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Self-assembled structures of amphiphiles regulating *via*

implanting of external stimuli

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Abstract

Natural or synthetic amphiphilic molecules in solutions can self-assemble to form variably-scaled structures such as micelles, discs, vesicles, tubes and fibers. Minor changes in the conformation and characteristics of amphiphiles can greatly adjust the packing parameters ($P = v/al_0$) and, in turn, the microstructures and the macroscopic properties of self-assembled systems, i.e., viscosity and elasticity, in some cases leading to a phase transition of spontaneous aggregates. This review focuses on how to controllably tune the phase transition of aggregates by changing the external conditions, e.g., pH, temperature, light, and ionic strength. Recent progress in phase transition of assembled structures induced by external stimuli was summarized. We do not attempt to be comprehensive in description of studies reported in literatures, but rather focus on those advances that come from our laboratory, which aim to give a comprehensive understanding of stimuli-responsive intelligent systems, including the transition process, transition mechanism and applications, and thus to provide a guideline for the preparation of smart systems and practical applications.

1. Introduction

The concept of self-assembly is that small structural units, such as atoms, molecules, macroions, or nanoclusters self-organize into more complicated structures via non-covalent interactions.[1-2] Molecular self-assembly has been recognized as one of the most significant issues in the science of 21st. It is a fascinating, practical, bottom-up approach to obtain stable, structurally well-defined, and functional objects at nano- and microscale in biological systems and materials synthesis.[3-7] The amphiphilic molecules contain both hydrophilic and hydrophobic parts. Dissolving in water, the hydrophilic part of the amphiphiles preferentially interact with water molecules, while the hydrophobic part tends to reside in air or nonpolar solvents.[8] The self-assembly of amphiphiles and inorganic-organic hybrid amphiphilic molecules in solutions has become one of the most important research items in soft matter field due to the advantages for fabricating the desired materials in terms of biological applications and enviromentally friendly processability.[9-12] Variably-scaledly self-assembled structures such as micelles (spherical, rod-like, wormlike, and disklike), vesicles, planar lamellae, tubes, and fibers can be produced in amphiphiles and inorganic-organic hybrid amphiphilic molecules solutions, which are driven by weak non-covalent interactions including hydrogen bonding, electrostatic interaction, hydrophobic interaction, and van der Waals interaction.[10-14]

These self-assembled structures of amphiphiles in solutions can be manipulated by tuning the environmental conditions, including pH, temperature, light, solvent polarity, ionic strength (the addition of salts), oxidation/reduction state, etc.[15-22] Since the

functions and properties of surfactant solutions strongly depend on the microstructure, to tune the microstructure of surfactant assemblies is of great importance for both theoretical investigations and practical applications.[23] In this review, recent progresses in regulating amphiphilic molecular self-assemblies *via* imparting external stimuli was summarized. We focus on the self-assembled microstructures and the structure transition under the change of environmental conditions. It is envisaged that the amphiphiles self-assembled microstructures, which respond to external stimuli, would not only be primarily utilized for high-end materials science, but also be possibilities for using stimuli-responsive surfactants in daily applications. The following parts are involved in this paper: (1) How to speculate the shape and size of aggregates formed by a given amphiphile in aqueous solutions. (2) The phase transition between self-assembled structures under the change in environmental conditions, e.g., pH, temperature, light, ionic strength, etc. (3) The applications of responsive amphiphiles systems.

2. Speculation of the shape and size of amphiphilic aggregates in aqueous solutions

Amphiphilic molecules, e.g., surfactants, phospholipids, and block copolymers, can form multitude of aggregates with different morphologies and sizes in aqueous solutions.[24] Depending on concentration, temperature and solvent property (dielectric constant, salinity, etc.), amphiphiles can either be dissolved in solutions or form aggregates like micelles (spherical or cylindrical) and bilayers structures.[25,26] The self-assembly of amphiphiles in solutions has been widely investigated both

