single-chain, single head group, surfactants, gemini surfactants typically have lower critical micelle concentrations (*cmc*), better wetting properties, lower limiting surface tensions, higher surface activity, stronger interaction with oppositely charged surfactants, unusual viscosity changes with an increase in surfactant concentration and unusual micellar structures and aggregation behaviors or morphologies [254,257-261]. The properties of gemini surfactants are influenced by the length of the spacer group [262], headgroup hydrophilicity [263], hydrophobic chain length and dissymmetry [264]. For a fixed length of both hydrophobic tails the *cmc* increases with the spacer length until it reaches a maximum value, and then the value decreases [262,265,266]. Furthermore, gemini surfactants with different headgroups – so-called heterogemini [267-269]– show very interesting properties; among these geminis we find zwitterionic surfactants which present an intermediate nature between ionic and non-ionic surfactants, and depending

on the type of the head groups they may show pH-dependent properties [270]. Aqueous solutions of some dimeric surfactants with short spacers show a very high viscosity at relative low concentrations and/or display viscoelasticity and shear induced viscoelasticity [271]. The ability of geminis to make organic compounds soluble in water makes them useful for applications in different fields such as drug formulations [272] and waste water treatment [231]. Other interesting and promising applications involve skin care [273], gene delivery vectors [274,275], antimicrobial effect [276], skin permeation enhancers [277], analytical methods [278,279], and synthesis of gold nanoparticles with tunable longitudinal surface plasmon resonance [280,281].

There are several reasons for studying interactions between gemini surfactants and cyclodextrins. The most straightforward one being the presence of *CD* has a strong influence on the surfactant self-assembly by shifting the *cmc* to higher values [213]. Other reasons are, e.g., the ability of *CD*-gemini-based formulations for solubilization of drugs [17,172,282] in aqueous media, and concomitantly showing excellent cellular selectivity [17]. *CD*-gemini complexes have also shown efficient ability for controlling DNA compaction/decompaction [283] and protein folding [284], and for gene therapy [285].

Despite the potential applications of *CD:G* complexes, studies on the complexation mechanism and corresponding complex properties are scarce.

Abrahmsén-Alami et al. [197,286] were the first to study the interactions between cyclodextrins (hydroxypropyl-cyclodextrins, HP-*CD*) and a gemini surfactant; the gemini used was a non-ionic heterogemini (labelled NIHG750) containing two hydrophobic and two hydrophilic groups: $(CH)_3(CH_2)_7$-CH[OH]-CH[$O(CH_2CH_2O)_{16}CH_3$]-$(CH_2)_7$CN. They found that HP-*CD* interacts mainly with the hydrophobic part of NIHG750 (methylene groups) resulting in the formation of rod-like complexes, which fact also indicates that the surfactant molecule takes an extended conformation in the complex. An important finding is that the complex is formed also by interactions between the hydrophilic part of the surfactant (EO-groups) and the HP-*CD*.

The first report on stability constants for G:CD formation was due to Sun *et al.* [287] They studied the complexation between α-*CD* and bis(alkyl dimethylammonium)-2-hydroxypropyl dichloride ($(C_iN)Cl_2$, i=12,14,16). The stoichiometry and the overall binding constants were determined by ITC measurements. Their findings of high order stoichiometries (*CD:G*) ranging from 2:1 (K_O= 5.1×10^{10} M^{-2}) and 1:4 (K_O=1.0×10^{16}

M^{-4}) for $(C_{12}N)Cl_2$ to 1:6 (K_O=1.4×10^{16} M^{-6}) have not been confirmed in later studies. Guerrero-Martinez *et al.* [288] studied the interaction between the gemini (dodecyldimethylammonium)diethyl ether dibromide (12-EO_1-12) and β-*CD*. They found that the complex stoichiometry (β-*CD*:*G*) is 2:1 at high β-*CD* concentrations with the first equilibrium constant ($K_{1,1}$=8(± 5)×10^3 M^{-1}) lower than the second ($K_{2,1}$=2.8(±0.9)×10^4 M^{-1}), as seen by chemical shifts analysis, indicating a co-operative process. These values have also been confirmed by self-diffusion analysis, resulting in the following binding constants: $K_{1,1}$=1(±0.5)×10^3 M^{-1} and $K_{2,1}$=5(±3)×10^4 M^{-1}) [289,290]. A structural analysis of the complex has been done by rotating frame nuclear Overhauser effect spectroscopy; it is suggested that the second binding induces a transfer to a deeper position (closer to the headgroup) of the first associated *CD* whereas the second *CD* is positioned at the ended of the remaining tail.

Similar structures have been described on the complexation of geminis, alkyl-α,ω-bis(dodecyldimethylammonium bromide), 12-*s*-12 (*s* = 2, 4, 6, 8 and 10) with β-*CD*. For these systems, the binding stoichiometry ranges from 1.6:1 for 12-2-12:*CD* to around 2:1 for 12-2-12:*CD*, depending on the method used. Assuming a two-step mechanism, binding constants were computed and they are given in Table 4.1. It is clear that the interaction between 12-*s*-12 and β-*CD* follows a non-cooperative mechanism which is contrary to what was observed for the previous discussed system. It was also found that $K_{1,1}$ is 5-10 times smaller than the corresponding value for the single chain dodecyltrimethylammonium bromide: $K_{1,1}$=18600(±4000) M^{-1} or $K_{1,1}$=17300(±1500) M^{-1}, as calculated from NMR self-diffusion or electrical conductivity experiments [134], respectively. The difference was explained on the basis of hydrophobic interactions between the two chains of the gemini. That is, from the ratio of the association constants for the gemini and the corresponding single chain surfactant, it is straightforward to estimate a change in free energy, between the two cases, of roughly 30 %. This value should be very similar to the difference in area exposed to water before and after association [213]. The importance of the interactions between hydrophobic chains of geminis has been highlighted with the studies on interactions between 12-EO_s-12 (*s*=1,5) and γ-*CD* [291]. This association is characterized by a 1:1 stoichiometry, with binding constants that do not depend on the spacer chain length – see Table 9. As is discussed above (see Section 4.1), the diameter of an alkyl chain allows two chains to reside inside the γ-*CD* cavity.

The non-cooperative interaction shown for 12-*s*-12 systems, on the other hand, was justified by steric constraints and electrostatic effects; in fact, once one *CD* molecule has associated with the gemini, the available space for the second *CD* to associate with the free chain is limited. Concerning the effect of electrostatic origin, it is expected that when both chains are complexed to *CD* molecules, the charges located at the ammonium groups will be surrounded by an environment rich in methyl groups, which is unfavorable from an electrostatic point of view. Another important finding, for this set of systems, is that by increasing the spacer chain length both tails approach a situation where they are independent of each other which is reflected in an increase of $K_{2,1}$, the value of which approaches $K_{1,1}$ values for the longest spacer [19,213].

The study of gemini:cyclodextrin interactions addresses another interesting issue: the possibility of complexation on the spacer, i.e. a binding of a *CD*-molecule between the two charged headgroups. Taking into account that the depth of the *CD* cavity is the same for α- and β-*CD*, it is reasonable to expect that a molecule of *CD* associates to the alkylchain spacer between the headgroups for 12-8-12 and 12-10-12, although with a weak association constant. Indeed, a stoichiometric ratio of 2.5:1 for β-*CD*:12-10-12 was found by self-diffusion measurements. This finding was supported by the study of Cabaleiro-Lago *et al*. [292], who reported the complexation with a bola surfactant having 12 carbons between the two charged groups (in the nomenclature used here, the bola surfactant would be designated 1-12-1). Although that high stoichiometric ratio has not been confirmed by Job's plots, from ^{1}H NMR chemical shift displacement studies, Carvalho et al. have found two distinct resonances for the ammonium methyl protons only for 12-10-12-containing systems, strongly indicating that the *CD* complexes with the surfactant's spacer, and it is also consistent with the occurrence of different complexes in solution in slow exchange. There is a considerable energy barrier for the process of pushing a charge trough the interior of the *CD* in order to form the complex with the *CD* positioned on the spacer, which explains the slow kinetics. The life time of the spacer complex can be estimated from the shift difference of the two peaks for high β-*CD:G* ratios to be in excess of 150 ms. Another important point observed is that the splitting is accompanied by the steady increase in the linewidths of both resonances, which are dependent on the gemini concentration. The situation was further supported by a ROESY-based analysis, which showed that the cross peak volumes between the inner cavity's protons of β-*CD* and those of methylene protons (of tails and spacer) of

gemini are reduced to less than 50 % when compared with those for 12-8-12. This reduction was explained by a less pronounced interaction between aliphatic tail protons and β-*CD*, as a result of an increase in the number of protons able to interact with β-CD, as should be the case if the insertion of a β-*CD* molecule in the spacer is considered.

