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PERSPECTIVE

Unveil the potential function of CD in surfactant systems

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CDs may have promising functions in surfactant systems far beyond simply being disadvantageous to the formation of micelles. In this paper we review the recent literature and our work on the interesting effect of CDs on amphiphilic systems, especially on the concentrated single surfactant systems and catanionic surfactant mixed systems, both of them have been scarcely focused upon in the literature. In concentrated single surfactant systems, the 2 : 1 surfactant–CD inclusion complexes may form hierarchical self-assemblies such as lamellae, microtubes, and vesicles which are driven by hydrogen bonding. In nonstoichiometrically mixed catanionic surfactant systems, CDs behave as a stoichiometry booster that always selectively binds to the excess component so as to shift the mixing ratio to electro-neutral in the aggregates. In this way, CDs reduce the electrorepulsion in the aggregates and trigger their growth. Upon analysis of literature work and our own results, we expect that a new era focusing on the new function of CDs on surfactant systems will come.

1. Introduction

Cyclodextrins (CDs) are oligosaccharides of six, seven, or eight D-glucopyranose ($C_6H_{10}O_5$) units (named as α, β, and γ-CD, respectively) linked by α-1,4 glycoside bonds. Overall these oligosaccharides form truncated doughnut-shaped structures with hydrophobic CH_2 groups in the cavity whereas hydrophilic OH groups at the exterior (Fig. 1). As a result, the hydrophobic cavity forms an ideal harbor in which poorly water-soluble molecules can shelter their most hydrophobic parts, whereas the formed complex is a soluble entity on its own. In the past century, CDs have been found to form molecular inclusion complexes with a variety of guest molecules ranging from inorganic to organic ones.[1–3] Among these, the complexes between CDs and surfactants have been widely investigated by surfactant chemists.[4–9]

The study of CD–surfactant inclusion complexes can be dated back to the early 1960s, when Schlenk and Sand for the first time reported the formation of inclusion complexes of

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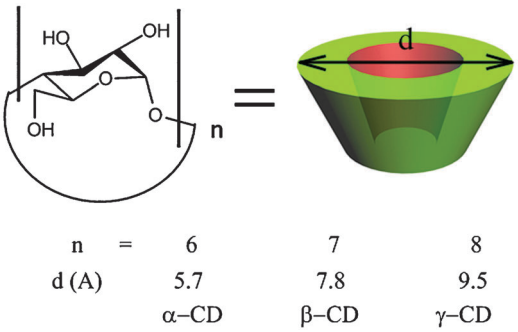

Fig. 1 Structures of cyclodextrins (CDs) and approximate values of the largest diameter of their nanocage.

β-CDs and fatty acids.[10] This discovery triggered a flourishing study about the formation of inclusion complexes between CDs and other amphiphiles, especially surfactants of various types.[4–9] So far it is well-known that the cavity size of α- and β-CDs fits the diameter of aliphatic chains very well, so that these two CDs are used frequently in CD–surfactant inclusion systems. It has been widely explored that α- and β-CDs can form inclusion complexes easily with single surfactant chains, including the single chain of a bola[7] (one aliphatic chain ended by two head groups) and a gemini[8] (two chains connected covalently by a spacer) surfactant. But due to the steric effect, no inclusion occurs if a double- or triple-chain surfactant is used.[11,12]

The binding stoichiometry between surfactants and CDs depends on the surfactant chain length and the molar ratio between surfactants and CDs.[13–18] Normally, 1 : 1 inclusion complexes can be formed easily in all cases; if the concentration of CD is high enough and the surfactant chain length is larger than 12 C, 2 : 1 complexes are also possible.[15,16,18] However, this normally leads to an orientation change of the CDs. As mentioned above, CDs are truncated doughnut-shaped structures. In cases where 1 : 1 inclusion complexes are formed, the head of the surfactants normally locates at the wider rim of the CDs;[19] in contrast, if 2 : 1 complexes are formed, the head of the surfactants locates at the narrower rim of the CDs,

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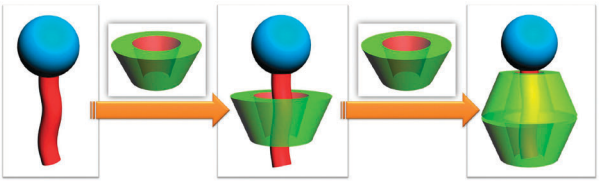

Fig. 2 Schemes of CD–surfactant complexes. For CD–surfactant 1 : 1 complexes, the mutual direction of CD and surfactant is not certain. The majority of the outer surface of 1 : 1 complexes is hydrophilic. As for CD–surfactant 2 : 1 complexes, two CD molecules are preferably aligned in a head-to-head fashion to maximize formation of H-bonds. Almost the entire outer surface of 2 : 1 complexes is hydrophilic. Image is adapted from Jiang *et al.* (2011).[50]

whereas the two wider rims connect together *via* hydrogen bonds to maximise hydrogen bond formation,[20,21] as illustrated in Fig. 2.

