Advances in Colloid and Interface Science 169 (2011) 13–25

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Versatility of cyclodextrins in self-assembly systems of amphiphiles

Lingxiang Jiang, Yun Yan, Jianbin Huang *

Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

Available online 27 July 2011

Keywords:
Surfactants
Cyclodextrins
Self-assembly
H-bonds
Unamphiphilic

ABSTRACT

Recently, cyclodextrins (CDs) were found to play important yet complicated (or even apparently opposite sometimes) roles in self-assembly systems of amphiphiles or surfactants. Herein, we try to review and clarify the versatility of CDs in surfactant assembly systems by 1) classifying the roles played by CDs into two groups (modulator and building unit) and four subgroups (destructive and constructive modulators, amphiphilic and unamphiphilic building units), 2) comparing these subgroups, and 3) analyzing mechanisms. As a modulator, although CDs by themselves do not participate into the final surfactant aggregates, they can greatly affect the aggregates in two ways. In most cases CDs will destroy the aggregates by depleting surfactant molecules from the aggregates (destructive), or in certain cases CDs can promote the aggregates to grow by selectively removing the less-aggregatable surfactant molecules from the aggregates (constructive). As an amphiphilic building unit, CDs can be chemically (by chemical bonds) or physically (by host–guest interaction) attached to a hydrophobic moiety, and the resultant compounds act as classic amphiphiles. As an unamphiphilic building unit, CD/surfactant complexes or even CDs on their own can assemble into aggregates in an unconventional, unamphiphilic manner driven by CD–CD H-bonds. Moreover, special emphasis is put on two recently appeared aspects: the constructive modulator and unamphiphilic building unit.

Contents

1. Introduction . . . 13
2. Molecular structures of CDs . . . 14
3. Basics of CD/surfactant complexes . . . 14
   3.1. Thermodynamics . . . 14
   3.2. Molecular conformation . . . 15
4. Destructive modulator . . . 16
   4.1. Surfactant micelles . . . 17
   4.2. Surfactant/polymer complexes . . . 18
   4.3. Surfactant/DNA complexes . . . 18
5. Constructive modulator . . . 18
6. Amphiphilic building unit . . . 20
   6.1. Amphiphilic CDs based on covalent modification . . . 20
   6.2. Amphiphilic CD complexes based on host–guest interaction . . . 21
7. Unamphiphilic building unit . . . 21
   7.1. Unamphiphilic self-assembly by natural CDs . . . 21
   7.2. Unamphiphilic self-assembly by CD/surfactant complexes at air/water surface . . . 22
   7.3. Unamphiphilic self-assembly by CD/surfactant complexes in bulk solution . . . 24
8. Conclusions and perspective . . . 24
Acknowledgments . . . 24
References . . . 24

1. Introduction

Amphiphiles (or surfactants) are molecules that consists hydrophobic and hydrophilic moieties. They can self assemble in solution into

* Corresponding author. Tel.: +86 10 62753557; fax: +86 10 62751708.
E-mail address: jbhuang@pku.edu.cn (J. Huang).

0001-8686/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cis.2011.07.002

structurally well-defined aggregates, as governed by a delicate balance between different noncovalent interactions, in particular hydrophobic and solvation interactions [1,2]. Not only is the self-assembly of amphiphiles ubiquitous in chemistry, materials science, industry, and commerce, but also does it provide a path towards ordered, functional assemblies, which might ultimately lead to intellectual organisms [3–5]. Construction and modulation of self-assembly therefore receives constant attention, for which many approaches have been developed ranging from molecular modification and additive introduction to stimuli responses [6–9]. Alternatively, cyclodextrins (CDs) may provide a host–guest approach to construct and modulate self-assembly.

CDs are donutlike oligosaccharides with hydrophobic cavities and hydrophilic outer surface, which can form inclusion complexes with most surfactants in high binding constants [10–15]. Loads of work has demonstrated that CDs can play important roles in surfactant or surfactant-based assembly systems with many applications such as viscoelasticity control [16–21], DNA decompaction [22–25], and protein reconstruction [26–28]. The roles played by CDs are, however, complicated and different (or even contradictory) from case to case. For example, it was generally accepted that CDs can destruct aggregates like surfactant micelles [29,30] or surfactant/polymer gel network [16], whereas it was recently revealed that CDs are able to transform mixed surfactant micelles into vesicles [31,32]. Moreover, the exterior of CDs (abundant with OH groups) was normally thought to be hydrophilic to dissolve CD/surfactant complexes into water or to maintain the solvation of CD based aggregates, but the OH-abundant exterior was found in recent reports to act as a "self-philic" moiety to drive the self-assembly of CD/surfactant complexes or even of the CDs themselves [33–44].

In this review, we attempt to elucidate the versatility and complexity of CDs in surfactant assembly systems according to the following vein. Sections 2 and 3 will briefly discuss some basic aspects of CDs and CD/surfactant complexes, with implication on the versatility of CDs. Sections 4 to 7, being the main contents of this review, will classify the roles played by CDs into two groups (modulator and building unit) and four subgroups (destructive and constructive modulators, amphiphilic and unamphiphilic building units) and will give in-depth comparison and analysis. At last, Section 8 would draw a conclusion and give a perspective.

2. Molecular structures of CDs

CDs consist of identical α-D-glucopyranose units, the C1 to C6 of which are marked in Fig. 1. These units are linked by α-1,4 glycosidic bonds to form a circle. The circle is shaped as a hollow, truncated cone rather than a perfect cylinder due to the chair conformation of the glucopyranose units. The bigger edge of the cone is usually called "head", while the smaller edge "tail". CD's secondary hydroxyl groups (C2-OH and C3-OH) locate at the head, whereas CD's primary hydroxyl groups (C6-OH) at the tail. Most commonly used CDs include natural α-, β- and γ-CD with six, seven, and eight glucopyranose units, respectively, as well as their hydroxypropyl and methylated derivatives (HPCDs and MCDs).

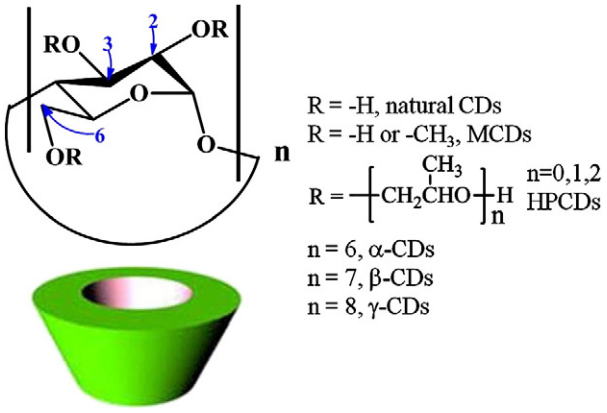

Fig. 1. Molecular structures of CD, HPCD, and MCD.

The central cavity of CDs is lined by the skeletal carbons and ethereal oxygens of the glucose residues, which makes it much less hydrophilic than the aqueous environment. The polarity of the cavity was estimated to be similar to that of a water/ethanol mixture, a somewhat hydrophobic environment. On the other hand, the hydroxyl groups of sugar residue at edges of the CD cone, giving a hydrophilic exterior. The hydrophobic potential map of α-CD is profiled in a very intuitive and informative way in Fig. 2 (calculated by Lichtenthaler et al. using a MOLCAD program [45,46]). It can be clearly seen that the cavity is hydrophobic while the exterior is hydrophilic (yet the tail is less hydrophilic). The hydrophobicity of the cavity enables the accommodation of a broad range of hydrophobic guests like alkyl chains of surfactants. The hosting ability of CDs is a key point for us to understand the behavior of CDs in CD/surfactant systems. The hydrophilic exterior usually imparts CDs and their complexes considerable solubility in water.

Although the OH groups on the exterior, in most cases, form H-bonds with water to dissolve the CDs or CD complexes (solvation), they can, in some situations, form CD–CD H-bonds to induce aggregation and even precipitation (self-assembly) [33–44]. For example, relatively strong CD–CD H-bonding in the crystal state was identified and was thought to be responsible for the limited aqueous solubility of natural CDs (in particular β-CD) in comparison to that of the comparable acyclic oligosaccharides. Substitution of any of the H-bond forming OH groups, even by relatively hydrophobic methoxy functions, will result in dramatic improvement of aqueous solubility. As will be shown, depending on the kind of H-bonds, the outer surface of CDs can be either hydrophilic (CD–water H-bonds, maintaining solvation, Sections 4 to 6) or "self-philic" (CD–CD H-bonds, driving self-assembly, Section 7).

3. Basics of CD/surfactant complexes

3.1. Thermodynamics

CDs are able to form host–guest complexes with most surfactants in 1:1 (denoted as surfactant@CD) or 2:1 (denoted as surfactant@2CD) stoichiometries with high binding constants by including surfactant's hydrophobic tails into CD cavities [47–74]. Fig. 3 lists the molecular structures and abbreviations of some common surfactants. The driving forces for CD/surfactant complex formation include, primarily, release of enthalpy-rich water molecules from the cavity (i.e. water molecules that cannot have a full complement of hydrogen bonds), van der Waals interactions, and hydrophobic interactions, as well as secondarily, hydrogen bonds, electrostatic interactions, release of conformational and steric strain, etc. The thermodynamic quantities for CD/surfactant complexation are, strictly speaking, a consequence of the weighted contributions of these interactions, which is, however, hard to handle in practice. Therefore, the size-match concept (a simple and effective concept that anticipates the highest binding constants for the best size-matching host–guest pairs) were more often used to explain and predict the thermodynamic quantities. The following discussion will demonstrate that the rather straightforward idea of size match does provide us a useful qualitative frame to understand the thermodynamic data.

1) For surfactant homologues, the binding constant increases substantially with the increase of tail length (Fig. 4, with data from [12,29,52,66,74]) because the CD cavity is more likely to be fully occupied by the longer tails. This increase, however, is much less pronounced for hydrocarbon chain longer than 14 carbons, probably because the CD cavity is "saturated" by the C14 chain.