experimentally and theoretically, numerous practical applications take advantage of the resulting multi-molecular aggregates.[27] The packing parameter, P, put forward by Israelachvili et al.,[28,29] used simple geometrical consideration to predict the shape and size of amphiphiles aggregates in aqueous solutions. The packing parameter was defined as: $P = v / a_0 l_0$, where v is the volume of the surfactant tail, l_0 is the length of the surfactant tail, and a_0 is the area of the hydrophilic groups of amphiphilic molecules. The packing parameter describes the geometry of the volume occupied by an amphiphilic molecule inside a micelle and determines the equilibrium structures formed.[30] If $P \leq 1/3$, the volume is a cone and the amphiphilic molecules will pack into spherical micelles; if $1/3 < P \leq 1/2$, the volume is a truncated cone and rod-like or wormlike micelles will produce; if $1/2 < P < 1$, the volume is a truncated cone and bilayers will be obtained; (within this region, vesicles appear at lower P, $1/2 < P \leq 7/10$, and tubular structures will appear at $7/10 < P < 1$); if $P = 1$, planar bilayer structures will appear; if $P > 1$, the volume is an inverted truncated cone and reverse structures will form.

The relation between the packing parameter and aggregates morphologies was shown in Table 1. For linear hydrocarbon surfactants, the v and l_0 can be calculated by the Tanford equation:

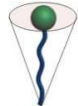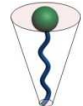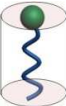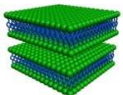$$v\,(\text{Å}) = 27.4 + 26.9n \quad (1)$$

$$l_0\,(\text{Å}) = 1.5 + 1.265n \quad (2)$$

where n is the number of carbon atoms of the alkyl chain.[31,32] The packing parameter theory can provide guideline for speculating the shape and morphology of surfactant

aggregates in aqueous solutions.

Table 1. Different aggregates predicted by the packing parameter P.[26,33]

P value	$P \leq 1/3$	$1/3 < P \leq 1/2$	$1/2 < P < 1$		$P = 1$	$P > 1$
			$1/2 < P \leq 7/10$	$7/10 < P < 1$		
Structure of amphiphiles						
Aggregates	spherical micelles	rod-like or wormlike micelles	vesicles	tubules	lamellae	reversed micelles
Model of aggregates						

3. Self-assembled structure transition *via* implanting of external-stimuli

Amphiphilic molecules can self-assemble to form diverse organized aggregates in aqueous solutions such as spherical micelles, rod-like or wormlike micelles, vesicles, or more complex structures, e.g., bicontinuous sponge or tubular structure, etc. These self-assembled structures are driven by multiple non-covalent interactions, which impart the self-assembled structures more sensitive to external stimuli.[34] In the past few decades, researches on the formation and transition between different self-assemblies have been performed in numerous works.[35] Here we summarized some typical examples in tuning the microstructures of surfactant self-assemblies *via* changing the environmental conditions, especially pH, temperature, ionic strength, and light, etc.

3.1. pH response

Surfactants that response to pH have been subject to increasing interest due to their broad potential applications, in which the variation of pH can be utilized to control self-assembly. The change of pH generally influences the solubility and configuration of surfactant molecules, thus affects their self-assembly properties. For instance, the fatty acids show pH response in water and can form fatty acid vesicles through strong hydrogen bonding within different certain pH ranges,[36] which depend on the chemical structure of fatty acids. Those compounds with longer aliphatic chains prone to form vesicles at higher pH in which the molecules can be packed more tightly in bilayer membranes.[37] Recently, our group reported the phase transition induced by pH in perfluorolauric acid (PFLA) aqueous solutions with alkaili.[38,39] In tetraethylene glycol monododecyl ether ($C_{12}EO_4$)/PFLA system, the densely packed vesicles formed at W_T = 15 wt% and R_{PFLA} = 0.2 (R_{PFLA} = $w_{PFLA}/(w_{PFLA}+w_{C12EO4})$), presenting the pH value of 2.56. When pH increased to 3.49, the sample showed flowing property which can be observed at the tilted test tubes (Figure 1a). Freeze fracture-transmission electron microscopy (FF-TEM) images (Figures 1b and c) indicated the microstructure transition from unilamellar and multilamellar vesicles to planar bilayers. Further increase in pH led the sample to be more fluid (Figure 1a). This transition can be ascribed to the decrease in the membrane charges with the addition of NaOH, due to the weakening of the electrostatic repulsion and the hydrogen bonding between the head-groups.
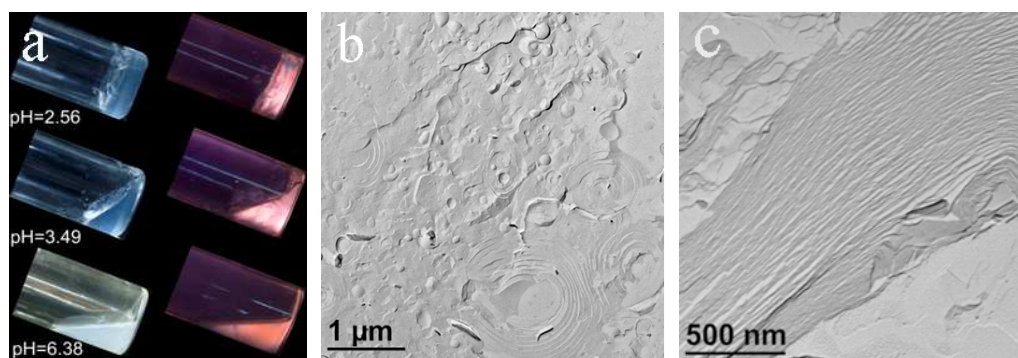
Figure 1. (a) Phase transition of PFLA/$C_{12}EO_4$ aqueous solution at W_T = 15 wt% and R_{PFLA} = 0.2 induced by increasing pH at 25.0 ± 0.1 °C. Left: without polarizers. Right: with polarizers. From top to bottom, pH = 2.56, 3.49 and 6.38. FF-TEM images of polydispersed vesicles in PFLA/$C_{12}EO_4$/H_2O system at W_T = 15 wt% and R_{PFLA} = 0.2 at pH = 2.56 (b) and lamellar phase at pH = 3.49 (c). Reprinted with permission from ref. 38 (copyright (2013) John Wiley and Sons).