More recently, interactions between β-*CD* and a dimeric cystine-derived urea surfactant ($(C_8Cys)_2$) [293] were reported. These anionic geminis with short hydrocarbon chains form a predominant 1:1 complex with stability constants ranging from 1200 to 13100 M^{-1} (see Table 9), depending on the experimental technique used. Such an order of magnitude disagreement, although not unusual in literature, suggests that the formation of high order complexes cannot be neglected.

4.4 Bolaform surfactants

In the previous section, hypothetical evidence was presented in favor of a situation where cyclodextrins thread the spacer of the geminis. This suggests the investigation of *CD* and bolaform surfactant interactions. Bolaforms are surface active agents having two water-soluble heads connected by a hydrophobic spacer [294-296]. These type of surfactants have weaker surface activities, higher critical micelle concentrations and smaller micelle sizes than the conventional homologous surfactants [297-299]. The dimeric features of these surfactants make them useful as coatings on smooth solid materials, where one end is attached to the surface of electrodes, polyelectrolyte, or nanoparticles, whereas the other headgroup is used for solubilization in water and for interactions with solutes [300]. The development of synthetic routes for novel bolaform surfactants [301-305] makes it possible to obtain diverse surfactant architectures and self-assembled structures. Those structures show a diverse range of morphologies, ranging from nanofibers [306,307] and nanotubes [308,309] to vesicles [310,311].

The use of bolaform surfactants for the synthesis of new catalysts is a promising field. For example, quaternary ammonium-based bolaform surfactants have been used as directing agents in the shape-controlled synthesis of gold nanostructures [312], and of metallosurfactants [313]. Bolaform surfactants are also used in template synthesis for the production of micro- and meso-porous silica [314,315], and hydrophobic nano-calcium carbonate [316].

Other applications include antifoaming agent in fermentation processes [317], metal and dye removal, either acting as an anchor [318-320] or by micellar extraction [321], formation of photosensitive structures [322-324] and the development of stimulus responsive gels [325,326]. Furthermore, bolaform surfactants are also relevant for biochemistry and pharmaceutical applications, by modeling lipid membranes [327-329], as permeability enhancers [330] or to be used for drugs encapsulation [331], respectively.

As pointed out before, surfactants are ideal guests that allow for the systematic study of *CD* complexation, since both hydrophobic and hydrophilic moieties can be systematically varied. Bolaform surfactants are of special interest as guest molecules due to the balance of several intermolecular forces: the hydrophobic effect which tends to protect the alkyl chain from the aqueous environment, the requirement of dehydration of the head groups during complex formation, as well as effects due to steric hindrances [153]. Bolaform amphiphiles also show inclusion dynamics significantly different from those of homologous univalent surfactants [332], due to the need of an ionic group to pass through the hydrophobic *CD* cavity and, consequently, depends on the size of cyclodextrin cavity, the surfactant end-groups and the size of alkyl chain.

Although the formation of pseudorotaxanes (complexes in which a linear chain rapidly and reversely threads through a cyclic molecular bead) between cyclodextrins and ligands with a structure similar to bolaform surfactants or surfactants [333,334] have been reported, we focus on systems involving bolaform surfactants.

The complexation between docosane 1,22-bis(trimethylammonium)bromide ($C_{22}Me_6Br_2$) and β-*CD* has been studied by speed of sound and density measurements and ^{1}H NMR [153]. The presence of β-*CD* is shifting the surfactant *cmc* to higher values, justified by the higher affinity of surfactant unimer for the cyclodextrin than for the micelle; however, the volume of the micelle is not affected by the presence of *CD*, in agreement with what happens for surfactants with a single headgroup [152,335]. By analyzing the *cmc* shift and the ^{1}H NMR chemical shifts (especially for inner *CD* protons: H_3 and H_5), a predominant 2:1 (*CD*:$C_{22}Me_6Br_2$) complex stoichiometry was suggested. Taking the depth of the cavity of β-*CD* as equal to 7.8 Å and the length of a methylene group as equal to 1.27 Å [336], 22 methylene groups will allow a maximum number of three *CD*s to thread the alky chain. Thus, the obtained stoichiometry suggests that both end-groups are located well outside of the *CD*s cavity.

A fully systematic studies on the interaction of shorter chain bolaform surfactants (with 12 methylene groups or less) with cyclodextrins were reported by Macartney [332] and Söderman [98,292]. Starting with β-*CD*-containing systems, the interaction of dodecane 1,12-bis(trimethylammonium bromide), $C_{12}Me_6Br_2$, with β-cyclodextrin leads to the formation of a 1:1 complex with binding constants of 3000 and 2500 M^{-1} (Table 10) as obtained by ^{1}H NMR self-diffusion and electrical conductivity, at 298.15 K, respectively [292]. The resulting complex shows a size similar to that of a bare *CD* as seen by NMR diffusometry. Considering the internal volume of the cavity (270 $Å^3$), it follows that the *CD* molecules can accommodate a chain with 10 methylene groups [337]. Therefore, in a crude picture, the carbon chain would be hidden inside the *CD* cavity to avoid unfavorable interactions with water but in a conformation which allows the bulky head groups to protrude out of the cavity and remain in the external aqueous environment. A thermodynamic study on the interactions between alkane-1,*s*-bis(trimethylammonium bromide), $C_sMe_6Br_2$ (*s*=8,10,12), and α-, β- and γ-*CD* were reported [98]. In general, it was found that for a given chain length, the binding is stronger for α-*CD* than for β-*CD* (in a 1:1 stoichiometry), and no interaction was observed for γ-CD. On the other hand the binding constant increased by increasing the surfactant alkyl chain length (Tables 10 and 11). Similar conclusion had previously been reached by studying the binding of alkane-1,*s*-bis(trimethylammonium bromide), $C_sMe_6Br_2$ (*s*=8-12) with α-*CD* by analysing the ^{1}H NMR chemical shifts deviations upon complexation [332]. The binding constants obtained by different techniques are in good agreement (Table 10). An important issue is that although it was found that complexes are mainly in a 1:1 stoichiometry, Lyon *et al.* found by electrospray mass spectrometry, an occurrence in gas phase of around 30 % of complexes with a 2:1 (*CD:S*) stoichiometry.