It is well-attested that upon addition of CD to a surfactant system, both the CMC and surface tension are increased; as the formed CD–surfactant inclusion complexes are hydrophilic they lose the ability to aggregate into micelles *via* hydrophobic interaction and the micelles are destroyed (Fig. 3).[19] Therefore, numerous reports claimed that the presence of CD is disadvantageous to the formation of micelles. To improve the association property of CD–surfactant systems, many efforts were made to hydrophobically modify CD molecules (HM-CD).[22] These HM-CDs on their own can self-assemble in a classic way similar to that of surfactant, where the CD portion acts as the hydrophilic head group of a surfactant. Interestingly, Hoffmann *et al.* found that HM-CDs may be disadvantageous to self-assembly formation as well: the wormlike micelles can be broken into spherical ones.[23] However, it is rather surprising that such an effect is not caused by the formation of inclusion complexes between HM-CDs and surfactant chains, but by the solubilization of HM-CDs in the micellar core.[23]

In contrast to the piles of literature that report on the disadvantages of CDs, especially unmodified CDs, for surfactant self-assembly, recent studies suggest that the formation of CD–surfactant inclusion complexes may be beneficial to self-assembling systems as well, if they are used properly. For instance, CDs were smartly exploited in controlled release of DNA or proteins.[24–26] As charged macromolecules, DNAs or proteins can form mixed micelles with oppositely charged surfactants; upon addition of β-CD, they are able to be released from the mixed micelles due to the formation of β-CD–surfactant inclusion complexes, which breaks the micelles (Fig. 4). The CD–surfactant complexation can also be used to tailor the rheological property of a fluid that contains hydrophobic chains. In many cases, viscous or viscoelastic fluid formed in telechelic associating polymers

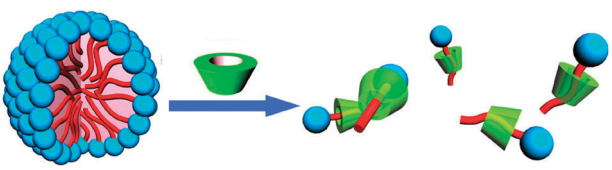

Fig. 3 A scheme for the destruction of a micelle induced by CD.

Fig. 4 Schematic representation of the proposed DNA decompaction mechanism. The different components are not at scale. Image is adapted from Carlstedta *et al.* (2010).[24]

composed of hydrophilic backbone and hydrophobic *n*-alkyl end-groups in water due to aggregation of the hydrophobes.[27,28] The addition of α-, β-, or γ-cyclodextrin (CD) substantially reduces the solution viscosity because the CD molecules envelop the hydrophobes which prevents association. A similar principle was copied to viscous systems made with polymer/surfactant mixtures, where the viscosity is produced by the connection of polymer chains by surfactant self-assemblies (micelles or vesicles). Upon addition of CDs, these self-assemblies were disassociated so that the viscosity is significantly reduced.[29] (Fig. 5)

Another flourishing area regarding the elegant use of CDs is to tailor the self-assembling properties of complicated amphiphiles in aqueous systems. Work in this category is mainly based on introduction of a well-known guest group, such as ferrocene (Fcc), adamantane (Ad), azobenzene *et al.*, to a complicated amphiphile, which normally has more than two hydrocarbon chains. Without CDs, these amphiphiles can self-assemble into some ordered structures; upon addition of CDs, owing to the inclusion of the hydrophobic bulky group into the cavity of CDs, the hydrophilicity of the CD–amphiphiles is significantly increased which results in transition of the self-assembled structures. For example, Chen *et al.* found that by mixing a 1-naphthylammonium chloride (NA)/β-CD inclusion complex with an anionic surfactant, aerosol AOT (sodium bis(2-ethyl-1-hexyl)sulfosuccinate), one obtains vesicles; in contrast, without the presence of β-CD, only flake-like structures are found (Fig. 6).[30] This different aggregate formation is actually constrained by the geometry rule proposed by Israelachvilli *et al.*,[31] which is described by the packing parameter *P*:

$$P = \frac{v}{a_0 l_c},$$

where v is the hydrocarbon chain volume, a_0 the head group area and l_c the hydrocarbon tail length, increases. According

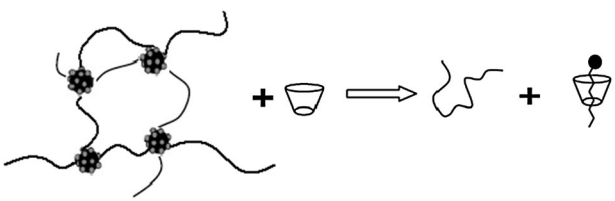

Fig. 5 Schematic representation of the interaction of CD with polymer/surfactant networks.