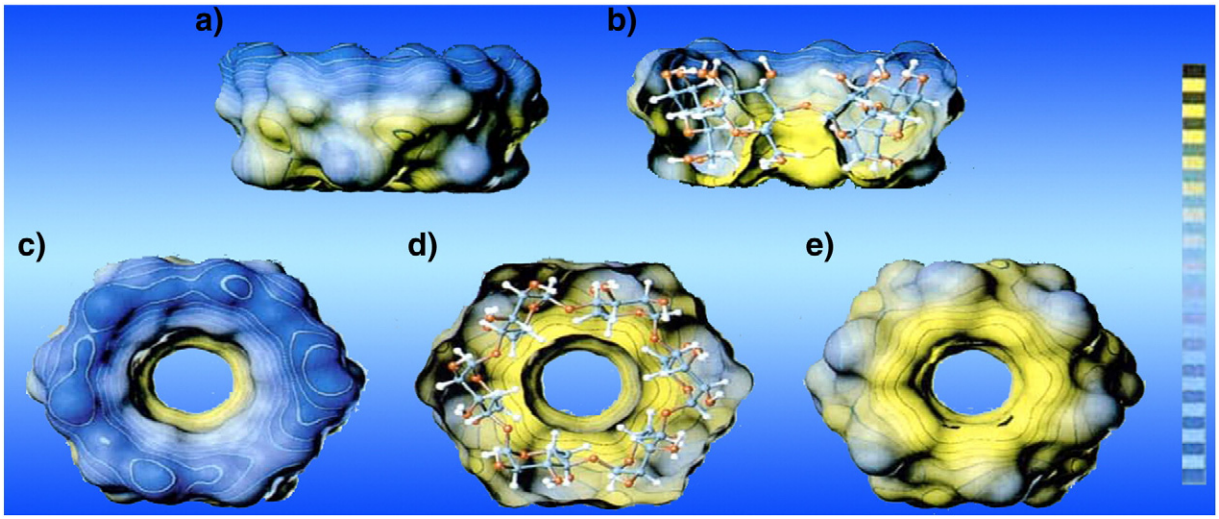

Fig. 2. Molecular hydrophilic potential of α-CD calculated by MOLCAD program in a) side view, b) side view of the cross section, c) top view, d) top view of the cross section, and e) bottom view. For visualization a two-color code graded into 32 shades is used. The color-coding is adopted to the range of relative hydrophobicity, using 16 colors ranging from dark blue (most hydrophilic surface areas) over light blue to full yellow (most hydrophobic regions) for mapping the computed values on the surface. The remaining 16 color shades (light blue to brown) indicate iso-contour lines in between former color scale, allowing for a more quantitative assessment of relative hydrophobicity on different surface regions. Adapted from [46]. Reprinted with permission from [46]. Copyright 1994 Elsevier.

2) For a hydrocarbon surfactant, its binding constant with α-CD is much higher than that with β-CD because the hydrocarbon chain fits the smaller cavity of α-CD better. For a fluorocarbon surfactant, it can bind barely with α-CD but strongly with β-CD because the fluorocarbon chain is too large for the α-CD cavity but fits the β-CD cavity. Xing et al. directly confirmed the respective preference of α-CD to hydrocarbon surfactants and β-CD to fluorocarbon surfactants [75].
3) For ionic surfactants with a certain chain length, the type of headgroups does not affect the binding constants significantly. However, for nonionic surfactants, a decrease in binding constant with the increasing EO chain length was observed, which was speculated to be related to EO–water H-bonds [76].
4) For some Gemini surfactants, their binding constants are much smaller than those of their single-chain analogs [77,78]. The authors attributed this phenomenon to the hydrophobic interaction and steric constraints between the two hydrocarbon tails on one Gemini surfactant. Moreover the binding constant rises with the increasing space chain length as a result of the separation of the two tails.

3.2. Molecular conformation

Generally, the most probable mode for surfactant@CD complexes involves the insertion of the nonpolar part of the surfactant into the CD cavity, while the polar (often charged) group of the surfactant is exposed to the bulk solvent just outside the wider opening of the cavity. But the exact molecular conformation of a specific CD/surfactant complex is usually case by case.

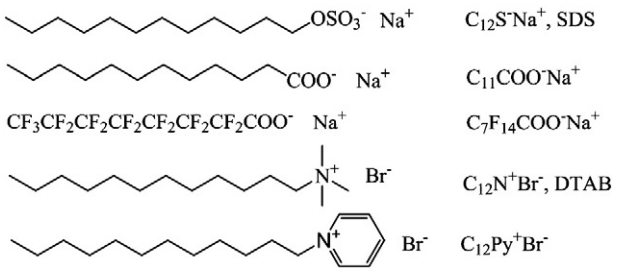

Fig. 3. Molecular structures and abbreviations of some common surfactants.

Funasaki et al. reported on the detailed conformation of aqueous α-CD/$C_nN^+Br^-$ (see Fig. 3) complexes based on ROESY spectra, as illustrated in Fig. 5[79–81]. For $C_nN^+Br^-$@α-CD complexes, with the increase of alkyl-chain length, the α-CD head is always oriented to the surfactant headgroup; the relative position of α-CD to the alkyl chain regularly changes, yet always close to the methyl end of the alkyl chain; the relative shuttle motion of the CD cavity with respect to the alkyl chain become wider. For $C_{12}N^+Br^-$@2α-CD complexes, the α-CD dimer adopts a head-to-head alignment along the alkyl chain, with one cavity not being fully filled by the alkyl chain.

An extensive dynamic and structural characterization is given by Brocos et al. on the complexes of SDS with α-, β- and γ-CD in water in virtue of molecular dynamics simulations (Fig. 6) [82]. For SDS@α-CD and SDS@β-CD complexes, CD's head can point to the SDS headgroup (Fig. 6a) or, slightly more preferred, to the tail of SDS (Fig. 6b); the CD cavity locates near SDS headgroup in the latter case. As for SDS@2CD complexes (Fig. 6c–e), the head-to-head conformation of CD dimer is tight and energetically favored over head-to-tail or tail-to-tail conformations, as stabilized by about 10 CD–CD H-bonds. As to 2SDS@CD complexes, the formation of 2SDS@α-CD or 2SDS@β-CD complexes is quite unlikely; 2SDS@γ-CD complexes with head-by-

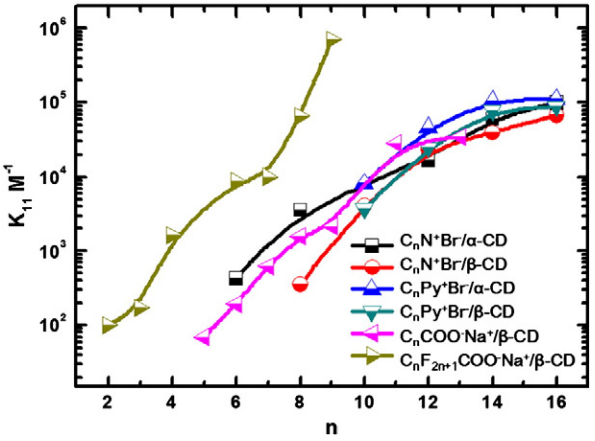

Fig. 4. The trend of binding constants on the increase of surfactant chain length (data from [12,29,52,66,74]).

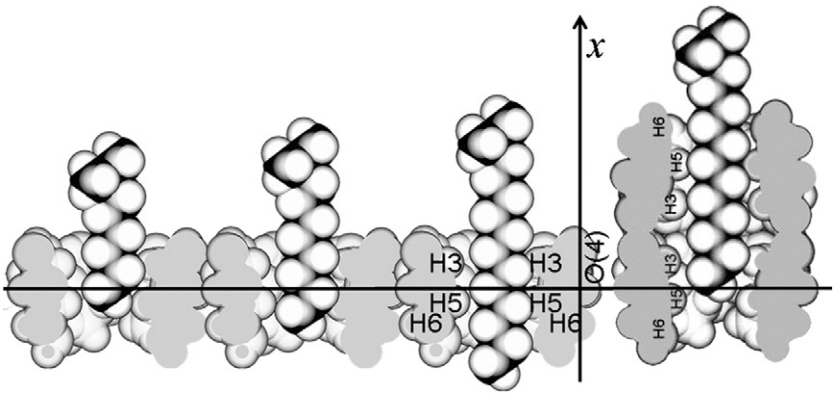

Fig. 5. Solution structures of $C_6N^+Br^-$@α-CD, $C_8N^+Br^-$@α-CD, $C_{12}N^+Br^-$@α-CD, and $C_{12}N^+Br^-$@2α-CD, as deduced according to ROESY results.
Adapted from [80,81]. Reprinted with permission from [80,81]. Copyright 2004 &2003 American Chemical Society.

head conformation of SDS are unexpectedly stable (Fig. 6f and g), which is speculated to be stabilized by Na^+ mediated salt bridges between sulfate groups.

4. Destructive modulator

As a modulator, although CDs by themselves do not participate into the final surfactant aggregates, they can exert import influence on the aggregates in virtue of their ability to include surfactants. We now consider the destructive influence of the CD/surfactant complexation on a coexisting surfactant-based aggregation equilibrium. Given the fact that CD/surfactant binding constants are generally high and that CD/surfactant complexes are quite water-soluble, it is reasonable to expect that 1) CD can compete a considerable amount of surfactant molecules from the surfactant-based aggregates, 2) the resultant complexes are unable to aggregate, and 3), as a result, the original

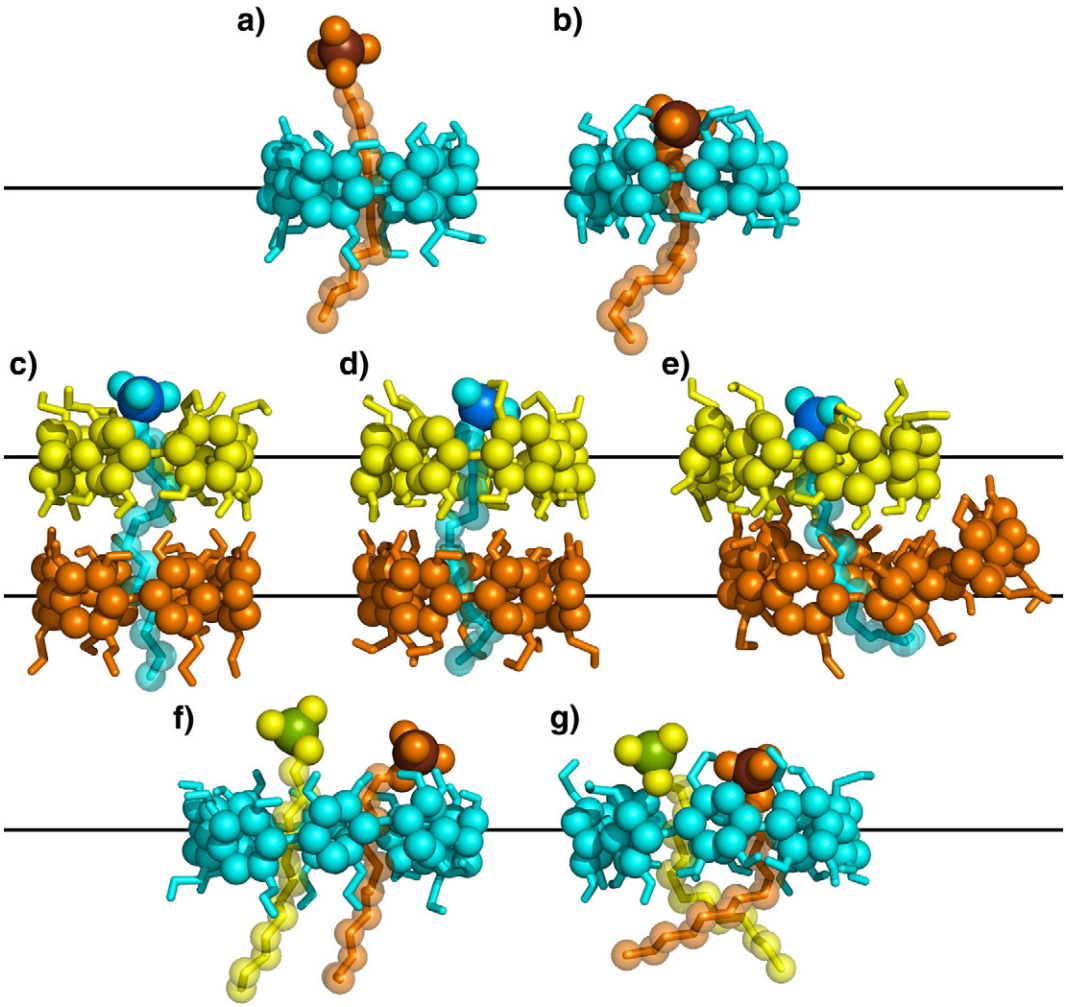

Fig. 6. Molecular conformation of a) SDS@α-CD, b) SDS@α-CD, c) SDS@2α-CD, d) SDS@2β-CD, e) SDS@2γ-CD, f) 2SDS@γ-CD, and g)2SDS@γ-CD, as calculated by molecular dynamics stimulation.
Adapted from [82]. Reprinted with permission from [82]. Copyright 2010 American Chemical Society.