Comparing the thermodynamics of complexation between α- and β-*CD*s, the binding is exothermic for both *CD*s, more so for α- than for β-*CD*, whilst the entropy change is negative for α- and positive for β-*CD*. Thus the strength of interaction clearly depends on the width of *CD* cavity. While the enthalpy change can be justified by a process dominated by hydrophobic interactions, resembling micelle formation, the explanation of the observed entropy changes is less trivial. For β-*CD*, an increase of ΔS^0 is justified by the release of water molecules, upon association, from the *CD* cavity and from the hydrocarbon chain; the binding process also contributes for a decrease in the

hydrophobic hydration that has a structure-making effect on the water [338]. The negative entropy change for α-*CD* complex formation indicates that the situation for water molecules inside the cavity is different. It was suggested that the effect was due to the inability of water molecules to develop a full hydrogen bonded network inside the *CD* cavity leading to an increased disorder, probably due to the high curvature inside of the cavity. When the water molecules are released, the hydrogen bonds reform, which leads to an increased order and release of heat. In fact, the heat capacity (C_p) per H_2O molecule in α-*CD*, is just 59 $JK^{-1}mol^{-1}$, while for β- and γ-*CD* it is ca. 70 $JK^{-1}mol^{-1}$, much closer to C_p for liquid water (75 $JK^{-1}mol^{-1}$) [339]. Another contribution to the entropy change is the conformational entropy of the hydrocarbon chain in the cavity. The two charges at the ends must reside outside the cavity and this leads to a stretching of the hydrocarbon chain when it enters the cavity, which leads to a lowering of the conformational entropy. This effect is expected to be larger for the narrower cavity of α-*CD* compared to β-*CD*.

5. Kinetic controlled association complexes

As discussed in section 4.2 it is possible that a molecule of *CD* associates to the alkyl chain spacer between the headgroups for 12-10-12, although with a weak association constant, on account of steric and electrostatic effects [19]. Also, one would expect a considerable activation barrier, for the formation of such a complex since the bulky polar head group has to go through the hydrophobic cavity of the cyclodextrin [340]. Bolaform surfactants are ideal guest molecules to study the kinetics of host-guest interactions as a consequence of its architecture (where both ends are constituted by polar heads).

Following previous work on the kinetics of α-*CD* with 1,1''-(α,ω-alkanediyl)bis(4,4'-bipyridinium) [341,342], Macartney *et al.* studied the kinetics of complexation, by ^1H NMR, of some bolaform surfactants with quaternary ammonium ($C_sMe_6Br_2$, *s*=8-12, and $C_{10}Et_2Me_4Br_2$) and phosphonium ($C_{10}PMe_6I_2$) head groups with α-*CD* [332]. Assuming a 1:1 binding stoichiometry between surfactant and cyclodextrin, the rate constants for the formation "on", k_{on}, and dissociation "off", k_{off}, processes can be represented by the following equation

$$S + CD \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} S - CD \quad (27)$$

Several aspects must be considered in the kinetic analysis. As pointed out by Park [343] the rate constants k_{on} and k_{off} in fact each depends on two microscopic rate constants. This follows since the *CD* molecule has the shape of a truncated cone with one opening smaller than the other, and threading and de-threading of the bolaform surfactant on the *CD* will be different depending on in which direction the process occurs. However, these microscopic rate constants cannot be determined separately. On the other hand, bolaform surfactants discussed in this review are centrosymmetric meaning that there is only one complex formed. Secondly, it has been suggested that the desolvation kinetics of the head group, preceding the incorporation into the CD cavity can modify, by several orders of magnitude, the rate constants for the "*on*" and "*off*" processes [344,345].

From the analysis of rate constants (Table 12) it can be concluded that values of k_{on} are very dependent on the size of the end group, decreasing by two and four orders of magnitude when one or both trimethyl ammonium groups are substituted by ethylmethyl ammonium and trimethyl phosphonium groups, respectively. Furthermore, k_{on} decreases by increasing the ionic strength: k_{on}=0.215 $M^{-1}s^{-1}$ (no salt added) to k_{on}=0.138 $M^{-1}s^{-1}$ for (I=1.0 M, NaCl) [343]. However, k_{on} shows only a weak dependence on the number of methylene groups in the surfactant. These results were confirmed by the analysis of the complexation kinetics, for similar systems, based on ITC and ^{1}H NMR measurements (see Table 12) [98]. The dependence of k_{on} on the head group and surfactant chain length can be rationalized by the fact that the barrier presumably has a large contribution originating from the necessity to push a charge through the non-polar cavity. In fact, the magnitude of this barrier can be estimated from the Born-equation. On the assumption that the size of the charged N-$(CH_3)_3$ head group is 100 $Å^3$ (giving a radius of 3 Å if assumed spherical), and that the permittivity of the inside and outside are 4 (twice that of a hydrocarbon) and 80, respectively, one arrives at a value of 50 kJ mol^{-1}. This value is of the same order of magnitude of the reported activation energy for the "*on*" process: 55 to 92 kJ mol^{-1} for $C_8Me_6Br_2$ to $C_{12}Me_6Br_2$, respectively [98]. This indicates that electrostatic effects contribute considerably to the barrier. Other contributions stem from the fact that only certain configurations of the bolaform surfactant hydrocarbon chain may get through the cavity.

The rates of the "*off*" process depend considerably more on the length of the surfactant, also reflected in a larger variation of the activation energies (70 kJ mol^{-1} for $C_8Me_6Br_2$ and 144 kJ mol^{-1} for $C_{12}Me_6Br_2$) [98]. This can be justified by considering the process as flow of charged head groups through a region of low concentrations of head groups inside the cavity. The flow rate will then depend on the concentration gradient of charged head groups outside the *CD* cavity. The gradient will be smaller for $C_{12}Me_6Br_2$ since its charged head groups have a larger effective volume to explore on either side of the *CD*-cavity. In other words, the probability of a charged head group exploring the entry to the *CD* cavity is considerably larger for C_8Me_6 than for $C_{12}Me_6$, and therefore its "*off*" rate is faster.

6. Conclusions and outlook

A detailed and critical review on the effect of surfactant architecture, tail hydrophobicity, headgroup, counter-ions and solvent, on the association with cyclodextrins, at different temperatures, with special emphasis on cationic surfactants and natural cyclodextrins, is provided.

For the majority of the complexes the stoichiometry is 1:1 or 2:1 (*CD*:*S*), depending on the type of surfactant, tail chain length and also the size of the cyclodextrin cavity. For example, for single tail surfactants, the stoichiometry is essentially 1:1 for tails up to 14 carbons, increasing to 2:1 for longer tails with a non-cooperative mechanism (i.e., $K_{2,1}<K_{1,1}$). However, there are exceptions: the interaction of, e.g., alkyltrimethylammonium bromides with γ-CD leads to a 1:2 association since the CD cavity can be threaded by two alkyl chains in a cooperative process. For gemini surfactants the stoichiometry of interactions clearly depends on the spacer chain length and ranges from 1.5:1 complexes for short spacers (say, with 2 methylene groups) to 2:1 for spacers with more than 8 methylene groups. Furthermore, both tails become independent of each other with longer spacer lengths; this explains why a non-cooperative 2:1 process for, e.g., β-*CD*:12-2-12 passes to a situation where $K_{1,1}$ is approximately equal to $K_{2,1}$ for 12-10-12. Indeed, double-chain surfactants seem to be more independent and flexible to interact with cyclodextrins than gemini surfactants. This can be justified by steric constrains and electrostatic effects between surfactants headgroups upon complexation. The interactions between bolaform (e.g., $C_nMe_6Br_2$, $8\leq n\leq 12$) surfactants with α-*CD* lead to a complex with a 1:1 stoichiometry.

The thermodynamic analysis of the binding reveals an enthalpy-driven process as expected on account of interactions between the surfactant tails and the cyclodextrin cavity. Depending on both surfactant and *CD*, the contribution of the entropy change to the Gibbs free energy, shows different algebraic values. For example, interactions involving α-*CD* leads, generally speaking, to negative entropy changes, which can be related to the state of water (less hydrogen-bonded) inside the cavity.

A relevant issue that also arises from this review is the difficulty to investigate correlations between different systems, when data are measured using different techniques and the thermodynamic functions are computed using different methods. To reach the goal of an accurate quantitative determination of stability constants and, consequently, thermodynamic functions, it is important to carry out a precise

stoichiometry determination and to obtain an adequate number of data points, in particular in the molar ratio range below the stoichiometric ratio. Moreover, one has to be aware of the assumptions behind the measured data and/or the fitting equations and carry out an overall critical assessment of all fitting parameters.