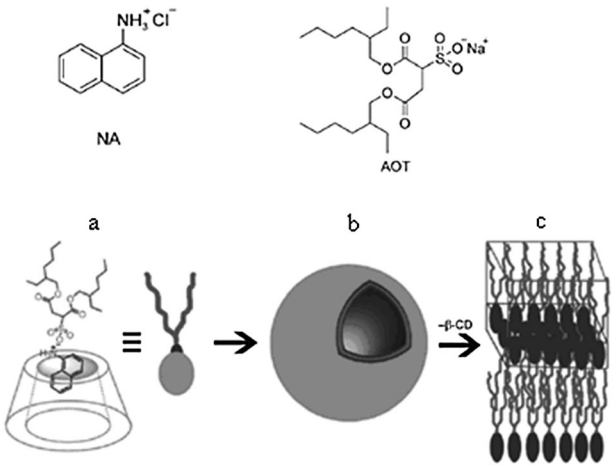

Fig. 6 Schematic representation of vesicle formation from a CD supramolecular complex. (a) Pseudoamphiphiles and (b) vesicular self-assembly of pseudoamphiphiles. The gap is exaggerated to display the structure of a vesicular membrane. (c) Aggregation of NA–AOT complexes. Image is adapted from Jing *et al.* (2007).[30]

to Israelachvilli, larger *P* values correspond to larger aggregates which have smaller curvature. Inclusion of NA into β-CD produces a new bulky hydrophilic headgroup, which increases a_0 and results in smaller *P*. Therefore, formation of aggregates with larger curvature (in this case, vesicles) occurred. In this way, Jiang *et al.* are able to make smart self-assemblies in a dispersion of a hydrophobic molecule that contains a *trans*-azobenzene moiety. Upon inclusion of the *trans*-azobenzene group into α- or β-CD's cavity, a bulky hydrophilic head group was created which transforms the molecule into an amphiphile, thus allowing the formation of vesicles.[32] Upon UV irradiation, the vesicles disassembled due to the change of the *trans*-azobenzene into its *cis* isomer, which doesn't fit the cavity of β-CDs any more. By utilizing this photo-sensitive complexation of the azobenzene group, which is attached to the aliphatic chain with CD, Zhang's group were able to create versatile smart molecular devices, such as photo-switched formation and disassembly of vesicles,[33] and a reversible 'molecular shuttle' that has photo-controlled wettability.[34]

Upon careful study of the literature, one may find that all the above examples are based on the well-known observation that CD inclusion complexes have stronger hydrophilicity, and most of the work was carried out in dilute solutions. This is especially true for the investigation of complexation between CDs and surfactants, where studies were mainly conducted at the premicellar region or around the CMC.[35–43] It is surprising that: (1) few studies focus on the concentrated or semi concentrated surfactant–CD mixed systems; and (2) little attention has been paid to the influence of CDs on the catanionic surfactant mixed systems. Since these two types of systems are very important in surfactant studies, we are very curious about what will occur if CDs were added to these systems. Excitingly, our recent work and some other literature reports indeed shed some light in this regard. In the following two sections, we will briefly summarize the progress about the effect of β-CD on semi-concentrated surfactant solutions and

on the mixed systems of catanionic surfactants, where β-CD is used smartly to endow surfactant self-assemblies with new life.

2. Hydrogen bond driven self-assembly in semi concentrated surfactant systems

Inspired by the emergence of nonamphiphilic self-assembly in polyoxometalate macroions,[44,45] oppositely charged polymers,[46,47] nonamphiphilic aromatic organic salts,[48] and so on, we wondered if any self-assembly driven by hydrogen bonds can occur in concentrated CD–surfactant mixed systems. As an exemplary system, we chose the concentrated aqueous mixtures of β-CD and sodium dodecyl sulfate (SDS, a most common anionic surfactant). The samples were prepared in the concentration range of 4–50% (wt%) at a molar ratio between β-CD and SDS of 2 : 1.[49,50] In this case, the 2 : 1 inclusion complex, namely SDS@2β-CD, was formed with the whole aliphatic chain of SDS embedded in the two cavities of β-CD so that the entire inclusion complex is completely hydrophilic.

It is very striking that vesicles,[50] microtubes,[49] and lamellae[50] were formed with increasing overall concentrations (Fig. 7b). Interestingly, the microtubes are multilamellar, and their cross-sections resemble annular rings (Fig. 7b and 8). Wide angle X-ray scattering (WAXS) results revealed that the SDS@2β-CD bilayer membrane has a channel-type crystalline structure, where β-CD molecules align in a head-to-head fashion along the "channels".