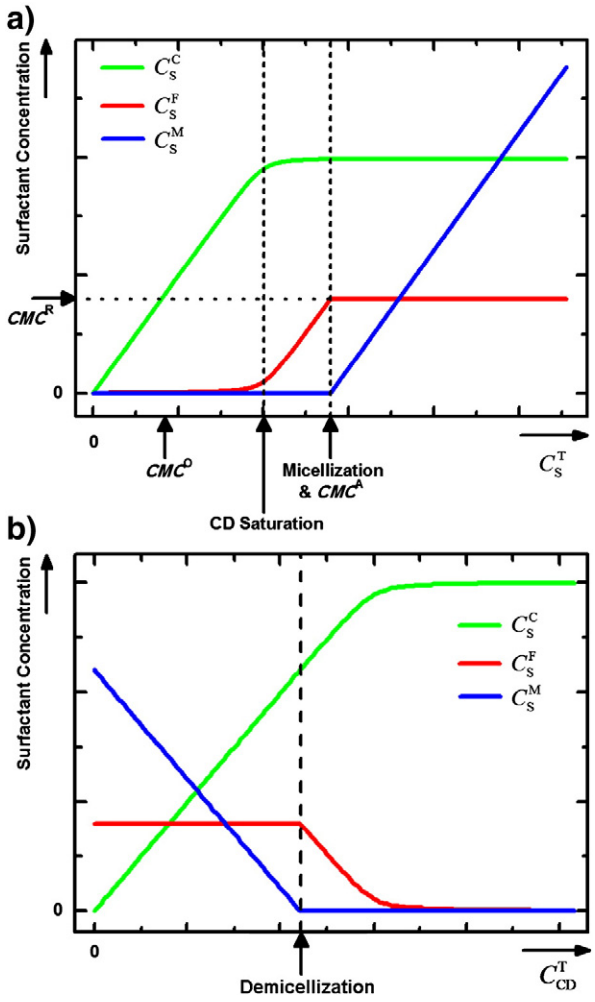

Fig. 7. Respective dependence of C_S^F, C_S^C, and C_S^M on C_S^T (a) as well as on C_{CD}^T (b).

aggregates are fully or partly destructed. Many works indeed reported CDs as a modulator to destruct surfactant micelles (Section 4.1), surfactant/polymer viscoelastic fluids (Section 4.2), surfactant/DNA complexes (Section 4.3), surfactant/protein complexes, etc.

4.1. Surfactant micelles

The interaction between CDs and surfactant micelles will be reviewed in a detailed manner because it is illuminative and thoroughly studied [15,29,60–66]. In the coexistence of complexation and micellization equilibriums, surfactant molecules can exist in free, complexed (with CDs), or micellized states. Accordingly, the total surfactant concentration (C_S^T) can be broken into C_S^F (free), C_S^C (complexed), and C_S^M(micellized). Here, we try to model the demicellization behavior of CDs by considering how the presence of CDs would affect C_S^M. Please note that the following discussion is based on general, simplified situations and may be subjected to variations for a specific CD/surfactant pair.

Consider the first scenario where a surfactant is gradually added to a CD solution step by step, that is, the total CD concentration (C_{CD}^T) is fixed and C_S^T is increased. The respective dependences of C_S^F, C_S^C, and C_S^M on C_S^T are plotted in Fig. 7a, which can be divided into three regions according to two curve breaks (vertical dashed lines).

- In the first region, C_S^C is close to C_S^T and C_S^F is close to 0, because the binding constant is generally high and most of the added surfactant molecules go to CD cavities. There is no micelle at all since C_S^F is much too low to give rise to micelles. The original *CMC* of the surfactant in the absence of the CD (CMC^O) is in this region or the second region, where no micellization would happen.
- Then at the first break, the CD cavities get almost saturated and the C_S^T at this point is usually close to the pre-fixed C_{CD}^T. So in the second region, C_S^C remains more or less constant and C_S^F increases significantly.
- At the second break, C_S^F reaches a critical value to initiate micellization. The C_S^F and C_S^T at this point are referred as CMC^R (real) and CMC^A (apparent), respectively. The CMC^R is essentially the same as CMC^O, increased or decreased slightly depending on the surfactant. Roughly speaking, CMC^A equals the sum of CMC^O and C_{CD}^T. Lastly, in the third region, almost all the newly added surfactant molecules go into micelles, whereas C_S^F and C_S^C basically keep unchanged. And the micelles, in terms of their aggregation numbers, shapes, or sizes, will basically not be affected by the coexisting uncomplexed CD or CD/surfactant complexes.

The destructive role of CDs in this scenario is reflected by the shift of CMC^A from CMC^O, which means that in the presence of CDs one has to add an extra amount of surfactant to commence micellization.

In the second scenario, C_S^T is fixed and C_{CD}^T is increased (Fig. 7b). Upon the addition of the CD, surfactant molecules are gradually transferred from micelles to CD cavities until the demicellization point, where all the micelles are consumed. After that, the newly added CD molecules start to bind with free surfactant molecules. In this scenario, the destruction is quite straightforward to understand.

Although CDs are nowadays routinely used as micelle-destructive agents where many reports and utilizations are within the above two scenarios, there are some interesting variations. For example, Wang et al. reported α-CD-induced disassembly of vesicles and further manipulation of the disassembly/assembly behavior by light (Fig. 8). The vesicles are formed by an azobenzene-ended cationic surfactant, and the manipulation was archived in virtue of the unique α-CD/azobenzene

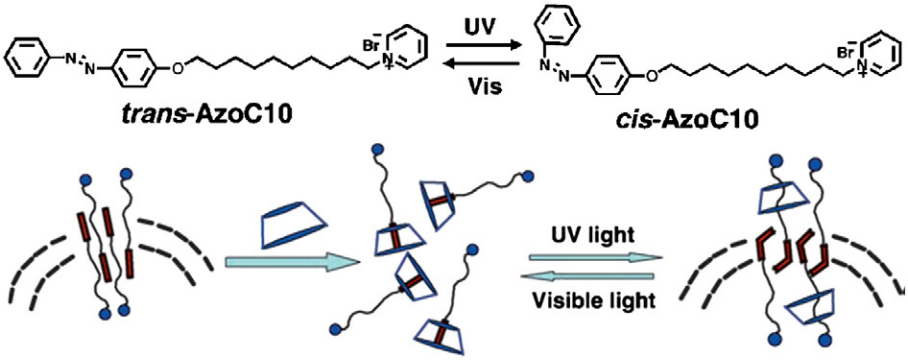

Fig. 8. Illustration of the photocontrolled reversible assembly and disassembly of AzoC10 vesicles; red bar: azobenzene moiety, blue spot: pyridinium group. Reprinted with permission from [83]. Copyright 2007 John Wiley and Sons.

interaction [83]. Two isomers of azobenzene, *trans*- and *cis*-forms, can be reversibly switched to each other upon photoirradiation. The *trans*-from can be well recognized by α-CD, leading to vesicle disassembly, whereas the *cis*-form is too bulky to be accommodated in the α-CD cavity, resulting in the shift of α-CD from azobenzene to alkyl chain and the restore of the vesicles.

4.2. Surfactant/polymer complexes

Polymers are often used in conjunction with surfactants in applications spread from cosmetics and pharmaceuticals to extraction of petroleum and processing of minerals, where the rheological properties are always important. Polymer/surfactant interaction is affected by their relative charge and hydrophobicity. In particular, strong interaction is observed in mixtures of polyelectrolytes with oppositely charged surfactants, where both electrostatic attraction and cooperative hydrophobic effect contribute. This strong interaction often leads to a pronounced viscosity enhancement and even gel formation. As displayed in Fig. 9a–c, association of surfactant micelles with polymers would lead to a physical cross-linking and viscosity increase, whereas CD/surfactant complex formation can result in micelle dissociation and viscosity decrease. Tsianou et al. [16] reported that, in a SDS (see Fig. 3)/cationic polymer system, the added α- and β-CD would form inclusion complexes with SDS, dissociating the SDS micelles which originally cross linked with polymer chains. Consequently, the viscosity enhancement induced by SDS is completely counteracted. Several other works by Khan et al. also involved CD/surfactant/polymer aqueous mixtures [17,19].

4.3. Surfactant/DNA complexes

Gene delivery received many attentions because it may enable the possibility to treat diseases by the insertion of genes into human cells and tissues, so-called gene therapy. In gene delivery, two steps are critical: compaction of DNA into small particles (to facilitate cell uptake through membranes and to protect DNA from nucleases) and decompaction of DNA into its natural state (to be proceed to following transcription into RNA). Cationic surfactants were widely used to compact DNA, the mechanism of which was considered as follows. Cationic surfactant molecules binds on oppositely charged DNA chains through electrostatic attraction, the bound surfactant molecules may further form micelle-like aggregates due to hydrophobic interaction, and the micellar aggregate may act as a nucleation center for DNA to wrap around it, leading to co-assembled bead-like or elongated aggregates. Given the CD's influence in oppositely charged surfactant/polymer complexes (Section 4.2), it is quite understandable that CDs are effective in the decompaction of the DNA/surfactant coassembly. Gonzalez-Perez et al. [22–24] reported that, in a CTAB (a cationic surfactant)/DNA system, α- and β-CD can disrupt DNA-wrapped CTAB micelles, leading to DNA decompaction from globules to coils. Cao et al. [25] reported β-CD-induced DNA decompaction in a 12-6-12 (a cationic Gemini surfactant)/DNA system (Fig. 10). It is worth to mention that although the DNA is decompacted, a considerable amount of β-CD/12-6-12 complex still binds on the DNA because of electrostatic attraction.

5. Constructive modulator

The above section shows that CDs can break the surfactant and surfactant-based aggregates. On the contrary, this section will show that CDs can induce growth of aggregates in mixed surfactant systems.