Nowadays, the application of cyclodextrins is facing new challenges through the use of *CD*-containing nanoparticles, *CD* aggregates or *CD*-grafted polymers and macromolecules. However, some different fundamental issues remain veiled or are not completely clarified as, for example, those involving the CD self-assembly, the anomalous aqueous solubility of β-CD, the structure of the water inside the *CD* cavity, the effect of non-centrosymmetric bolaform surfactants on the interaction mechanism with *CD*s or even the supramolecular structures formed essentially by hydrogen bonds instead of hydrophobic interactions. All these make this area a promising field with plenty of challenges.

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FIGURE CAPTIONS

Figure 1. (A) Raw calorimetric data and (B) heat, *Q*, per injection versus the injection number, at 308.20 K for injections of 4.16 μL of [$C_{12}Me_6$]=0.116 mol/kg in 0.900 g of β-CD solution at a concentration of 4.746 mmol kg^{-1}. Adapted from ref. [98].

Figure 2. Effect of the binding constant on the measureable parameter of *CD-S* association by using titration (left) and a Job's plot (right) methods. Data have been obtained by using Eq. (9), with $\Delta Y=\Delta\delta$, and assuming a $[S]_T$=0.5 mM, ΔY_{CD-S} =0.5 and in the left-hand panel *K* is equal to: 1) 5; 2) 10; 3) 100; 4) 500; and 5) 1000 M^{-1}.

Figure 3. Schematic representation of the solution composition as seen by ^{1}H NMR self-diffusion measurements. a) [C_8G_1]/[β-*CD*]=1; b) Critical aggregation concentration (*cac*=*cmc*+[*CD*]).

Figure 4. Evolution of concentration of different species occurring in a CD:S mixed solution as a function of total concentration of surfactant. $[CD]_T$=5 mM and *cmc*=15 mM.