The driving force for the above marvellous hierarchical self-assemblies in SDS@2β-CD systems is hydrogen bond. This conclusion was obtained by first ruling out the hydrophobic interaction in these systems since the β-CD/SDS solutions exhibit water-like surface tension (~69 mN m^{-1}), revealing that SDS@2β-CD is fully hydrophilic. Secondly, the role of the electrostatic repulsive force between the SDS head groups was identified to be responsible for stabilization (macro phase stability), because both salt addition and substituting SDS with nonionic surfactants ($C_{12}EO_{10}$ or C_{14}DMAO) resulted in precipitation. Finally, hydrogen bond formation was proved to be the driving force by the following indirect experiment: when replacing β-CD with its "H-bond-poor" analogue (HP-β-CD), the solutions are transparent and no aggregate can be found, indicating that the H-bonds between β-CD molecules (including the direct ones and those bridged by water) contribute to the assembly of SDS@2β-CD.[49]

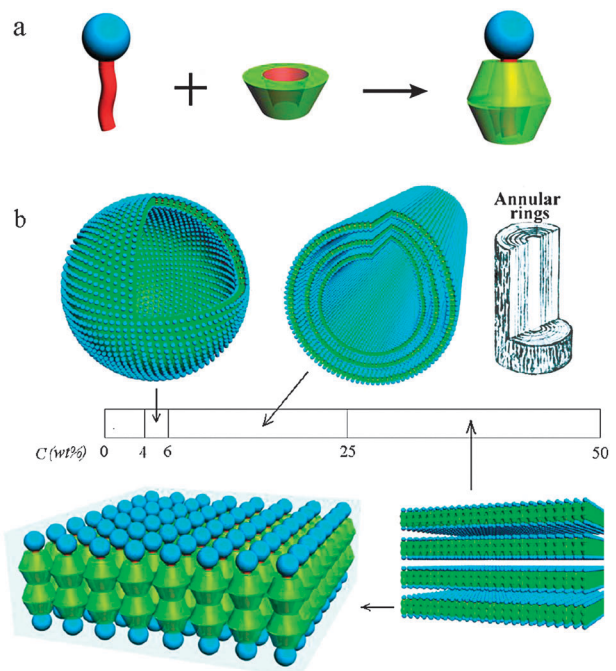

Fig. 7 Schematic self-assembly behavior of SDS@2β-CD, at different concentrations. Image is modified from Jiang *et al.* (2010, 2011).[49,50]

The most important finding is that such a hydrogen bond driven self-assembly can be generalized in other CD/ionic surfactant systems:[49] when SDS was replaced by anionic $SDSO_3$ and SDBS, cationic CTAB, or zwitterionic TDPS, tubular structures were observed at a CD/surfactant molar ratio of 2 : 1 and a typical total concentration of 10 wt% (Fig. 9), although these structures are different in some details. For instance, in the $SDSO_3$/β-CD system, the microtubes are in equilibrium with a considerable amount of giant vesicles, as highlighted by different colors (Fig. 9a); in the SDBS/β-CD and TDPS/β-CD systems, the tubes are of diameters ~3 μm and ~200 nm, respectively (Fig. 9b and c).

The hydrogen bond driven self-assemblies of semi-concentrated CD inclusion complexes was found by Hennink *et al.* as well in a recent study,[51] where the formation of biocompatible hydrogels was found in the aqueous solution of β-CD and 8-arm or linear cholesterol-ended poly(ethylene glycol) (PEG–chol) (Fig. 10). In their case, the inclusion occurs between β-CD and the cholesterol group. XRD examination demonstrates the presence of crystalline domains of β-CD. In their studies, the concentration of β-CD is 5.5% which is high enough to allow close contact (Fig. 10). In contrast, it was found in other works that disruption of the hydrogels occurred by adding small amounts of β-CD (<16 mM).[52–54] For example, Akiyoshi *et al.* reported that addition of less than 1% β-CD to hydrogel nanoparticles based on cholesterol-grafted pullulan60 or poly(L-lysine) disrupted the nanogels due to the capture of the hydrophobic cholesterol groups by β-CD. We expect that at high enough CD concentrations where formation of hydrogen bond between CDs is possible, the scenario might be completely different.

3. CDs as stoichiometry booster in catanionic surfactant mixed systems

In literature, one can find some work regarding the effect of CD on the mixed surfactant systems, which can be mainly classified into two groups: one is the mixed systems of like-charged surfactant systems[55–58] or nonionic/zwitterionic ones;[59] the other is hydrocarbon and fluorocarbon surfactant systems.[60,61] In both types of systems, the authors focus a lot on the competition of the two surfactant components binding with CDs. As a result, in the fluorocarbon containing systems, one observes breaking of the mixed micelles caused by continuous removal of the fluorocarbon surfactants from the mixed micelles, because the binding strength between CDs and fluorocarbons is much stronger;[60,61] in the like charged