In recent papers by Jiang et al. [31,32], β-CD-induced aggregate growth was identified in nonstoichiometrical mixed cationic/anionic surfactant systems. The aggregate growth typically undergoes a micellar elongation and a following micelle-to-vesicle transition with β-CD addition, which in turn greatly influences viscosity and absorbance of the solutions. Preliminary analysis on the mechanism showed that the selective binding of β-CD towards the major component (molar fraction>0.5) of the cationic/anionic surfactant mixture is responsible for the aggregate growth: this selectivity

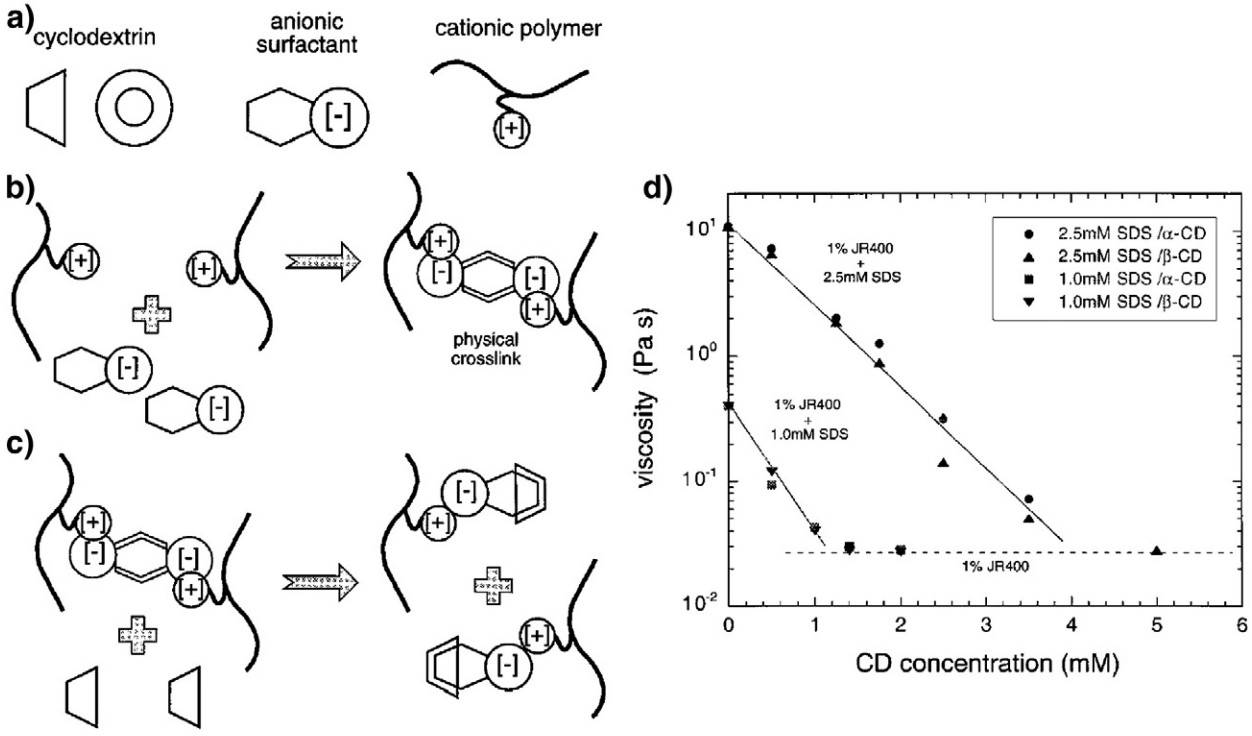

Fig. 9. a) to c), Schematic representation of the interactions between cationic polymers, anionic surfactants, and cyclodextrins. d) Decrease in zero-shear viscosity of solutions of the cationic polymer JR400 and the anionic surfactant SDS, resulting from the addition of α- or β-CD at different concentrations. The dashed line indicates the zero-shear viscosity value of 1 wt.% JR400 aqueous solution.
Reprinted with permission from [16]. Copyright 1999 American Chemical Society.

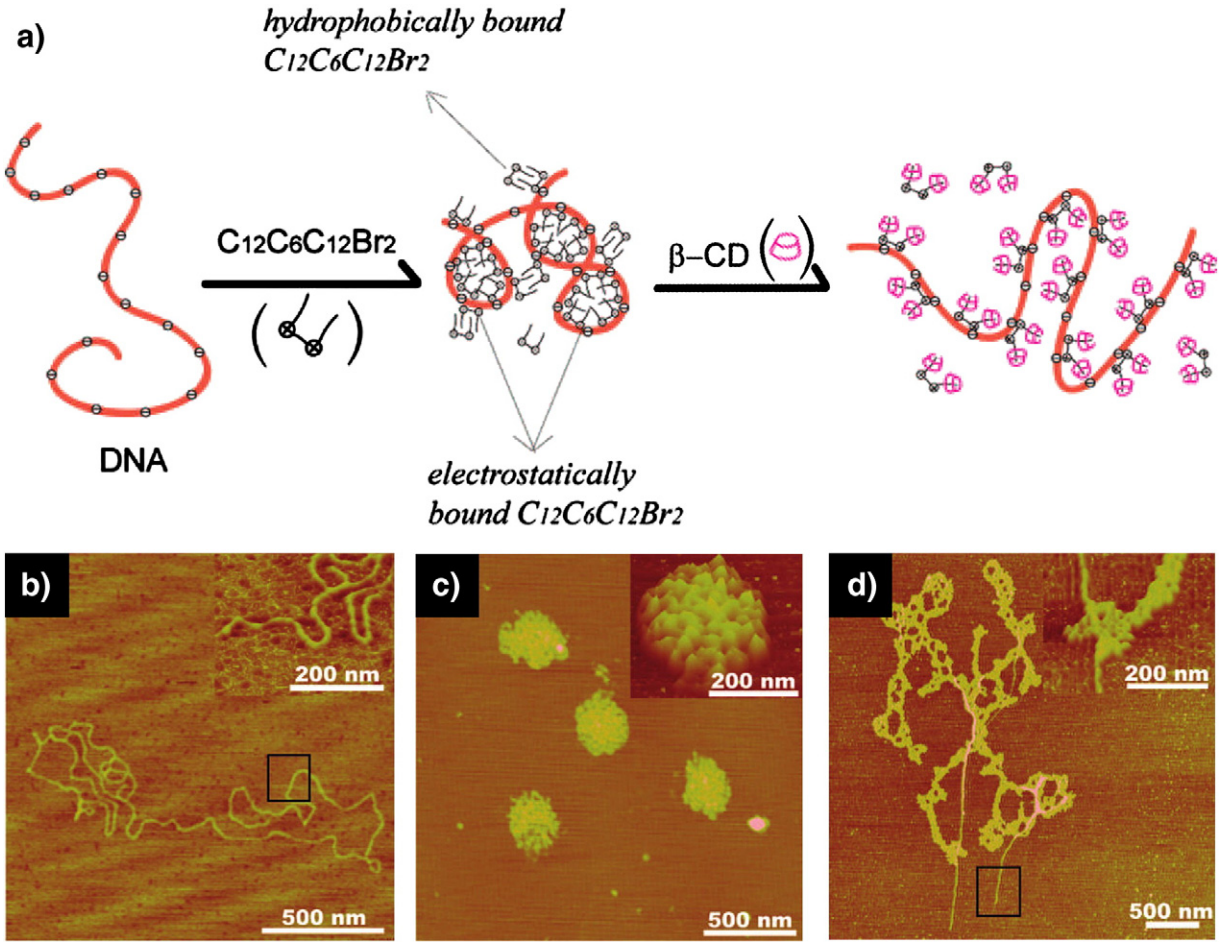

Fig. 10. a) Illustration of the mechanisms of the cationic surfactant-induced DNA compaction and decompaction of the surfactant/DNA complexes by β-CD. b), c), and d), AFM images of natural DNA coils, surfactant/DNA globules, and DNA coils decompacted by β-CD, respectively.
Adapted from [25]. Reprinted with permission from [25]. Copyright 2008 American Chemical Society.

removes the excess part of the major component from the aggregates, shifts the surfactant compositions in the aggregates towards electroneutral mixing stoichiometry which favors low-curved aggregates like vesicles, and thus gives rise to the observed aggregate growth and concomitant variations in solution properties (Fig. 11).

Following work attributed the selectivity of β-CD towards the major surfactant to the interplay between the host–guest (β-CD/surfactant) equilibrium and the biased aggregation (monomeric/aggregated surfactants) equilibrium. This interplay dominates the systems in the following way: 1) nonstoichiometric cationic/anionic surfactant systems are characterized by a great bias in the aggregation equilibrium, that is, the charged aggregates considerably prefer the countercharged, minor surfactant over the cocharged, major one due to electrostatic reasons, 2) the biased aggregation equilibrium imposes an apparent

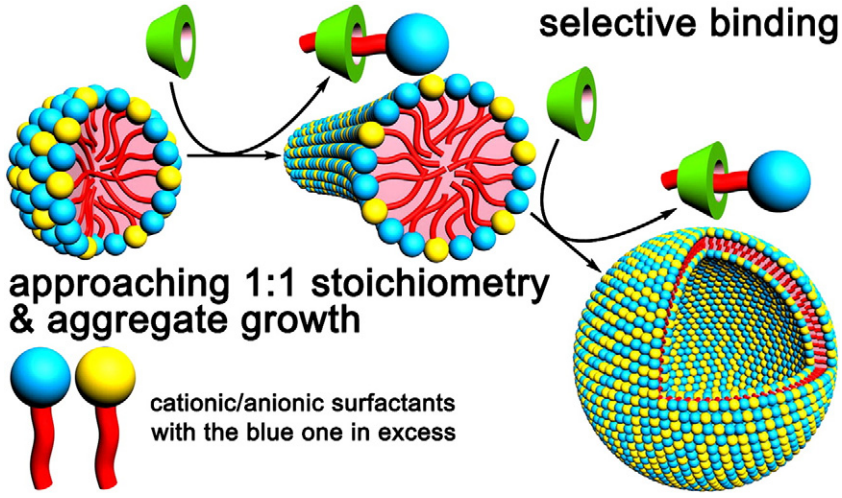

Fig. 11. Scheme of the aggregate growth induced by β-CD in nonstoichiometrical cationic/anionic surfactant systems.
Reprinted with permission from [31]. Copyright 2009 American Chemical Society.