The imine bond, formed by aldehyde groups and amino groups, is a kind of dynamic covalent bond. Zhang et al. reported some novel H-shaped amphiphiles, for which the imine bond was utilized to bind two bola amphiphiles together.[40] As shown in Figure 2, micelles formed by the self-assembly of H-shaped amphiphiles were observed. When pH was adjusted from basicity to slight acidity, the imine bond was hydrolyzed, leading to the dissociation of H-shaped amphiphiles and the transition between different aggregates.
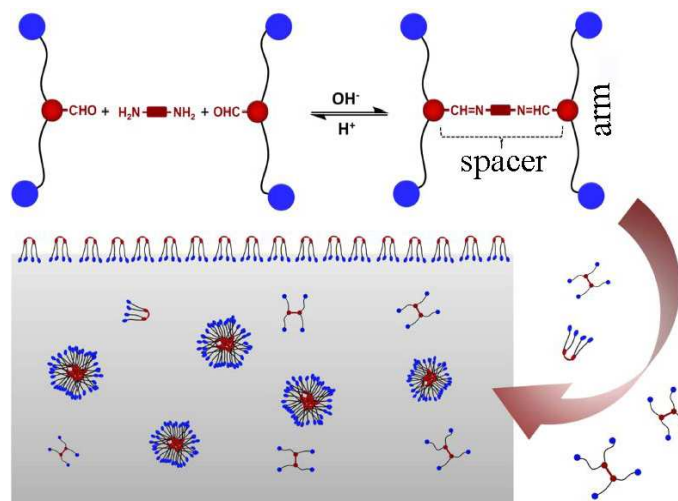
Figure 2. The H-shaped amphiphile and its aggregation behavior in water at water/air interface. Reprinted with permission from ref. 40 (copyright (2012) American Chemical Society).

Another typical pH-responsive system is the amino acid derived surfactant systems. The amino acids always have certain pK_a values, corresponding to the protonation of COO^- and the dissociation of NH_3^+. The environmental pH can greatly affect the existence form of amine acid molecules. The amine acid derived surfactants can exist in anionic, cantionic and zwitterionic forms depending upon the solution pH, which causes the formation of different aggregates. Dey et al.[41] reported a histidine derived surfactant, sodium N-(4-n-octyloxybenzoyl)-L-histidinate (SOBH), which self-assembled to form vesicles with diameters in the range of 30 - 200 nm at pH = 8. When pH increased to 12, the diameters of vesicles also increased. Ranganathan et al.[42] synthesized a series of tyrosine derivatives, sodium salts of maleamic acid of lauryl esters of tyrosine (MTNa), and phenylalanine derivatives, sodium salts of maleamic acid of lauryl esters of phenylalanine (MPNa). The transition between different aggregates with the variation of pH was demonstrated in MTNa aqueous

solutions. Small micelles produced at pH of about 7.54 and the coexistence of micelles and vesicles ($\sim$ 50 nm) were found at pH near 6.5. With the continuous decrease of pH, vesicles and precipitates presented at pH nearly above 6 and below 6, respectively. In MPNa aqueous solutions, large vesicles and precipitates were observed at pH about 7.60 and below 7, respectively.