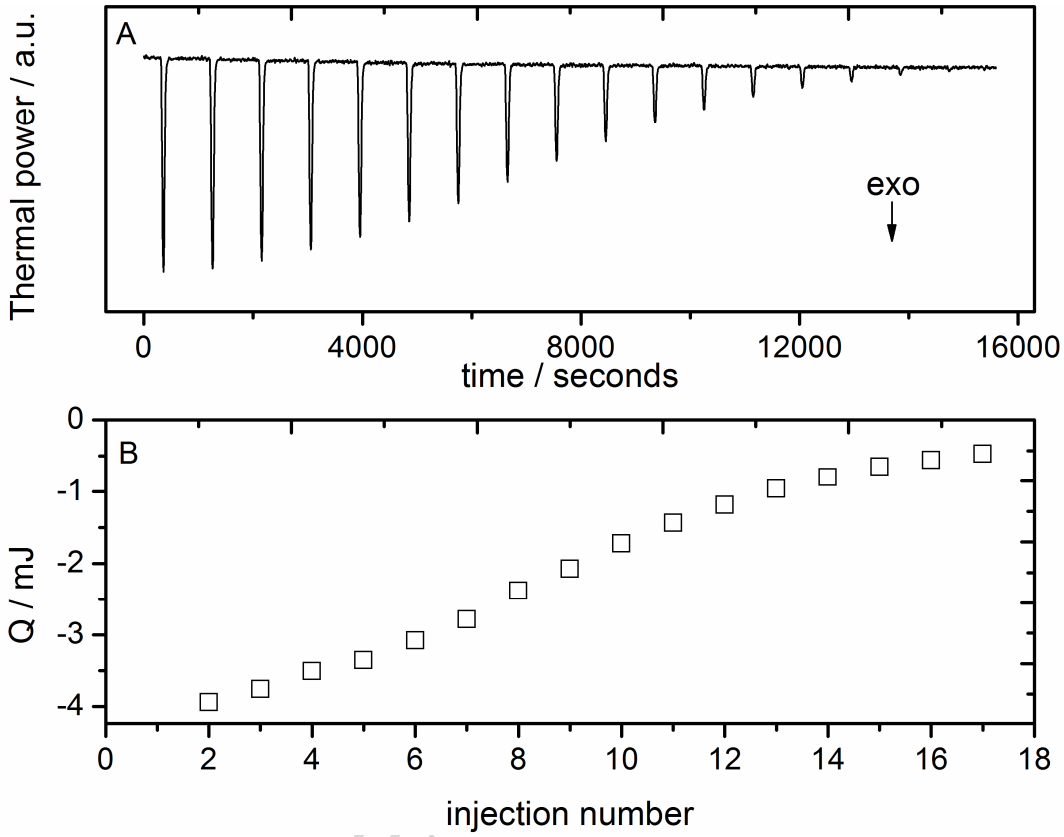


Fig. 1

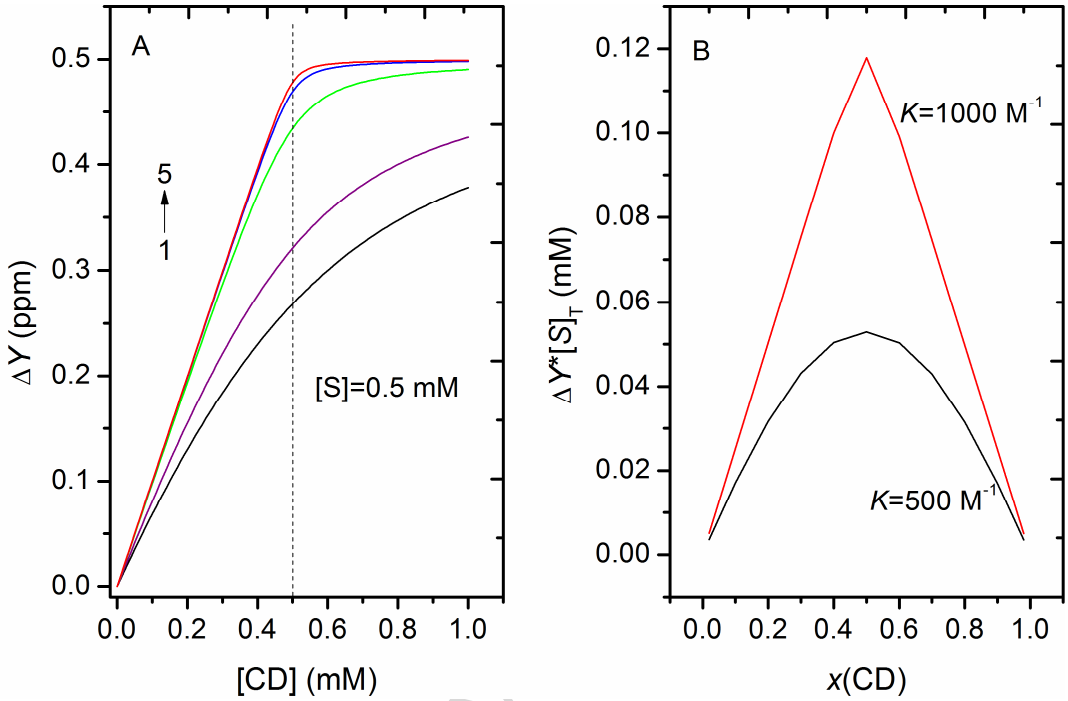


Fig. 2

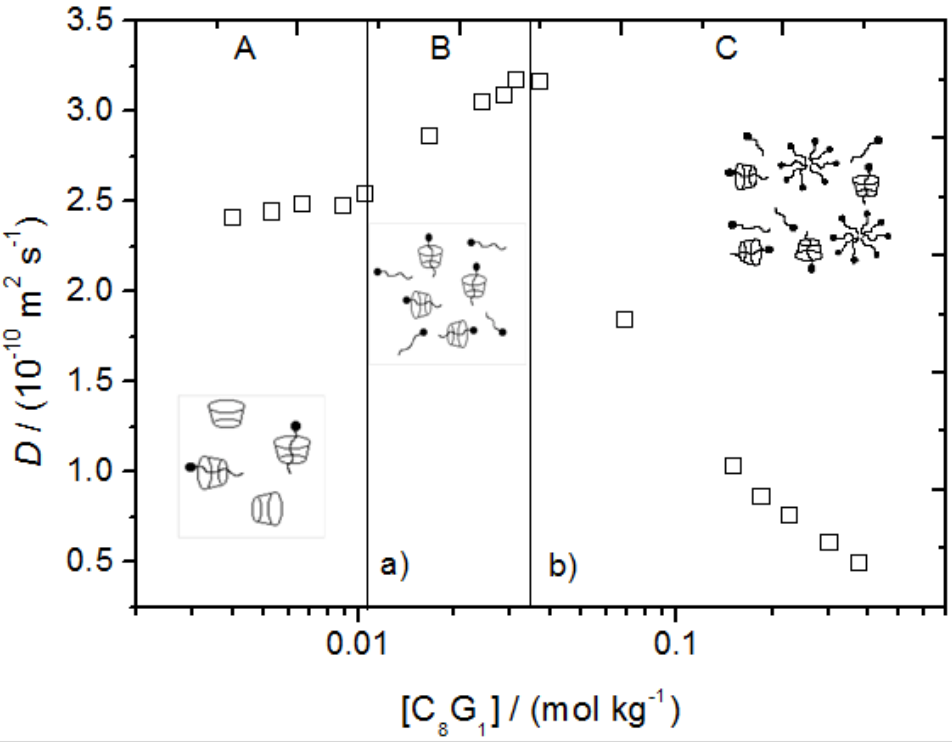


Fig. 3

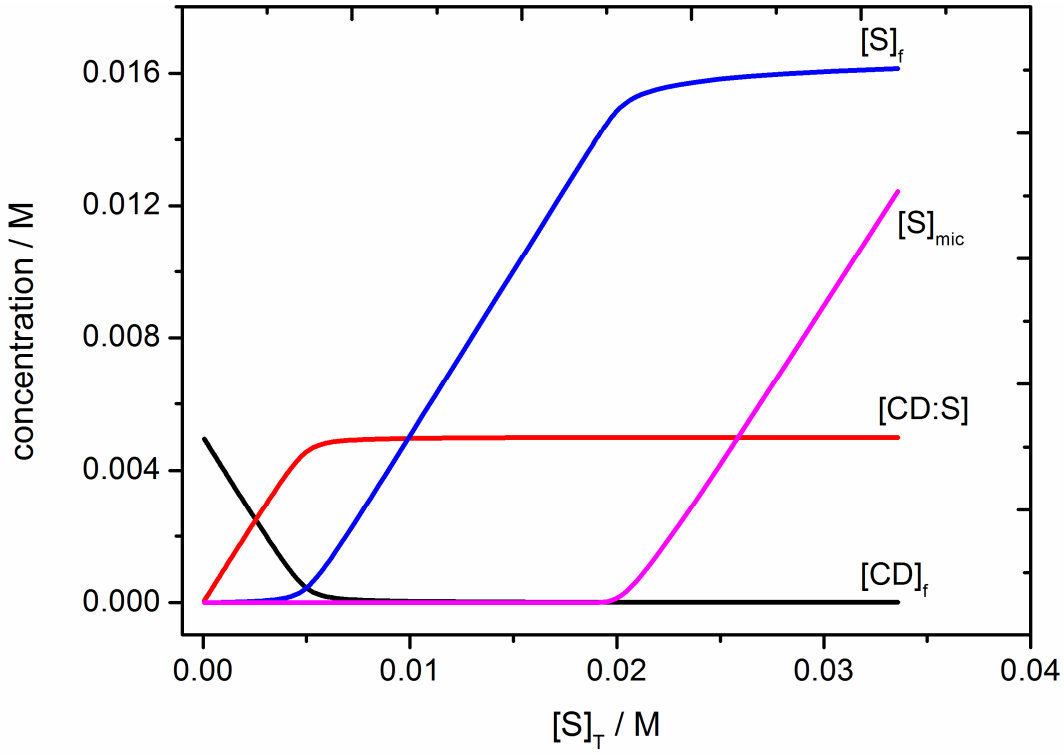


Fig. 4

Table 1. Binding constants and other fitting parameters for the inclusion complexes β-*CD* (0.25 mM):12-6-12, at 25 ºC.

	δ^{T}_{CD} / ppm	$\delta^{T}_{CD\text{-}S}$ / ppm	$\delta^{T}_{CD2\text{-}S}$ / ppm	$\delta^{J}_{CD\text{-}S}$ / ppm	$K_{1,1}$ / (10^4 M^{-1})	$K_{2,1}$ / (10^3 M^{-1})
H_3	3.94 (±0.01)	3.94 ± (0.01)	3.4 (±0.1)		0.17 (±0.04)	2.4 (±0.7)
H_5	3.84 (±0.01)	3.94 (±0.01)	3.3 (±0.1)			
H_3	3.86 (±0.01)	3.83 (±0.03)		3.86 (±0.01)	3.7 (±1.1)	7.5 (±0.7)
H_5	3.70 (±0.02)	3.69 (±0.03)		3.70 (±0.02)		

H_3 and H_5 are located inside the cavity near the wide and narrow rims of the *CD*, respectively. Superscripts J and T denote the chemical shifts calculated by using experimental data points from Job's plot and titration experiments, respectively; the values inside parentheses are the standard deviation of the values obtained from the fitting.

Table 2. Thermodynamic parameters for interactions between β-*CD* and salts of alkyltrimethylammonium, at different temperatures.

	$K_{1,1}$ / M^{-1}	$K_{2,1}$ / M^{-1}	ΔH^0 / (kJ mol^{-1})	$T\Delta S^0$ / (kJ mol^{-1})	Obs.
			25 ºC		
C_6TAB	66.2 (±2)				(1) [130]
C_8TAB	7.7 (±0.3)×10^2				(1) [130]
	3.56 (±0.16)×10^2				(2) [162]
C_{10}TAB	4.0 (±0.3)×10^3				(1) [130]
	3.843×10^3		−74.85*	−54.38	(3) [140]
	1.2 (±0.3)×10^3		−7.2 (±0.2)	10.4	(4) [230]
	4143 (± 27)				(2) [162]
	394 (±80)				(5) [146]
	3981	<3			(6) [154]
C_{12}TAB	21 (±3)×10^3				(1) [130]
	13.81 (±0.45)×10^3				(2) [162]
	18.633 ×10^3		−58.73*	−34.35	(3) [140]
	1.1 (±0.4)×10^3		−9.2 (±0.4)	8.1	(4) [230]
	1.9 (±0.4)×10^3				(7) [192]
	0.9×10^3				(8) [231]
	2.4 (±0.6)×10^3				(3) [232]
	17783	<25			(6) [154]
	23.7×10^3		−2.3		(4)[117]
	18.1×10^3				(6) [233]
	22.1(±5.5)×10^3	52 (±32)			(9) [234]
	1.45 (±0.3)×10^3				(5) [235]
	2.9 (±0.75)×10^3 ***				(3) [232]
	2.4 (±0.5)×10^3 ****				(5) [235]
C_{14}TAB	23 (±5)×10^3				(1) [130]
	14.8 (±0.4)×10^3		−12.4 (±0.4)	11.4	(4) [230]
	62.742×10^3	1.226×10^3	−54.41*	−27.04	(3) [140]
	49.5 (±0.5)×10^3				(10) [220]
	36050 (±1749)				(2) [162]
	39811	56			(6) [154]
	10655**				(3) [121]
	39750	3060			(4) [117]
	44 (±6.5)×10^3	118 (±12)			(9) [234]
	51150 **				(6) [236]
	64270 (±1680)	182 (±106)	1st bind: −19.84; 2nd bind: −96.06	1st bind: 8.22; 2nd bind: −90.14	(6) [155]
C_{15}TAB	54891 (±1749)				(2) [162]
C_{16}TAB	45.5 (±10.5)×10^3	76 (±40)			(1) [130]
	61.76×10^3	50			(6) [119]
	60733 (±11484)				(2) [162]
	67.7×10^3	9.6×10^3			(4) [117]
	65.5×10^3	398			(7) [194]
	70.795×10^3	126			(6) [154]
	59.8 (±15)×10^3	390 (±70)			(9) [234]
	20×10^3				(3) [139]
	2.24×10^3				(3) [237]
			30 ºC		
C_{10}TAB	2.855 ×10^3		−74.85*	−54.81	(3) [140]
C_{12}TAB	14.996 ×10^3		−58.73*	−34.50	(3) [140]
C_{14}TAB	48.396 ×10^3	0.964 ×10^3	−54.41*	−27.22	(3) [140]
	54747 (±1713)	124 (±24)	1st bind: −19.84; 2nd bind: −96.06	1st bind: 8.15; 2nd bind: −89.46	(6) [155]
			35 ºC		
C_{10}TAB	1.438×10^3		−74.85*	−56.24	(3) [140]
C_{12}TAB	11.180×10^3		−58.73*	−34.85	(3) [140]
C_{14}TAB	44.334×10^3	1.131×10^3	−54.41*	−26.99	(3) [140]
	48.93 (±1.06)×10^3	107 (±38)	1st bind: −19.84; 2nd bind: −96.06	1st bind: 8.19; 2nd bind: −88.18	(6) [155]
C_{16}TAB	1.85×10^3				(3) [237]
			40 ºC		
C_{10}TAB	0.967×10^3		−74.85*	−56.96	(3) [140]