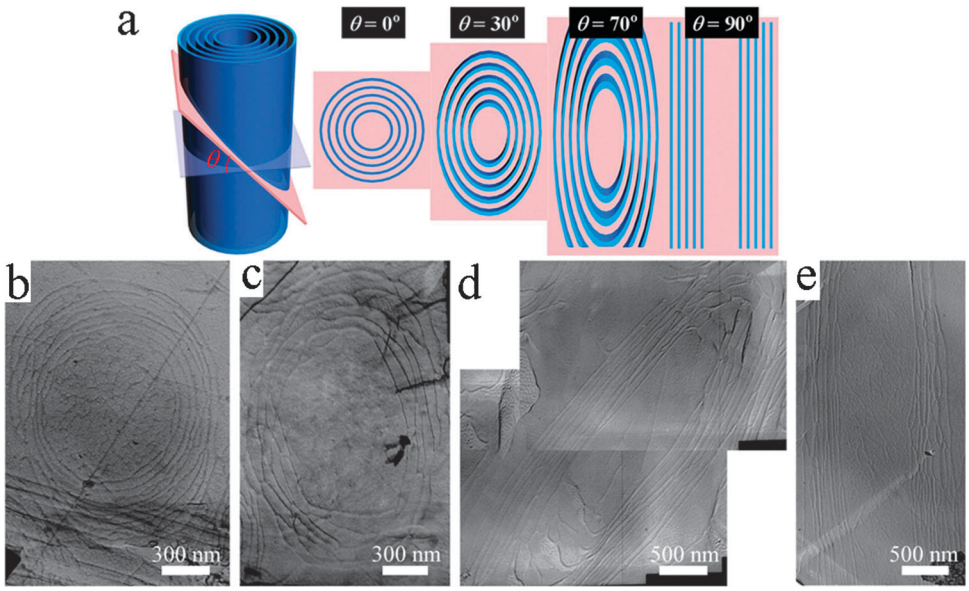

Fig. 8 Demonstration of the "annular ring" structure of the microtubes. The cross sections of such a microtube with increases of θ (a) and FF-TEM micrographs of the microtubes with the fracture section at different angles (b–e). Image is modified from Jiang *et al.* (2010).[49]

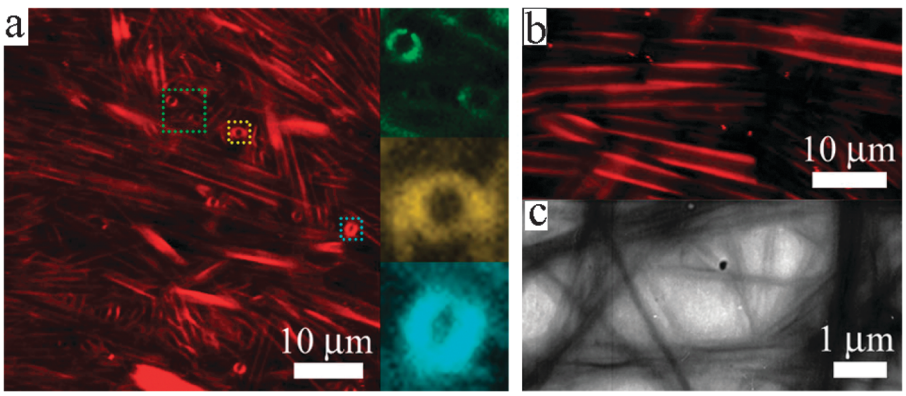

Fig. 9 Aggregates formed by other CD/IS complexes. Microtube/vesicle coexistence for $SDSO_3$/β-CD (a). Microtubes of SDBS/β-CD and TDPS/β-CD, respectively (b, c). Image is modified from Jiang *et al.* (2010).[49]

surfactant systems, one observes the competition of binding whereas there is no breaking of micelles.[59] It is surprising that little work has been done to study the influence of CDs on catanionic surfactant mixed systems.[62,63]

Catanionic surfactant systems are very attractive since they enable the formation of a full spectrum of self-assembled structures, ranging from micelles (spherical, rodlike, and wormlike) and [64–66] vesicles,[67–71] to other bilayer structures,[72,73] simply by variation of the cationic-to-anionic surfactant ratio. Such rich aggregate morphologies in catanionic surfactant systems can be related with the variation of the packing parameter triggered by changing the mixing ratio. It is known that in catanionic solutions oppositely charged surfactants can form ion-pair complexes which greatly reduce the average head group size of each component. As a result, the packing parameter, P, increases. Then, with shifting the mixing ratio gradually to charge-neutralization, the electrostatic repulsion in the aggregates decreases. This means that the average head group area of the surfactants decreases, which leads to an increase in P. Correspondingly, the aggregates transform from small micelles into vesicles and other larger aggregates.