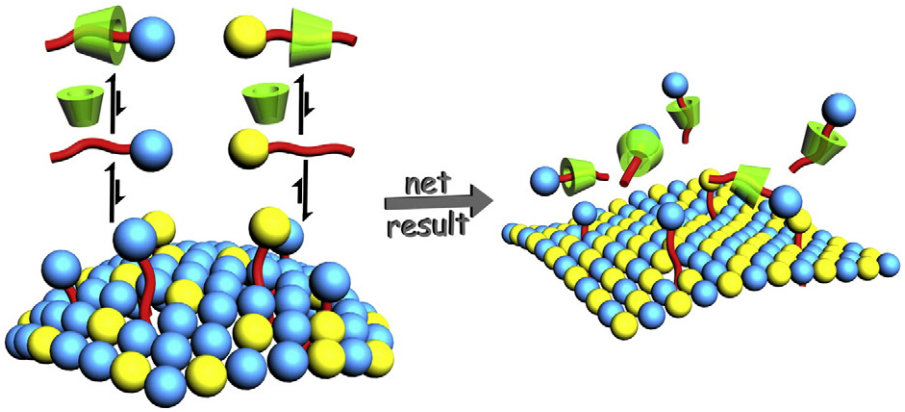

Fig. 12. A schematic illustration of the interplay between the host–guest and biased aggregation equilibriums, the apparent binding selectivity of β-CD, and the resultant reduction on aggregate curvature.
Reprinted with permission from [32]. Copyright 2010 American Chemical Society.

selectivity to the host–guest equilibrium, namely, β-CD has to always selectively bind the major surfactant even if binding constants of β-CD to the two surfactants are quite similar, 3) in return, the host–guest equilibrium amplifies the bias of the aggregation equilibrium, that is, the selective binding partly removes the major surfactant from the aggregates and leaves the aggregate composition approaching the electroneutral mixing stoichiometry, and 4) this composition variation enhances electrostatic attractions between oppositely charged surfactant headgroups, at last resulting in less-curved aggregates as we observed (Fig. 12). In particular, the present apparent host–guest selectivity is of remarkably high values, and the selectivity stems from the bias of the aggregation equilibrium rather than the difference in binding constants. Moreover, β-CD is defined as a "stoichiometry booster" for the whole class of cationic/anionic surfactant systems, which provides an additional degree of freedom to directly adjust aggregate compositions of the systems. The stoichiometry boosting of the compositions can in turn affect or even determine micro-structures and macro-properties of the systems.

Another example of CD-induced aggregate growth was found in detergent/lipid/protein systems. Before CD addition, the detergent/lipid/protein mixture forms mixed micelles due to the presence of a considerable amount of the micelle-forming detergent. After CD addition, the detergent will be selectively extracted by CDs, whereas the vesicle-forming lipid and the protein will be leave to form protein-contained vesicles (a micelle-to-vesicle transition). For instance, Signorell et al. [27] and Degrip et al. [28] utilized the selective extraction of detergents from mixed detergent/lipid/protein micelles to prepare proteoliposomes of a defined lipid/protein ratio for 2D crystallization of protein.

Interestingly, CDs can be either a destructive or constructive modulator through the very action, extracting surfactant from the aggregates. The difference is that CDs need to selectively bind the "less-aggregatable" component (the major surfactant in cationic/anionic surfactant mixtures or the detergent in detergent/lipid/protein mixtures) to be constructive.

6. Amphiphilic building unit

As an amphiphilic building unit, CDs can be chemically (by chemical bonds) or physically (by host–guest interaction) attached to a hydrophobic moiety, where the CD outer surface acts as a hydrophilic moiety and the resultant compound as a classic amphiphile.

6.1. Amphiphilic CDs based on covalent modification

CDs can be modified with hydrophobic parts such as alkyl chain or cholesterol, giving rise to the so-called "amphiphilic CDs" [84–92]. The amphiphilic CDs can self assemble in a classic way similar to that of surfactant, where the CD portion acts like the hydrophilic headgroup of a surfactant. Till now many amphiphilic CDs were developed and were found to be able to form micelles, monolayers at air/water surface, vesicles, and fibers. Compare to surfactant aggregates, the amphiphilic CD-based aggregates provide macrocyclic hosting sites on the surface, creating new possibilities for host–guest interaction

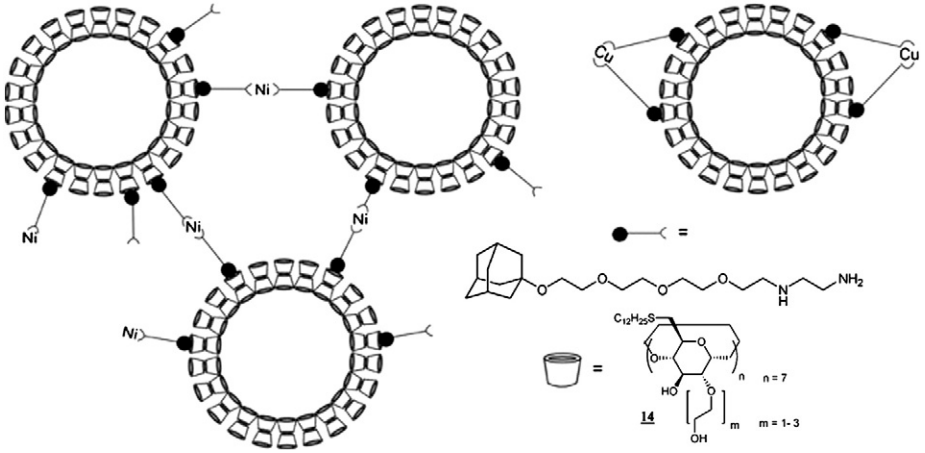

Fig. 13. Intervesicular clustering of cyclodextrin vesicles induced by Ni^{2+} and ligand L, as well as intravesicular complexation to cyclodextrin vesicles by Cu^{2+} and ligand L. Adapted from [88]. Reprinted with permission from [88]. Copyright 2007 National Academy of Sciences of the United States of America.

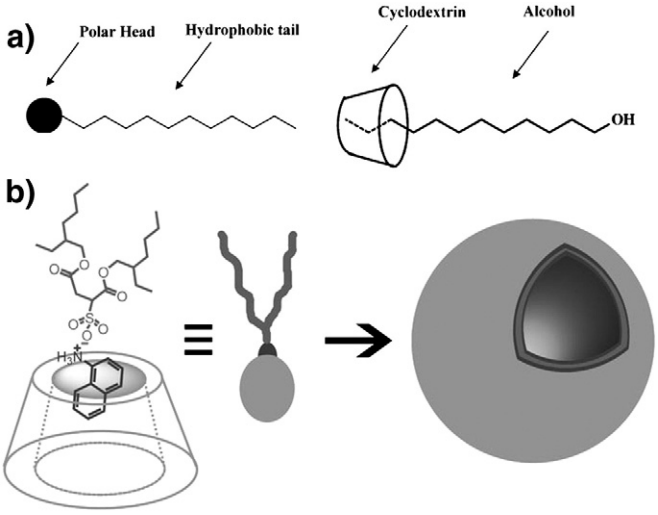

Fig. 14. a) Analog between covalent amphiphiles and noncovalent CD-based amphiphiles (pseudoamphiphiles). b) Schematic representation of vesicle formation from a CD-based supramolecular pseudoamphiphiles.
Adapted from [93,94]. Reprinted with permission from [93,94]. Copyright 2007 John Wiley and Sons. Copyright 2008 American Chemical Society.

and recognition. For example, Lim et al. [88] investigated orthogonal complexation-mediated intra- and intervesicular interaction in an amphiphilic CD–vesicle system (Fig. 13). Host vesicles composed of amphiphilic β-CD recognize metal-coordination complexes of the adamantyl-functionalized ethylenediamine ligand (L) via hydrophobic inclusion in the CD cavities at the vesicle surface. In the case of Cu (II) and L, the resulting coordination complex was exclusively CuL_2, and the interaction with the host vesicles was intravesicular. In the case of Ni(II) and L, a mixture was formed consisting of mainly NiL and NiL2, the interaction with the host vesicles was effectively intervesicular, and addition of the guest–metal complex resulted in aggregation of the vesicles into dense, multilamellar clusters.

6.2. Amphiphilic CD complexes based on host–guest interaction

Amphiphilic CD complexes can be obtained if a hydrophobic guest is appropriately chosen so that a part of the guest is included in CD cavity and another part is exposed [93–97]. Bojinova et al. [93] proposed that β-CD/alcohol complexes, in which a considerable part of the alkyl chain is exposed outside of the CD cavity, can act as surfactants (Fig. 14a). Their proposition was confirmed by the surface tension reduction and micelle formation in aqueous solution of the complexes. Jing et al. [94] reported self-assembly behavior in a β-CD/NA (1-naphthylammonium chloride)/AOT (sodium di-2-ethylhexyl sulfosuccinate) ternary aqueous system, where β-CD forms inclusion complexes with NA and NA forms ionic complexes with AOT. The resulting β-CD/NA/AOT complex (can be regarded as a double-tail nonionic surfactant) can assemble into vesicles (Fig. 14b). The key of this complex is a double-binding nature of NA, that is, the naphthene group to be included into CD cavities on one side and the cationic group to be bind to anionic AOT on the other side. NA can be replaced by other molecules with a double-binding nature, such as 1-adamantanamine hydrochloride [95] and (ferrocenylmethyl) trimethylammonium iodide [96,97].

7. Unamphiphilic building unit

Recently, nonamphiphilic self-assembly is emerging as a new form of assembly and drawing increasing attentions [98–102]. Classic amphiphilic self-assembly is mainly governed by a delicate balance between two opposite effects: the hydrophobic effect, which drives the hydrophobic moiety to aggregate to minimize contact with water, and the solvation of the hydrophilic moiety, which tends to maintain contact with water. As the driving force of amphiphilic assembly, the hydrophobic effect, however, appears to be relatively weak and nondirectional; the resultant structures are inherently soft, fluid, and less-ordered. In contrast, nonamphiphilic self-assembly does not rely on hydrophobic effect, for example, assembly of polyoxometalate macroions, oppositely charged polymers, and nonamphiphilic aromatic organic salts may be governed by electrostatic interactions, including counterion mediation, direct attractions between opposite charges, or salt bridges [98–102]. The nonamphiphilic self-assembly, although still in its infancy, has begun to manifest superiorities in some aspects over its conventional amphiphilic counterpart. In this section, we will review CDs' role as a unamphiphilic building unit, where natural CDs themselves or CD/surfactant complexes can self assemble into various aggregates as driven by CD–CD H-bonds.

7.1. Unamphiphilic self-assembly by natural CDs

It has been known for some time that natural CDs are able to self assemble into aggregates [33–37]. Abundant data were obtained by light scattering methods, both dynamic and static, where Fig. 15 cites the data summarized by Messner et al. [33]. A general observation is that the aggregates of the natural CDs tend to grow with increasing CD concentration. The largest aggregates are observed for β-CD, up to several micrometers in diameter. The anomalously low solubility of β-CD may be related to the intensity of aggregate formation, which becomes notable at β-CD concentrations above 3 mM. It should be emphasized that formation of large aggregates does not necessarily indicate extensive aggregate formation. Actually, the fraction of CD molecules participating in aggregates is often very low. For example, the mass contribution of the α-CD aggregates in aqueous 12 mM α-CD solution does not exceed 0.8%.