C_{12}TAB	5.794×10^{3}		−58.73*	−36.17	(3) [140]
C_{14}TAB	19.966×10^{3}	0.929×10^{3}	−54.41*	−28.62	(3) [140]
	$50.277\ (\pm0.963)\times10^{3}$	24 (±4)	1st bind: −19.84; 2nd bind: −96.06	1st bind: 8.21; 2nd bind: −90.59	(6) [155]
			45 ºC		
C_{16}TAB	1.56×10^{3}				(2) [237]

(1) ^{1}H NMR diffusometry; (2) visible spectroscopy; (3) electrical conductivity; (4) ITC; (5) speed of sound; (6) potentiometry; (7) surface tension; (8) ^{1}H NMR chemical shifts; (9) fluorescence; (10) kinetic methods. * Values obtained by using the van't Hoff equation in a concentration range from 25 to 40 ºC. ** An average of several independent experiments, carried out with different initial concentrations of surfactant, has been calculated. *** HP-β-CD. **** DM-β-CD;

Table 3. Thermodynamic parameters for interactions between α-*CD* and alkyltrimethylammonium bromide at different temperatures.

	$K_{1,1}$/ M^{-1}	$K_{2,1}$/ M^{-1}	ΔH^0 / (kJ mol^{-1})	$T\Delta S^0$ / (kJ mol^{-1})	Obs.
C_6TEB	268**		−16.1	−11.0	(1) [238]
C_{10}TAB	3.7×10^3	3.7×10^3			(2) [151]
C_{12}TAB	$4.9 (\pm 0.3) \times 10^6$		−51.8 (±0.5)	−13.6	(1) [230]
	1.82×10^4	3.5×10^2			(3) [239]
	1.7×10^4	1.0×10^3			(4) [233]
C_{14}TAB	42975 *	3132 *			(4) [236]
	$6.5 (\pm 0.3) \times 10^6$		−66.1 (±0.5)	−27.2	(1) [230]
	4500				(5) [121]
	6.1×10^4	0.7×10^4			(1) [117]
C_{16}TAB	9.49×10^4	3.06×10^3			(4) [119]
	1.11×10^3				(5) [237]
	9.92×10^4	2.04×10^4			(1) [117]

(1) ITC; (2) ultrasonic attenuation spectra; (3) ^{1}H NMR chemical shifts; (4) potentiometry; (5) electrical conductivity. * Average values. ** C_6TEB: hexyltryethylammonium bromide. *K* values are given in mol^{-1} kg;

Table 4. Thermodynamic parameters for interactions between γ-*CD* and alkyltrimethylammonium bromide at different temperatures.

	$K_{1,1}$/ M^{-1}	$K_{1,2}$/ M^{-1}	ΔH^0 / (kJ mol^{-1})	$T\Delta S^0$ / (kJ mol^{-1})	Obs.
C_{10}TAB	37.4 (±0.3)	3.3 (±0.3) $\times 10^3$	−7.5 (±0.4)*; −9.7 (±0.3)**	16.5*; 10.4**	(1) [230]
C_{12}TAB	0.2 (±0.1) $\times 10^3$	33.9 (±0.1) $\times 10^3$	−3.8(±0.1)*; −15.3(±0.2)**	9.4*; 10.5**	(1) [230]
C_{14}TAB	0.3 (±0.2) $\times 10^3$	61.6 (±0.2) $\times 10^6$	−7.3 (±0.2)*; −15.6 (±0.3)**	6.3*; 28.8**	(1) [230]
	2.3×10^3				(2) [121]
	0.567×10^3 ***	5.57×10^3 ***			(3) [236]

(1) ITC; (2) ^{1}H NMR diffusometry; (3) potentiometry. * Enthalpy change for the 1st surfactant binding. ** Enthalpy change for the 2nd surfactant binding. *** An average of several independent experiments, carried out with different initial concentrations of surfactant, has been calculated.

Table 5. Stability constants for interactions between alkyltrimethylammonium chlorides and dodecyldimethylethylammonium bromide and *CD*s, at 25 ºC.

	CD	$K_{1,1}$/ M^{-1}	Obs.
C_{12}TAC	α	102 (±0.08) [(1)]; 887 (±50) [(2)]	[224]
		2270	(1) [240]
	β	219 (±0.06) [(1)]; 13391 (±175) [(2)]	[224]
	β	1290	(3) [121]
	HP-β	313 (±0.07) [(1)]; 5544 (±288) [(2)]	[224]
	γ	727 (±0.27) [(1)]; 20032 (±350) [(2)]	[224]
C_{14}TAC	α	102 (±0.08) [(1)]; 1116 (±78) [(2)]	[224]
	β	219 (±0.06) [(1)]; 13806 (±200) [(2)]	[224]
	HP-β	313 (±0.07) [(1)]; 9099 (±312) [(2)]	[224]
	γ	727 (±0.27) [(1)]; 36922 (±427) [(2)]	[224]
C_{16}TAC	α	2480	(1) [240]
C_{12}DMEAB	α	132 (±0.8) [(1)]; 707 (±35) [(2)]	[224]
	β	210 (±0.05) [(1)]; 13272 (±155) [(2)]	[224]
	β	2100 (± 400)	(4) [235]
	HP-β	211 (±0.07) [(1)]; 5248 (±250) [(2)]	[224]
		3200	(1)[241]
	β-DM	2600 (± 500)	(4) [235]
	γ	211 (±0.07) [(1)]; 14007 (±345) [(2)]	[224]

(1) electrical conductivity; (2) fluorescence; (3) ^{1}H NMR diffusometry; (4) speed of sound. C_{12}DMEAB: dodecyldimethylethylammonium bromide.

Table 6. Thermodynamic parameters for interactions between β-*CD* and alkylpyridinium salts (bromide (C_nPB) and chloride (C_nPC)), at different temperatures.