Compared with the situation in single or like-charged surfactant systems, where addition of CD simply weakens the formation of micelles upon formation of inclusion complex with the surfactant molecules, we found that the addition of CDs to catanionic surfactant systems leads to growth of the micelles. The first sign for this transition is a significant macroscopic change induced by β-CD in a nonstoichiometrically mixed catanionic system, SDS/DEAB, with $x_{SDS} = 0.8$, $C_T = 10$ mM.[21] Upon addition of β-CD, the relative viscosity rises and reaches a maximum at $C_{\beta\text{-CD}} = 3.5$ mM (Fig. 11a), then drops back to that of water at $C_{\beta\text{-CD}}$ up to 5 mM but an intense increase of the turbidity (Fig. 11b). FF-TEM micrograph, DLS, and fluorescence quenching experiments revealed that the system has undergone a micellar growth process before transformation into a vesicular suspension.[21]

Such an increase of aggregate sizes was observed in the DEAB-rich side as well. Actually, in a broad category of

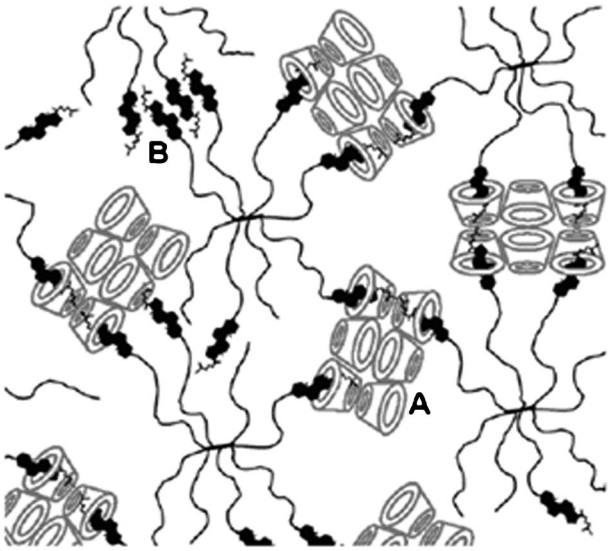

Fig. 10 Schematic representation of 8-arm PEG–chol/β-CD gels. Cholesterol groups at the termini of the 8-arm PEGs form inclusion complexes with crystalline nanoclusters of β-CDs (A). β-CD clusters with arbitrary size and crystal packing are shown. Dependent on the relative number of cholesterol and β-CD moieties, hydrophobic cholesterol–cholesterol interactions might also occur (B). Image is adapted from van de Manakker *et al.* (2010).[51]

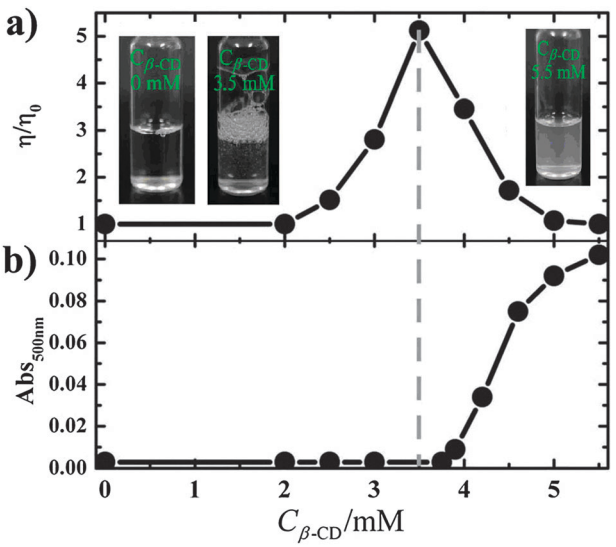

Fig. 11 The variations of relative viscosity (a) and absorbance (b) inSDS/DEAB (x_{SDS} = 0.8, C_T = 10 mM) solutions with varied β-CD concentration, $C_{β\text{-CD}}$. The inset photographs in (a) show the appearance of the typical solutions. Image is adapted from Jiang *et al.* (2010).[21]

catanionic surfactant systems where nonstoichiometry mixing exists, we found that the excess component is always found predominantly removed from the aggregates by β-CD, which shifts the mixing ratio between the two oppositely charged surfactants gradually to 1 : 1.[21] As a result, a growth of micelles is promoted, rather than their breaking (Fig. 12).