The morphology of β-CD aggregates in water were investigated by Bonini et al. [38,39], revealing polydispersed, nearly spherical objects (~100 nm) at lower concentrations and micrometer planar aggregates at higher concentrations. As shown in the Cryo-TEM images (Fig. 16), 3 mM β-CD solution gives polyhedral aggregates in mutual contact to

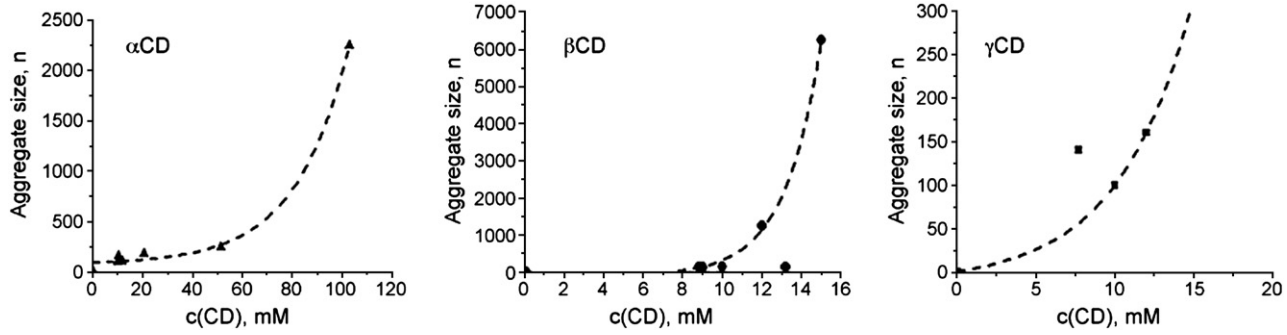

Fig. 15. An average size of native CD aggregates (n is the number of molecules) versus CD concentration observed by light scattering taken from literature.
Reprinted with permission from [33]. Copyright 2006 Elsevier.

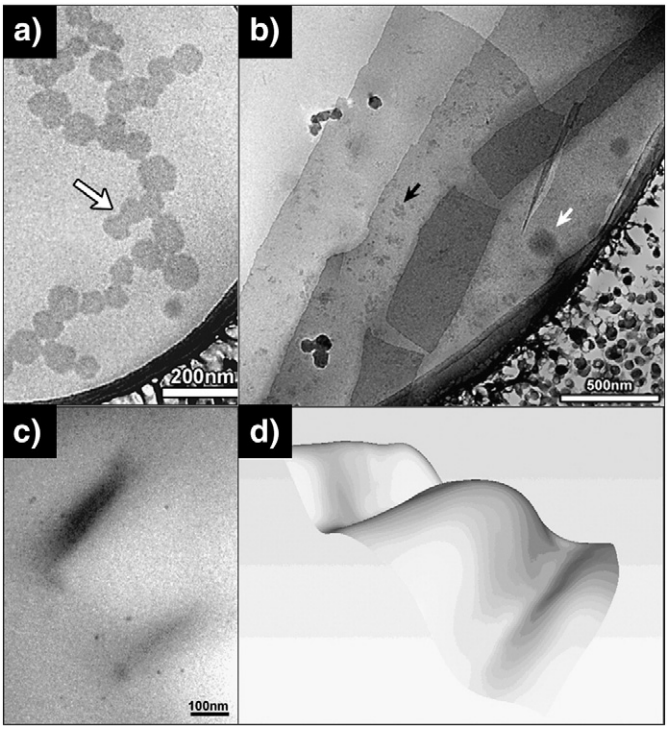

Fig. 16. Cryo-TEM micrographs of β-CD aqueous solutions at a) 3 mM, b) 6 mM, and c) 12 mM. The stimulated undulated sheetlike aggregate (d) is believed to produce the electronic pattern in (c).
Adapted from [38]. Reprinted with permission from [38]. Copyright 2006 American Chemical Society.

form a branched structure (Fig. 16a); 6 mM β-CD solution is predominant by large sheetlike aggregates, in coexistence with globular particles (black arrow, Fig. 16b) and discoidal aggregates (white arrow, Fig. 16b); the sheetlike aggregates still prevail in 12 mM β-CD solution, in which the undulation of a sheet structure in Fig. 16d is believed to produce the electronic pattern in Fig. 16c. In another work, Polarz et al., however, proposed wormlike structures for CD aggregates, where CD molecules line up in ideally parallel or staggered parallel arrangement, as supported by silica nanocasting, DLS, and SAXS results.

The driving force for nature CDs to aggregate is generally believed to be CD–CD H-bonds. This opinion was mainly supported by three observations: 1) Substitution of any OH groups of CDs (such as MCD and HPCD) would give them significantly increased solubility and decreased (or even abolished) tendency of self-assembly, 2) when the solution pH is increased to 12 or above, the OH groups of the CD molecule become ionized, resulting in dissociation of the CD aggregates, and 3) chaotropic additives that break hydrogen bonds, such as urea or sodium chloride, can cause notable depression of the CD self-assembly.

7.2. Unamphiphilic self-assembly by CD/surfactant complexes at air/water surface

In an interesting work by Hernandez-Pascacio et al. [40,41], it was reported that native α-CD as well as its complex with SDS can self-assemble into nanotubes at water/air surface. Although the surface tension of aqueous α-CD or α-CD/SDS complex are close to (or even a little higher than) that of pure water, α-CD and its complex were found to enrich themselves at the surface to form multilayer films.

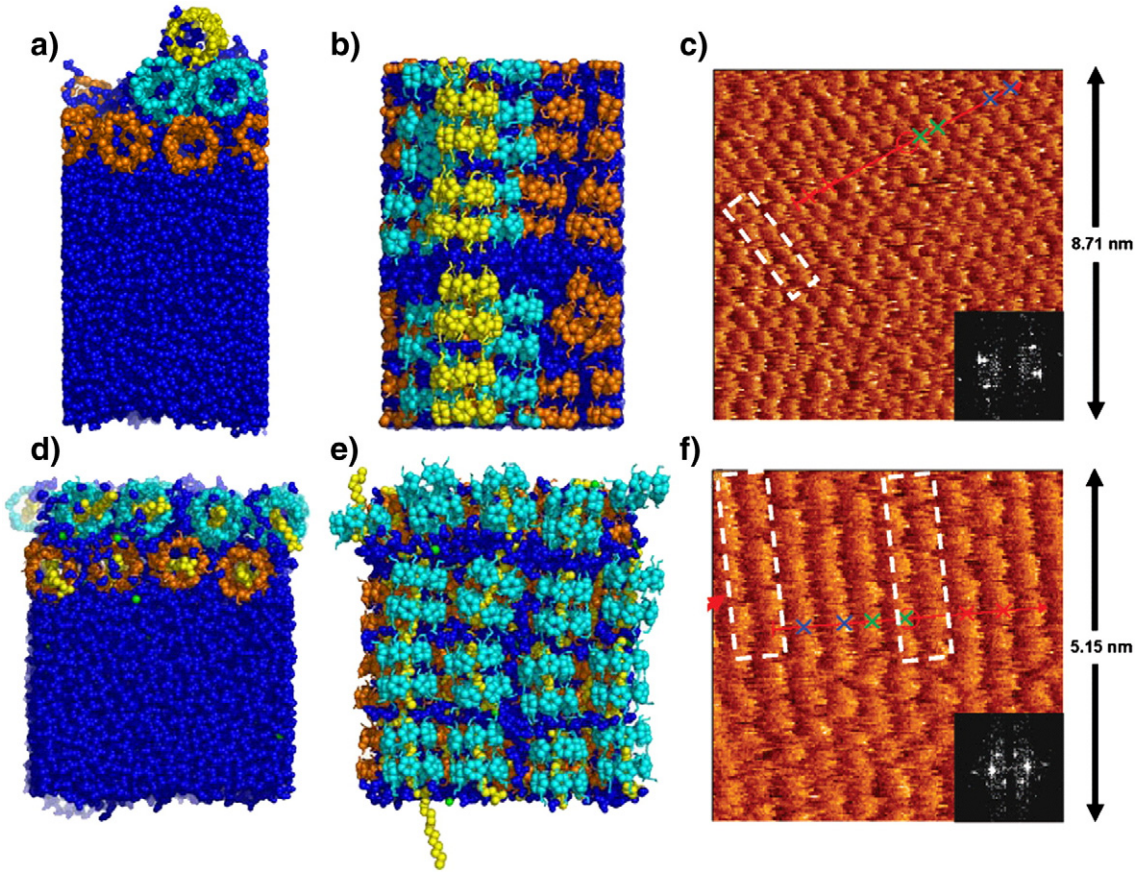

Fig. 17. a) to c), Self-assembly of α-CD dimers at water/air surface: structures from molecular dynamics trajectories at 283 K (a, top view; b, lateral view) and AFM force image (c). d) to f), Self-assembly of SDS@2α-CD complexes at water/air surface: structures from molecular dynamics trajectories at 283 K (d, top view; e, lateral view) and AFM force image (f).
Adapted from [41]. Reprinted with permission from [41]. Copyright 2007 American Chemical Society.

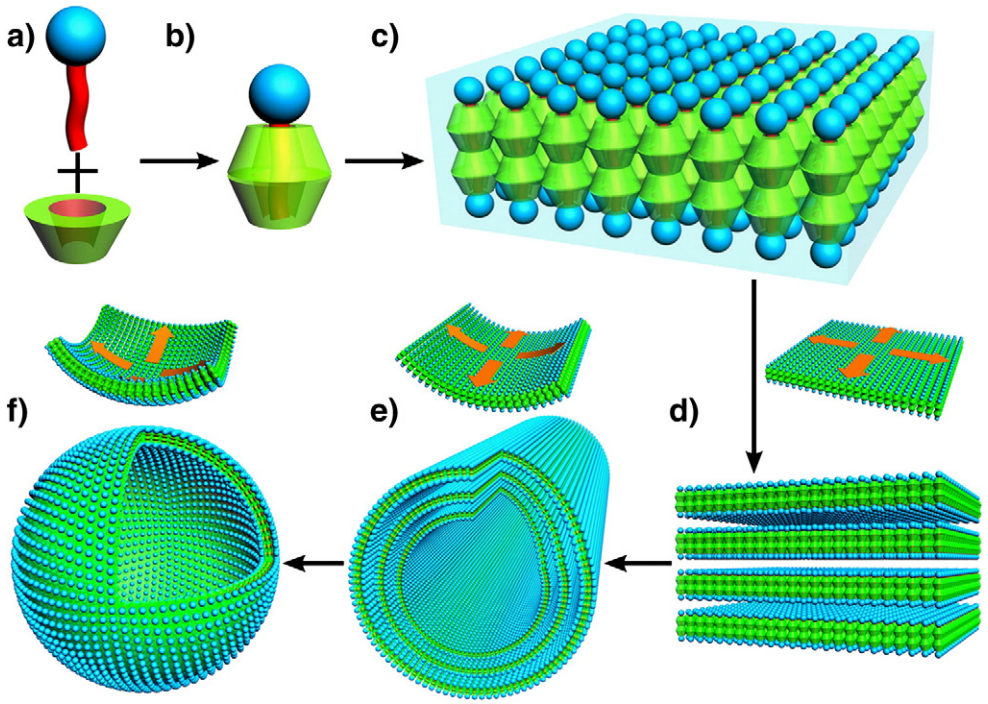

Fig. 18. Schematic self-assembly behavior of SDS@2β-CD. a), SDS and β-CD monomers. b), SDS@2β-CD complex. c), The SDS@2β-CD bilayer membrane with a channel-type crystalline structure. d), e), and f), The aggregates transform upon dilution from lamellae via microtubes to vesicles.
Reprinted with permission from [43]. Copyright 2011 American Chemical Society.