	$K_{1,1}$ / M^{-1}	$K_{2,1}$ / M^{-1}	ΔH^0 / (kJ mol^{-1})	$T\Delta S^0$ / (kJ mol^{-1})	Obs.
			20 ºC		
C_{14}PC	78320	29	−16.43*	11.04	(1) [243]
C_{16}PC	104948	919	−16.04*	12.13	(1) [243]
			25 ºC		
C_{10}PB	81190 (±1040) ¥				(2) [159]
	3740 (±50)				(2) [159]
C_{12}PC	17220		−41.59*	−17.42	(1) [243]
	2800 ¥				(1) [240]
C_{12}PB	44200 (±2700) ¥	310 (±280)			(2) [159]
	24900 (±1300)				(2) [159]
	18700		−2.3		(3) [117]
C_{14}PB	99700 (±660) ¥	1600 (±460)			(2) [159]
	66300 (±9020)	830 (±420)			(2) [159]
C_{14}PC	67518	94	−16.43*	11.14	(1) [243]
C_{16}PC	93749	356	−16.04*	12.33	(1) [243]
	$4.88 (\pm 0.18)\times 10^4$	265 (±95)			(4) [194]
	5×10^4				(1) [139]
C_{16}PB	4×10^4				(1) [139]
	110070 (±970) ¥	1600 (±460)			(2) [159]
	88850 (±250)	1.5 (±0.6)			(2) [159]
			30 ºC		
C_{12}PC	13731		−41.59*	−15.58	(1) [243]
C_{14}PC	60588	61	−16.43*	11.33	(1) [243]
C_{16}PC	82737	1523	−16.04*	12.50	(1) [243]
			35 ºC		
C_{12}PC	12238		−41.59*	−17.48	(1) [243]
C_{14}PC	55127	66	−16.43*	11.54	(1) [243]
C_{16}PC	76664	920	−16.04*	12.77	(1) [243]
			40 ºC		
C_{12}PC	7302		−41.59*	−18.43	(1) [243]
C_{14}PC	50664	83	−16.43*	11.78	(1) [243]
C_{16}PC	57511	99	−16.04*	12.49	(1) [243]

(1) Electrical conductivity; (2) potentiometry; (3) ITC; (4) surface tension. ¥ Experiments with α-*CD*. C_{12}DEAB: dodecyldimethylethylammonium bromide.* Values obtained by using the van't Hoff equation in a concentration range from 20 to 40 ºC.

Table 7. Thermodynamic parameters for interactions between 3-alkoxyl-2-hydroxypropyltrimethylammonium bromides (C_nNBr) and *CD*s, at 25 ºC.

	$K_{1,1}$/ M^{-1}	$K_{2,1}$/ M^{-1}	ΔH^0 / (kJ mol^{-1})	$T\Delta S^0$ / (kJ mol^{-1})	Obs.
			α-*CD*		
C_7NBr	1.95×10^3		−18.89 (±0.53)	−0.11	(1) [244]
C_8NBr	2.62×10^3		−24.87 (±0.32)	−5.36	(1) [244]
C_{12}NBr	0.02148	3.06×10^6	1×10^{6} *; −57.95(±0.45)**	−20.93	(1) [244]
C_{14}NBr	0.0663	13.75×10^6	1×10^{6} *; −67.75(±0.49)**	−27.02	(1) [244]
			β-*CD*		
C_8NBr	1.08×10^3		−2.97 (±0.36)	14.35	(1) [245]
C_{12}NBr	34.85×10^3		−12.65 (±0. 60)	13.28	(1) [245]
C_{14}NBr	141.9×10^{3} ***		−23.96(±0.48)	5.44	(1) [245]

(1) ITC. * Enthalpy change for the 1st surfactant binding. ** Enthalpy change for the 2nd surfactant binding. *** Value for overall association constant ($K_{1,1}$*$K_{2,1}$)

Table 8. Stability constants for interactions between double tailed surfactants and *CD*s, at 25 ºC.

	$K_{1,1}/(10^3\ M^{-1})$	$K_{2,1}/(10^3\ M^{-1})$	Obs.
		α-CD	
DOAB	3.6	17.16×10^3	(1) [252]
DDAB	17.16	2.22×10^3	(1) [252]
DDAB	15.9	5.7	(2) [158]
DDAC	26	7.5×10^3	(1) [248]
		HP-α-CD	
DDAC	8.4	2.8×10^3	(1) [248]
		β-CD	
DDAB	16.1	0.73×10^3	(2) [158]
DDAC	9.7	2.9×10^3	(1) [248]
		HP-β-CD	
DDAC	26.1	n.d.	(1) [248]
		CM-β-CD	
DDAC	86.4		(1) [248]
		γ-CD	
DDAB	4.44	1.8×10^{-6}	(2) [158]
DDAC	7.6	n.d.	(1) [248]

(1) ^{1}H NMR chemical shifts; (2) potentiometry. DOAB: *N*,*N*-dioctyldimethylammonium bromide; DDAB: *N*,*N*-didecyldimethylammonium bromide; DDAC: *N*,*N*-didecyldimethylammonium chloride; HP-α-CD: Hydroxypropyl-alpha-cyclodextrin; HP-β-CD: hydroxypropyl-beta-cyclodextrin; CM-β-CD: carboxymethyl-beta-cyclodextrin; n.d.: not detected, $K_{1,1}>>K_{2,1}$.

Table 9. Binding constants and stoichiometry ratios for *CD*:gemini surfactants interactions, at 298.15 K.

		Stoichiometry *CD:S*	$K_{1,1}$/ M^{-1}	$K_{2,1}$/ M^{-1}	Obs.
$(C_{12}N)_2Cl_2$	α-CD	2:1		3.80×10^{10} a)	(1) [293]
$(C_{14}N)_2Cl_2$				4.20×10^{6} a)	
$(C_{16}N)_2Cl_2$				4.00×10^{7} a)	
$(C_{12}N)_2Cl_2$	β-CD	2:1		4.7×10^{6} a)	
$(C_{14}N)_2Cl_2$				0.98×10^{6} a)	
$(C_{12}N)_2Cl_2$	γ-CD	2:1		3.00×10^{7} a)	
$(C_{14}N)_2Cl_2$				2.70×10^{6} a)	
$(C_{16}N)_2Cl_2$				0.62×10^{16} a)	
12-2-12	β-CD	2:1	$1.97(\pm0.15)\times10^{3}$	$0.60(\pm0.24)\times10^{3}$	(2) [203]
12-2-12			$4.0(\pm1.4)\times10^{4}$	$3.6(\pm0.5)\times10^{3}$	(3) [19]
12-4-12			$5.6(\pm2.3)\times10^{4}$	$4.7(\pm0.6)\times10^{3}$	(3) [19]
12-6-12			$3.7(\pm1.1)\times10^{4}$	$7.5(\pm0.7)\times10^{3}$	(3) [19]
12-8-12			$3.15(\pm0.53)\times10^{3}$	$1.34(\pm0.27)\times10^{3}$	(2) [203]
12-8-12			$9.8(\pm4.1)\times10^{4}$	$5.6(\pm0.6)\times10^{3}$	(3) [19]
12-10-12			$3.13(\pm0.79)\times10^{3}$	$2.12(\pm0.43)\times10^{3}$	(2) [203]
12-10-12			$2.0(\pm0.7)\times10^{4}$	$8.3(\pm1.0)\times10^{3}$	(3) [19]
12-EO_1-12			$8(\pm2)\times10^{3}$	$2.8(\pm0.9)\times10^{4}$	(3) [288]
12-EO_1-12			$1.0(\pm0.5)\times10^{3}$	$5(\pm3)\times10^{4}$	(4) [288]
12-EO_1-12	γ-CD	1:1	$2.9(\pm0.5)\times10^{4}$		(4) [290]
12-EO_5-12			$2.0(\pm0.5)\times10^{4}$		(4) [290]
$(C_8Cys)_2$	β-CD	1:1	$13.1(\pm0.2)\times10^{2}$; $9.6(\pm0.3)\times10^{2}$ b)		(2) [161]
$(C_8Cys)_2$			$8.2(\pm0.1)\times10^{2}$		(5) [161]
$(C_8Cys)_2$			$7.0(\pm0.6)\times10^{2}$; $6.5(\pm0.7)\times10^{2}$; $1.2(\pm0.3)\times10^{2}$; $4.5(\pm0.7)\times10^{2}$ b)		(3) [161]

(1) ITC; (2) electrical conductivity; (3) ^{1}H NMR chemical shifts; (4) ^{1}H NMR diffusometry; (5) UV-visible spectroscopy. a) Overall binding constants: $K_O=K_{1,1}*K_{2,1}$ in M^{-2}; b) Different K values result from different experimental initial conditions or measurements.