3.2. CO_2 response

Although pH as a trigger to regulate the surfactant self-assembly has been used broadly, some disadvantages still exist. For instance, acids or bases must be used in stoichiometric quantities, which results in the formation of by-products after each switching cycle. The production and disposal are environmentally and economically costly.[43] Thus, CO_2, a widely available, inexpensive, biocompatible and renewable resource, has been used as a trigger to tune the self-assembled structures in some pH-switchable systems for its easy removal by bubbling to air.[44,45] The key point for the CO_2 controllable systems is that the surfactant molecules are able to reversible uptake and release CO_2.

Pioneering work was made by George and Weiss, who developed the CO_2 sensitive systems.[46] In these systems, the long-chain alkylamine reacted with CO_2 to form surfactants charged by ammonium carbamates (Scheme 1). When the solutions were bubbled by N_2, Ar or air or slightly heated, CO_2 was released from the solution, which imparted the systems more convenient controllability. The capture and release of CO_2 were reversibility and repeatability, which were confirmed by monitoring the change of conductivity of compound 1a (Scheme 1) in wet dimethyl sulfoxide (DMSO) treated by CO_2 and then by argon over three cycles (Figure 3).[23,47] The conductivity

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increased when CO_2 was bubbled into the solution and decreased upon the addition of

argon, indicating the transition between different aggregates during this process.[47]
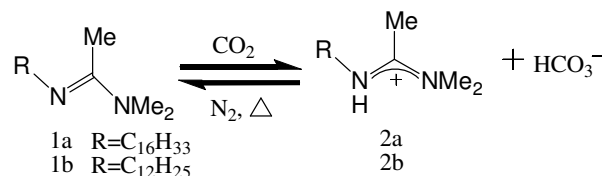
Scheme 1. Long-chain alkylamine reacted with CO_2 to form ammonium

carbamates.[47]
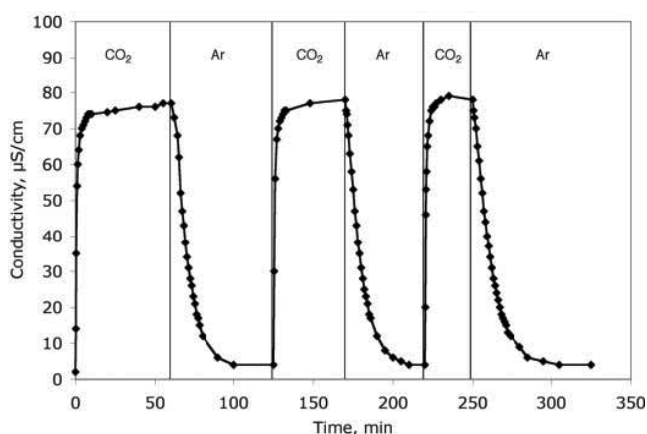
Figure 3. The conductivity of compound 1a in DMSO solution at 23 ^{o}C as a function

of time during three cycles of treatment with CO_2 and followed by argon. Reprinted

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Very recently, Feng and coworkers[44,45,48] reported the CO_2-switchable wormlike

micelles formed by an amine based surfactant (Figure 4). They developed complex

fluids composed of CO_2-switchable viscoelastic wormlike micelles utilizing

N,N,N′,N′-tetramethyl-1,3-propanediamine (TMPDA, Figure 4a) and an

commercially available anionic surfactant, sodium dodecyl sulfate (SDS), with the

stoichiometric ratio of 2:1.[45] When CO_2 was bubbled into the mixture solution, the