Why does the excess component selectively bind with CDs? Why does the difference in binding constants become

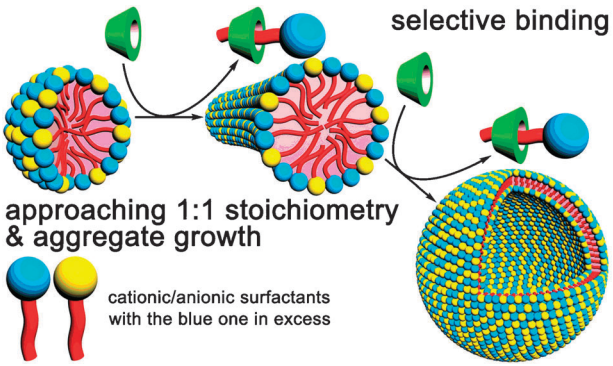

Fig. 12 A scheme of the aggregate growth induced by β-CD in nonstoichiometrical cationic/anionic surfactant systems. Image is adapted from Jiang *et al.* (2010).[21]

unimportant in catanionic surfactant systems? These questions were solved by our thermodynamic model.[74] For a given aqueous mixture of surfactant **1**, surfactant **2**, and β-CD, where their respective bulk concentrations are C_1, C_2 ($C_1 + C_2 = C_T$), and $C_{β\text{-CD}}$. In a 1 : 1 surfactant/β-CD binding model, the host–guest equilibrium is governed by

$$K_i^b = \frac{C_i^c}{C_i^m C_{β\text{-CD}}^f} \quad (1)$$

where K_i^b is the binding constant of CD to surfactant **i** (**i** = **1** or **2**) and C_i^c, C_i^m, and $C_{β\text{-CD}}^f$ are the concentrations of **i**/β-CD complex, monomeric (uncomplexed and unaggregated) **i**, and free (uncomplexed) β-CD, respectively. Then the apparent selectivity of β-CD to surfactant **i**, S_i, can be defined as the ratio of C_i^c weighed by C_i:

$$S_1 \equiv \frac{C_1^c C_2}{C_2^c C_1} = \frac{K_1^b C_1^m C_2}{K_2^b C_2^m C_1} \quad (2)$$

Clearly, $S_1 \gg 1$, $S_1 \ll 1$, and $S_1 \sim 1$ correspond to a high selectivity to **1**, a high selectivity to **2**, and a low selectivity, respectively. At $C_T <$ critical aggregation concentration (CAC), the aggregation equilibrium is not yet established and the selectivity is simply governed by binding constants. For the mixtures of SDS/DEAB (molar ratio 3 : 1) and β-CD, the apparent selectivity is found very close to 1. This suggests if we study the catanionic surfactant system at concentrations below CAC, binding competition of the two components with CD will occur, which depends only on the binding strength of each components with CD. In this case, the catanionic systems are similar to those nonionic ones or hydrocarbon/fluorocarbon surfactant systems.

However, at $C_T \geq$ CAC, the aggregation equilibrium emerges and the selectivity can be expressed as[74]

$$S_1 = \lim_{C_{β\text{-CD}} \to 0} \frac{K_1^b \mathrm{CMC}_1 x_1^a C_2}{K_2^b \mathrm{CMC}_2 x_2^a C_1} \exp(\beta((x_2^a)^2 - (x_1^a)^2)) = \frac{K_1^b \mathrm{CMC}_1 x_1^{a0} C_2}{K_2^b \mathrm{CMC}_2 x_2^{a0} C_1} \exp(\beta((x_2^{a0})^2 - (x_1^{a0})^2)) \quad (3)$$

in which x_i^{a0} is the molar fraction of **i** in the aggregates without

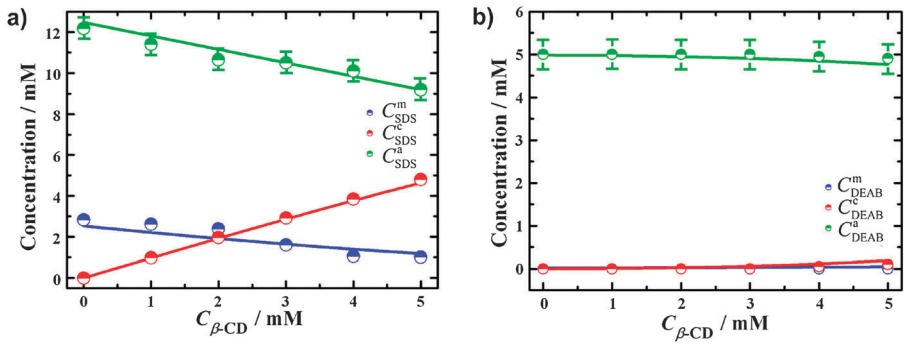

Fig. 13 The selective binding of β-CD upon its addition to a SDS-rich SDS/DEAB (15/5 mM) system as predicated by the thermodynamic model and experimentally confirmed by PGSE-NMR. (a) and (b), Variations of concentrations of SDS and DEAB in different states. Image is adapted from Jiang *et al.* (2010).[74]