Further analysis on the films showed that 1) head-to-head α-CD dimers and SDS@2α-CD complexes are the building blocks to line up into channel-type nanotubes, 2) the nanotubes are orientated parallel to the surface and are stacked into multilayer films, and 3) H-bonds between CD molecules, both direct and water-bridged ones, are critical to stabilize the nanotube films. The conformation of the α-CD nanotube films is simulated by MD in a side (Fig. 17a) and top (Fig. 17b) view and is detected by AFM (Fig. 17c). Similar results for SDS@2α-CD nanotubes are given in Fig. 17d–f. However, it is not clear why would α-CD and SDS@2α-CD complex enrich themselves into the surface if the surface tension (or say surface energy) is not reduced by the enrichment.

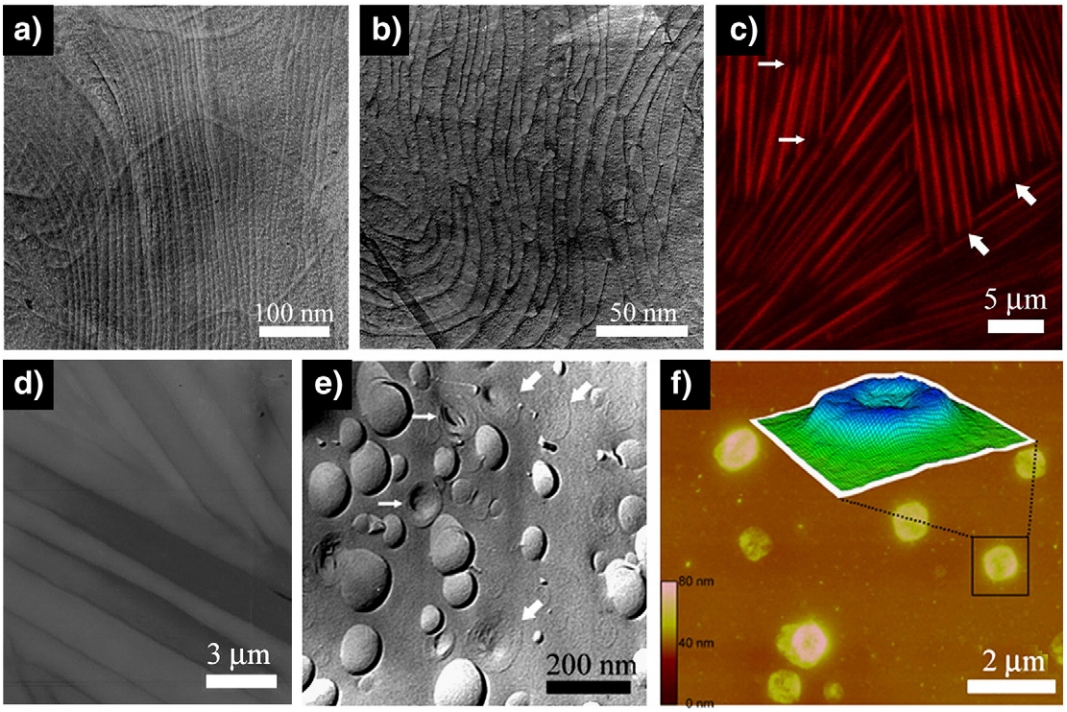

Fig. 19. Morphology of SDS@2β-CD aggregates. a) and b), FF-TEM images of lamellae. c) and d), CLSM and TEM graphics of microtubes, respectively. e) and f), FF-TEM and AFM images of vesicles, respectively.
Adapted from [42,43]. Reprinted with permission from [42,43]. Copyright 2010 & 2011 American Chemical Society.

7.3. Unamphiphilic self-assembly by CD/surfactant complexes in bulk solution

Recently, Jiang et al. found that SDS@2β-CD complex is able to self-assemble into well-defined lamellae, tubes, and vesicles, in concentrated or semi-concentrated aqueous solution [42–44]. As shown in Fig. 18, all the three classes of aggregates share a consistent building block, the channel-type crystalline bilayer membrane (Fig. 18c); the membranes will laterally expand into infinite two-dimensional lamellar structures at high concentrations (Fig. 18d), extend in one direction and scroll up in the perpendicular direction to form one-dimensional multilayer microtubes upon dilution (Fig. 18e), and close up along two in-plane axis to generate dispersed vesicles upon further dilution (Fig. 18f).

Detailed structure of the SDS@2β-CD bilayer (Fig. 18c) was identified in a molecular level on the basis of SAXS and WAXS results. Morphologies of the aggregates (Fig. 18d–f) were determined by a combination of CLSM, FF-TEM, AFM, and SAXS. Fig. 19a and b are full of numerous parallel lines with a uniform interval, typical for cross sections of lamellar structures. Fig. 19c and d are prevailed by pairs of parallel lines, consistent with the longitudinal-sectional view of hollow tubular structures. Fig. 19e and f are predominant by spherical and donut-like structures, respectively, corresponding to vesicles. Moreover, the present lamellae exhibit unprecedented in-plane crystalline architecture in addition to classical out-of-plane liquid-crystalline order, and therefore can be regard as an intermediate phase between a liquid crystal and a solid. The microtubes are constituted by a set of coaxial, equally spaced, hollow cylinders, resembling the annular rings of trees (thus termed as "annular ring" microtubes), featuring an unbundling nature, ultralong persistence lengths, highly monodispersed diameters, and remarkable rigidity.

Further effort was exerted on unveiling the mechanism of the SDS@2β-CD self-assembly. Firstly, the hydrophilic outer surface of SDS@2β-CD complex rules out the possibility that its self-assembly is driven by hydrophobic effect. Based on control experiments, we proposed that it is mainly driven by H-bonds between CD molecules and is mediated by electrostatic interactions between SDS headgroups. Secondly, an important issue immediately rises if the present assembly is not driven by hydrophobic effect, that is, why would the SDS@2β-CD bilayer fold up into tubes and vesicles upon dilution just like typical lipid bilayers do? It is well known that lipid bilayers tend to fold up to minimize unfavorable contact between water and hydrophobic tails at the ends of a bilayer sheet. In this case, SDS@2β-CD bilayers also tend to fold up and eliminate edges of a bilayer sheet, as we speculated, to maximize lateral H-bonding network between CD molecules.

Combining the discussion of Sections 4 to 7, we can see that the OH groups of CDs can form H-bonds with water to dissolve the CDs or CD/surfactant complexes (Sections 4 and 5) or to balance the hydrophobic effect in amphiphilic aggregates (Section 6), or on the contrary they can form H-bonds with other CD molecules to drive self-assembly of the unamphiphilic aggregates (Section 7). According to the above results, it appears that lower concentrations prefer CD–water H-bonds while higher concentrations prefer CD–CD H-bonds. However, this speculation is not strongly or systematically evidenced, and the key factors to determine the H-bonds are still not clear at this stage.

It is worth to note that the self-assembly behavior of CDs or CD/surfactant complexes actually did not, to our knowledge, receive enough attention. Most of the papers in the literature assimilated them to molecularly dispersed solute in water, and interactions between CD molecules or CD/surfactant complexes were not taken into account. Although this approximation did not introduce any major error (probably because those studies were limited to low concentrations and the fraction of assembled CDs is often quite low), a more rigorous consideration is desirable.

8. Conclusions and perspective

In conclusion, CDs can play crucial roles in self-assembly systems of amphiphiles either as a modulator or as a building block. As a modulator, CDs and their complexes remain in the solution other than join the aggregates, yet they affect the aggregates by extracting surfactants from the aggregates. In most cases, the depletion of surfactants results in the destruction of the surfactant-based aggregates like micelles and polymer/surfactant gel network. The destructive modulation by CDs was applied to DNA decompaction and protein reconstruction. In certain cases where the aggregates are formed by surfactant mixtures, CDs would selectively bind the "less-aggregatable" component and promote the aggregates to grow, acting as a constructive modulator.

As a building block, CDs are incorporated into the final aggregates where they might be a hydrophilic or "self-philic" moiety depending on the kind of H-bonds. Being an amphiphilic building unit, CDs can be chemically (by chemical bonds) or physically (by host–guest interaction) attached to a hydrophobic moiety, where the CD outer surface acts as a hydrophilic moiety (CD–water H-bonds are favored) and the resultant compound as a classic amphiphile. As a unamphiphilic building unit, CD/surfactant complexes or even CDs on their own can self-assembly into aggregates in an unamphiphilic way, in which the CD exterior appears to be "self-philic" (CD–CD H-bonds are favored) to drive the self-assembly.

As the cited examples show, CDs provide a handful and effective approach to control the self-assembly of amphiphiles, which in turn affect the solution properties (like viscosity, absorbance, and surface tension) and even lead to DNA decompaction and protein reconstitution. Considering the wide and extensive utilizations of surfactants or amphiphiles, we would expect the involvement of CD modulation in many more applications.

Furthermore, the unamphiphilic self-assembly behavior of CDs and CD/surfactant complexes differentiate itself from the classic amphiphilic behavior in a most fundamental way: the former is mainly driven by CD–CD H-bonds whereas the latter by hydrophobic interaction. Such a unamphiphilic self-assembly may offer us a new angle to understand, construct, and control self-assembly.

Acknowledgments

This work was supported by National Natural Science Foundation of China (20873001, 20633010, 21073006, and 50821061) and National Basic Research Program of China (Grant No. 2007CB936201).

References

[1] Israelachivili JN. Intermolecular and Surface Forces. London: Academic Press; 1985.
[2] Tanford C. The Hydrophobic Effect: Formation of Micelles and Biological Membranes. New York: John Wiley & Sons; 1973.
[3] Whitesides GM, Mathias JP, Seto CT. Science 1991;254:1312.
[4] Lehn J-M. Proc Natl Acad Sci USA 2002;99:4763.
[5] Menger FM. Proc Natl Acad Sci USA 2002;99:4819.
[6] Shimizu T, Masuda M, Minamikawa H. Chem Rev 2005;105:1401.
[7] Jiang LX, Wang K, Deng ML, Wang YL, Huang JB. Langmuir 2008;24:4600.
[8] Jiang LX, Wang K, Ke FY, Liang DH, Huang JB. Soft Matter 2009;5:599.
[9] Lin YY, Cheng XH, Qiao Y, Yu CL, Li ZB, Yan Y, et al. Soft Matter 2010;6:902.
[10] Palepu R, Richardson JE, Reinsborough VC. Langmuir 1989;5:218.
[11] Rekharsky MV, Inoue Y. Chem Rev 1998;98:1875.
[12] Yunus WMZW, Taylor J, Bloor DM, Hall DG, Wynjones E. J Phys Chem 1992;96:8979.
[13] Junquera E, Aicart E, Tardajos G. J Phys Chem 1992;96:4533.
[14] Dorrego AB, Garcia-Rio L, Herves P, Leis JR, Mejuto JC, Perez-Juste J. Angew Chem Int Ed 2000;39:2945.
[15] De Lisi R, Milioto S, De Giacomo A, Inglese A. Langmuir 1999;15:5014.
[16] Tsianou M, Alexandridis P. Langmuir 1999;15:8105.
[17] Talwar S, Harding J, Oleson KR, Khan SA. Langmuir 2009;25:794.
[18] Liao DS, Dai S, Tam KC. J Rheol 2009;53:293.
[19] Mahammad S, Roberts GW, Khan SA. Soft Matter 2007;3:1185.
[20] Galant C, Amiel C, Auvray L. J Phys Chem B 2004;108:19218.
[21] Abdala AA, Tonelli AE, Khan SA. Macromolecules 2003;36:7833.