Table 10. Stability constants for bolaform surfactants:cyclodextrins (1:1) interactions, at 298.15 K.

		$K_{1,1}$/(kg mol^{-1})	Obs.
$C_{12}Me_6$ Br_2	β-CD	2.5 (±0.1)×10^3	(1) [291]
		3.0 (±0.4)×10^3	(2) [291]
C_8Me_6 Br_2	α-CD	44	(3) [98]
		44 (±5) [a)]	(4) [332]
$C_9Me_6Br_2$		240 (±50) [a)]	(4) [332]
$C_{10}Me_6$ Br_2		1121 [a)]	(3) [98]
		1360 (±290) [a)]	(4) [332]
$C_{11}Me_6$ Br_2		3170 (±970) [a)]	(4) [332]
$C_{12}Me_6$ Br_2		6900	(3) [98]
		6760 (±850) [a)]	(4) [332]

(1) electrical conductivity; (2) ^{1}H NMR diffusometry; (3) ITC coupled to ^{1}H NMR chemical shifts; (4) ^{1}H NMR chemical shifts. [a)] Unities of $K_{1,1}$ in (M^{-1}); solutions were prepared in D_2O, with a constant ionic strength (I=0.01 M NaCl).

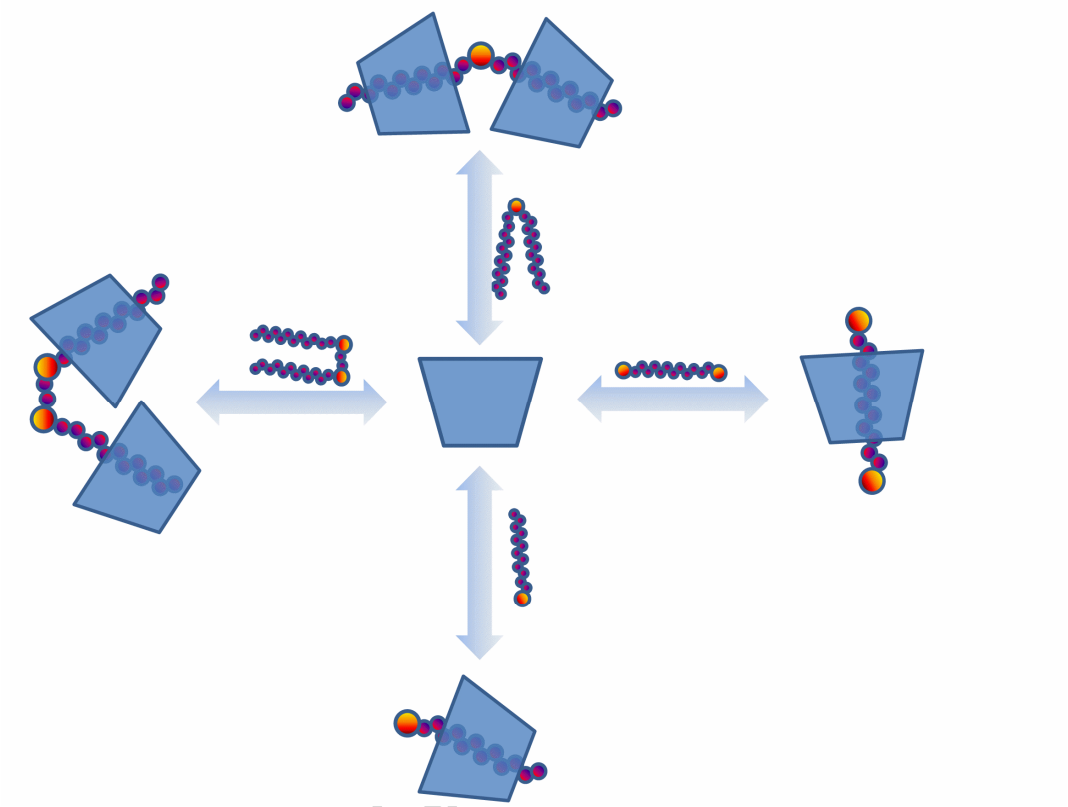
Table 11. Thermodyamic parameters for bolaform surfactants:cyclodextrins (1:1) interactions, at 308.15 K, as seen by ITC [98].

		$K_{1,1}$/(kg mol^{-1})	ΔH^0 / (kJmol^{-1})	ΔS^0/ (JK^{-1}mol^{-1})
$C_8Me_6\ Br_2$	α-CD	35 (±1)	−16.8 (±0.1)	−25.0 (±0.4)
$C_{10}Me_6\ Br_2$		764 (±100)	−25 (±1)	−25 (±3)
$C_{12}Me_6\ Br_2$		3817 (±340)	−31 (±1)	−31 (±2)
$C_{10}Me_6\ Br_2$	β-CD	137 (±100)	−4.7 (±0.1)	25.6 (±0.2)
$C_{12}Me_6\ Br_2$		3817 (±340)	−9.7 (±0.1)	31.5 (±0.5)

Table 12. Kinetic parameters for the formation, k_{on}, and dissociation, k_{off}, of α-cyclodextrin:bolaform surfactants (1:1) complexes.

	k_{on} / (mol^{-1} dm^3 s^{-1})	k_{off} / (10^{-4} s^{-1})	$\tau_{1/2}$ [c] / s
		298.15 K	
$C_8Me_6Br_2$	0.16 (± 0.01) [a]	37.3	186
$C_9Me_6Br_2$	0.187 (± 0.015) [b]	5.23 (±0.14)	1325
$C_{10}Me_6Br_2$	0.143 (± 0.001) [a]	1.276	5432
	0.164 (± 0.022) [b]	1.04 (±0.01)	6665
$C_{11}Me_6Br_2$	0.104 (± 0.011) [b]	0.341 (±0.004)	20327
$C_{12}Me_6Br_2$	0.126 (± 0.001) [a]	0.183	37877
	0.121 (± 0.013) [b]	0.132 (±0.004)	52511
$C_{12}Et_2Me_4Br_2$	5.83 (± 0.38) × 10^{-3} [b]	0.54 (±0.02)×10^{-1}	128361
		308.20 K	
$C_8Me_6Br_2$	0.30 (±0.02) [a]	84.6	82
$C_{10}Me_6Br_2$	0.322 (± 0.001) [a]	4.215	1644
$C_{12}Me_6Br_2$	0.349 (±0.001) [a]	0.914	7584
		348.15 K	
$C_{10}PMe_6I_2$	7.9 (± 0.6)×10^{-5} [b]	—	—

[a] Unities of (mol^{-1} kg s^{-1}); values from ref. [98]. [b] Values from ref. [332]. [c] $\tau_{1/2}=\ln(2)/k_{off}$ and represents the half-life of the complex.



Graphical Abstract

Highlights

Surfactants form host-guest supramolecular structures with cyclodextrins;

Values of stability constants depend on techniques and methods of evaluation;

Cyclodextrin-surfactant interactions are exothermic;

Disordered water inside the α-cyclodextrin cavity leads, in general, to a negative binding entropy change.