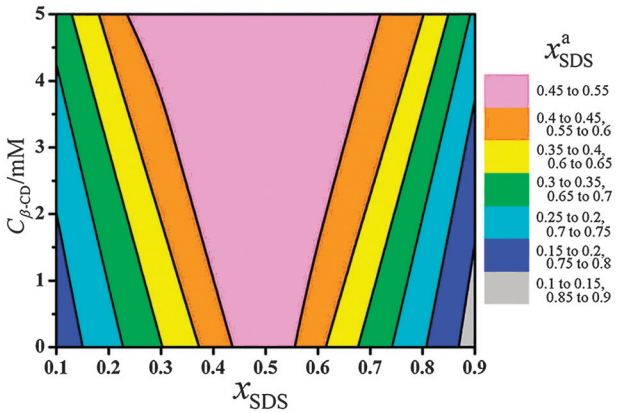

Fig. 14 Predicted contour map for SDS/DEAB (C_T = 10 mM) and β-CD mixed systems, x^{a}_{SDS} against the surfactant composition in bulk solution (x_{SDS}) and against $C_{\beta\text{-CD}}$. Image is adapted from Jiang *et al.* (2010).[74]

β-CD addition (*i.e.*, $C_{\beta\text{-CD}} = 0$), β is the interaction parameter of the two surfactants and represents a net energy difference between the mixed (**1** + **2**) aggregation phase and the pure (**1** or **2**) micellar phases. In this stage, the combination of the host–guest and aggregation equilibria dominates the systems. For the SDS/DEAB/β-CD systems, the thermodynamic model generally gives high selectivity of β-CD to the major surfactant regardless of the similarity between K^{b}_{SDS} and K^{b}_{DEAB}. It is found that the concentration of complexed SDS (C^{c}_{SDS}, the red curve in Fig. 13a) is almost proportional to $C_{\beta\text{-CD}}$, whereas the concentration of complexed DEAB (C^{c}_{DEAB}, the red curve in Fig. 13b) is always close to 0, qualitatively revealing a high selectivity to SDS (S_{SDS}). This leads to the predominant removal of the excess SDS from aggregates (the green line in Fig. 13a), while the concentration of DEAB in aggregates C^{a}_{DEAB} is not affected (the green line in Fig. 13b).

Since β-CD always shifts the compositions in the aggregates to 1 : 1, it was defined as a stoichiometry booster for nonstoichiometric cationic/anionic surfactant systems, which is analogous to a pH buffer that always adjusts the ratio of H^+/OH^- to a certain value. Fig. 14 demonstrates this stoichiometry boosting effect in a contour map for SDS/DEAB/β-CD systems. It is clearly found that with increasing $C_{\beta\text{-CD}}$, the fraction of SDS in aggregates (x^{a}_{SDS}) shows resistance to variations of the overall molar fraction of SDS in the system (x_{SDS}). The higher $C_{\beta\text{-CD}}$, the stronger the resistance.

4. Conclusions

The function of CDs in manipulating the properties of surfactant systems can be very promising if we liberate our mind. For more than half a century it has been known that CDs form inclusion complexes with surfactants, yet it is rather surprising that the knowledge has stopped at this stage for such a long period. The latest work of us and others may become a corner stone that unveils a new vista in this field. Both fine tuning of aggregates in catanionic surfactant mixed systems and building of unconventional self-assemblies become possible by employing CDs properly. However, examples given in this review article are only the first explorations. We expect to see much more comprehensive work in this regard. For example, can be various catanionic surfactant systems depending on the structure and type of the employed surfactants. What will occur if CDs are added to the mixture of a conventional surfactant and an oppositely charged gemini or bola type amphiphile? What will occur to the aqueous two-phase systems of catanionic systems? The answer to the latter may shed some light on phase transitions that can be used in bioseparation. In addition, by tuning the aggregates in catanionic systems in our study, we impose only 1 : 1 inclusion complex on the surfactant systems; what will occur if 2 : 1 inclusion complexes are formed? In a recent study by Xing and Xiao,[63] they found that with the formation of 1 : 1 complexes, the 1 : 1 mixed catanionic surfactant mixtures become clear and transparent, whereas precipitates are observed as 2 : 1 inclusion complexes are formed. These precipitates are found to be composed of aggregates of channel type CD–surfactant inclusion complexes which exhibit thermo-dependent phase behavior. This example clearly shows that a complete understanding of the function of CDs in the catanionic surfactant mixed systems is lacking.

Furthermore, in regard of the formation of hydrogen bond-driven hierarchical self-assemblies, the smart use of them as molecular devices is also very promising. As described in our study, all the self-assemblies are channel type structures with

the hydrophobic surfactant tails fully embedded in the cavity of the CDs. This means that the sheltered hydrophobic molecules are finely aligned. Can this be employed in future materials science? The hydrogen-bond driven lamellar systems can also be competitive hydrogel reservoirs. In a word, with the development of molecular self-assemblies, which aims at organizing various building blocks into hierarchical structures, smart use of CDs in surfactant systems has become attractive virgin ground that deserves more attention. We expect that our knowledge of CDs on surfactant systems will step out of the ''binding'' and ''micellar breaking'' times and move forward to a more interesting, and challenging era.

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