[22] Gonzalez-Perez A, Carlstedt J, Dias RS, Lindman B. Colloids Surf, B 2010;76:20.
[23] Carlstedt J, Gonzalez-Perez A, Alatorre-Meda M, Dias RS, Lindman B. Int J Biol Macromol 2010;46:153.
[24] Gonzalez-Perez A, Dias RS, Nylander T, Lindman B. Biomacromolecules 2008;9:772.
[25] Cao MW, Deng ML, Wang XL, Wang YL. J Phys Chem B 2008;112:13648.
[26] Li L, Nachtergaele S, Seddon AM, Tereshko V, Ponomarenko N, Ismagilov RF. J Am Chem Soc 2008;130:14324.
[27] Signorell GA, Kaufmann TC, Kukulski W, Engel A, Remigy HWJ. Struct Biol 2007;157:321.
[28] DeGrip WJ, VanOostrum J, Bovee-Geurts PHM. Biochem J 1998;330:667.
[29] Mwakibete H, Bloor DM, Wynjones E. Langmuir 1994;10:3328.
[30] Nicolle GM, Merbach AE. Chem Commun 2004:854.
[31] Jiang LX, Deng ML, Wang YL, Liang DH, Yan Y, Huang JB. J Phys Chem B 2009;113:7498.
[32] Jiang LX, Yan Y, Huang JB, Yu CF, Jin CW, Deng ML, et al. J Phys Chem B 2010;114:2165.
[33] Messner M, Kurkov SV, Jansook P, Loftsson T. Int J Pharm 2010;387:199.
[34] Coleman AW, Nicolis I, Keller N, Dalbiez JP. J Inclusion Phenom Mol 1992;13:139.
[35] Gonzalez-Gaitano G, Rodriguez P, Isasi JR, Fuentes M, Tardajos G, Sanchez M. J Inclusion Phenom Macrocyclic 2002;44:101.
[36] Wu AH, Shen XH, He YK. J Colloid Interface Sci 2006;297:525.
[37] Wu AH, Shen XH, He YK. J Colloid Interface Sci 2006;302:87.
[38] Bonini M, Rossi S, Karlsson G, Almgren M, Lo Nostro P, Baglioni P. Langmuir 2006;22:1478.
[39] Rossi S, Bonini M, Lo Nostro P, Baglioni P. Langmuir 2007;23:10959.
[40] Hernandez-Pascacio J, Banquy X, Perez-Casas S, Costas M, Amigo A, Pineiro A. J Colloid Interface Sci 2008;328:391.
[41] Hernandez-Pascacio J, Garza C, Banquy X, Diaz-Vergara N, Amigo A, Ramos S, et al. J Phys Chem B 2007;111:12625.
[42] Jiang LX, Peng Y, Yan Y, Deng ML, Wang YL, Huang JB. Soft Matter 2010;6:1731.
[43] Jiang LX, Peng Y, Yan Y, Huang JB. Soft Matter 2011;7:1726.
[44] Yan Y, Jiang LX, Huang JB. Phys Chem Chem Phys 2011, doi:10.1039/c0cp02651d.
[45] Immel S, Brickmann J, Lichtenthaler FW. Liebigs Ann 1995:929.
[46] Lichtenthaler FW, Immel S. Tetrahedron: Asymmetry 1994;5:2045.
[47] Nilsson M, Valente AJM, Olofsson G, Soderman O, Bonini M. J Phys Chem B 2008;112:11310.
[48] Mehta SK, Bhasin KK, Mama S, Singla ML. J Colloid Interface Sci 2008;321:442.
[49] Bernat V, Ringard-Lefebvre C, Le Bas G, Perly B, Djedaini-Pilard F, Lesieur S. Langmuir 2008;24:3140.
[50] Pineiro A, Banquy X, Perez-Casas S, Tovar E, Garcia A, Villa A, et al. J Phys Chem B 2007;111:4383.
[51] Cabaleiro-Lago C, Nilsson M, Valente AJM, Bonini M, Soderman O. J Colloid Interface Sci 2006;300:782.
[52] Tutaj B, Kasprzyk A, Czapkiewicz J. J Inclusion Phenom Macrocyclic 2003;47:133.
[53] De Lisi R, Lazzara G, Milioto S, Muratore N. Phys Chem Chem Phys 2003;5:5084.
[54] Wilson LD, Verrall RE. J Phys Chem B 2000;104:1880.
[55] Funasaki N, Neya S. Langmuir 2000;16:5343.
[56] Gharibi H, Safarpour MA, Rafati AA. J Colloid Interface Sci 1999;219:217.
[57] Tominaga T, Hachisu D, Kamado M. Langmuir 1994;10:4676.
[58] Buschmann HJ, Cleve E, Schollmeyer E. J Inclusion Phenom Macrocyclic 1999;33:233.
[59] Bakshi MS. J Inclusion Phenom Macrocyclic 1999;33:263.
[60] Alvarez AR, Garcia-Rio L, Herves P, Leis JR, Mejuto JC, Perez-Juste J. Langmuir 1999;15:8368.
[61] Wilson LD, Verrall RE. Langmuir 1998;14:4710.
[62] Wilson LD, Verrall RE. J Phys Chem B 1998;102:480.
[63] Shen XH, Belletete M, Durocher G. J Phys Chem B 1998;102:1877.
[64] Garcia-Rio L, Leis JR, Mejuto JC, Perez-Juste J. J Phys Chem B 1998;102:4581.
[65] De Lisi R, Milioto S, Pellerito A, Inglese A. Langmuir 1998;14:6045.
[66] Wilson LD, Verrall RE. J Phys Chem B 1997;101:9270.
[67] Qi ZHH, Zhu LZ, Chen HW, Qi WB. J Inclusion Phenom Mol 1997;27:279.
[68] Lu RH, Hao JC, Wang HQ, Tong LH. J Inclusion Phenom Mol 1997;28:213.
[69] Lu RH, Hao JC, Wang HQ, Tong LH. J Colloid Interface Sci 1997;192:37.
[70] Junquera E, Pena L, Aicart E. Langmuir 1997;13:219.
[71] Jobe DJ, Verrall RE, Junquera E, Aicart E. J Colloid Interface Sci 1997;189:294.
[72] GonzalezGaitano G, Compostizo A, SanchezMartin L, Tardajos G. Langmuir 1997;13:2235.
[73] GarciaRio L, Leis JR, Mejuto JC, PerezJuste J. J Phys Chem B 1997;101:7383.
[74] Mwakibete H, Cristantino R, Bloor DM, Wynjones E, Holzwarth JF. Langmuir 1995;11:57.
[75] Xing H, Lin SS, Yan P, Xiao JX, Chen YM. J Phys Chem B 2007;111:8089.
[76] Eli W, Chen WH, Xue QJ. J Inclusion Phenom Macrocyclic 2000;36:439.
[77] Nilsson M, Cabaleiro-Lago C, Valente AJM, Soderman O. Langmuir 2006;22:8663.
[78] Guerrero-Martinez A, Gonzalez-Gaitano G, Vinas MH, Tardajos G. J Phys Chem B 2006;110:13819.
[79] Funasaki N, Ishikawa S, Neya S. Pure Appl Chem 2008;80:1511.
[80] Funasaki N, Ishikawa S, Neya S. J Phys Chem B 2004;108:9593.
[81] Funasaki N, Ishikawa S, Neya S. J Phys Chem B 2003;107:10094.
[82] Brocos P, Diaz-Vergara N, Banquy X, Perez-Casas S, Costas M, Pineiro A. J Phys Chem B 2010;114:12455.
[83] Wang YP, Ma N, Wang ZQ, Zhang X. Angew Chem Int Ed 2007;46:2823.
[84] Han YB, Cheng K, Simon KA, Lan Y, Sejwal P, Luk YY. J Am Chem Soc 2006;128:13913.
[85] Silva OF, Fernandez MA, Pennie SL, Gil RR, de Rossi RH. Langmuir 2008;24:3718.
[86] Sallas F, Darcy R. Eur J Org Chem 2008:957.
[87] Ravoo BJ, Darcy R. Angew Chem Int Ed 2000;39:4324.
[88] Lim CW, Crespo-Biel O, Stuart MCA, Reinhoudt DN, Huskens J, Ravoo BJ. Proc Nat Acad Sci USA 2007;104:6986.
[89] Nalluri SKM, Ravoo BJ. Angew Chem Int Ed 2010;49:5371.
[90] Voskuhl J, Ravoo BJ. Chem Soc Rev 2009;38:495.
[91] Versluis F, Tomatsu I, Kehr S, Fregonese C, Tepper AWJW, Stuart MCA, et al. J Am Chem Soc 2009;131:13186.
[92] Auzely-Velty R, Pean C, Djeddaini-Pilard F, Zemb T, Perly B. Langmuir 2001;17:504.
[93] Bojinova T, Coppel Y, Lauth-de Viguerie N, Milius A, Rico-Lattes I, Lattes A. Langmuir 2003;19:5233.
[94] Jing B, Chen X, Wang XD, Yang CJ, Xie YZ, Qiu HY. Chem Eur J 2007;13:9137.
[95] Jing B, Chen X, Zhao YR, Wang XD, Cai JG, Qiu HY. J Phys Chem B 2008;112:7191.
[96] Li QH, Chen X, Jing B, Zhao YR, Ma FM. Colloids Surf, A 2010;355:146.
[97] Li QH, Chen XA, Wang XD, Zhao YR, Ma FM. J Phys Chem B 2010;114:10384.
[98] Liu T, Diemann E, Li H, Dress AW, Muller A. Nature 2003;426:59.
[99] Li D, Zhang J, Landskron K, Liu T. J Am Chem Soc 2008;130:4226.
[100] Voets IK, Keizer A, Cohen Stuart MA. Adv Colloid Interface Sci 2009;147–148:300.
[101] Harada A, Kataoka K. Science 1999;283:65.
[102] Wu L, Lal J, Simon KA, Burton EA, Luk Y-Y. J Am Chem Soc 2009;131:7430.