TMPDA molecules were protonated to ammonium species. Two protonated TMPDA

molecules 'bridged' two SDS molecules through electrostatic interaction to form a

pseudo-gemini surfactant, resulting in a macroscopic increase of viscosity because of

the formation of wormlike micelles. After CO_2 was removed, the ammonium groups

were deprotonated back to tertiary, inducing a transition from wormlike micelles to

spherical micelles. Such self-assembled structure transition can be reversibly tuned by

cyclically bubbling and removing CO_2. Afterwards, the single component systems,

octadecyl   dipropylene   triamine   (ODPTA,   Figure   4b),   and

N-erucamidopropyl-N,N-dimethylamine ($UC_{22}AMPM$, Figure 4c), were performed to

construct the CO_2 tuning wormlike micelles in aqueous solutions, respectively.[44,48]

Before the introduction of CO_2, the ODPTA solution was emulsion-like fluid with

low-viscosity, consisting of vesicles.[48] However, after bubbling CO_2 for only 2

minutes, vesicles transformed into wormlike micelles, accompanying with a

significant increase of viscoelasticity. When CO_2 was displaced by N_2, vesicles

re-formed again. The reversible microstructure transition between spherical micelles

and wormlike micelles regulating by bubbling CO_2 was also observed in $UC_{22}AMPM$

solutions.[44] Zhao et al.[49] synthesized some amphiphiles and focused on the

modulation of the size, shape, and morphology of their self-assembled structures

under the controlled CO_2 stimulation levels. The obtained regulation was conducive to

understanding the stimuli-triggered dynamically reshaping process in self-assembly of

amphiphilic molecules in aqueous solutions.[49]
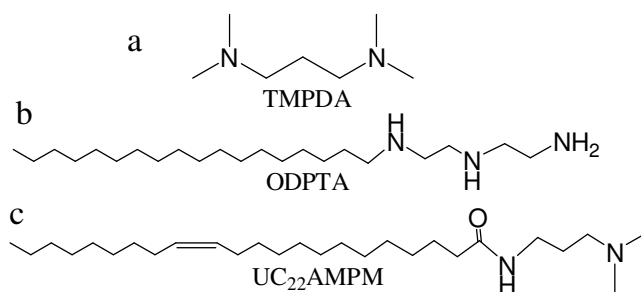
Figure 4. Chemical structures of TMPDA (a), ODPTA (b), and UC$_{22}$AMPM (c).

3.3. Temperature response

Temperature is often considered an excellent way to tailor self-assembles due to three main reasons: i) no additives added; ii) easy to control; iii) a wide range of applications in various fields. The temperature-sensitive systems are convenient for investigating the stage of individual surfactants in the aggregates transition process because the transition can be cycled or stopped at any required step during the measurements. Kinetic aspects can also be examined by controlling the heating and cooling rates.[23]

Temperature has great effect on solubility of surfactants, which induces the transition between different aggregates. For most nonionic surfactants, the dissolution mechanism in aqueous solutions is the hydrogen bonding between the hydrophilic heads (usually ethylene oxide chains) and water molecules. The introduction of thermal energy, i.e., rising temperature intensifies the molecular thermal motion and weakens or breaks the hydrogen bonding. Thus, the transparent aqueous solutions turn turbid above a certain temperature owing to the dehydration of ethylene oxide (EO) units and the consequent aggregation.[50] This temperature is called "cloud point temperature" and is dependent on the length of EO chains, the size and structure of hydrophobic tails.[51] In contrast, for ionic surfactants, the solubility increases with

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temperature rising. When temperature is above a critical value, the so-called "Krafft point temperature", the solubility can increase rapidly. In ionic surfactant systems, the size of aggregates normally decreases with the increase of temperature. Aggregates transition from vesicles to micelles with temperature increasing usually occurs in most vesicular systems.[52,53] As exceptions, Huang et al. reported a number of cationic/anionic surfactant systems, in which they observed the heating-induced transition from micelles to vesicles in a number of cationic/anionic (catanionic) surfactant systems,[34,54] and they predicted that it was a general phenomenon in catanionic surfactant systems with stronger molecular interactions and larger micelle aggregation numbers.

Hao et al. reported a series of temperature-sensitive aqueous three-phase surfactant systems (A3PS).[55] For these systems, a constant temperature within 20 - 30 $^{\circ}$C was favorable to the formation of three-phase systems (Figure 5). When temperature decreases, one phase among the three phases can be compressed, leading to the formation of two-phase solutions. On the other hand, with increasing temperature, the lamellar phase gradually disappears and a micellar phase was observed due to the dehydration of the surfactant headgroups and the unfavorable entropy contributions, which favors the formation of micelles.
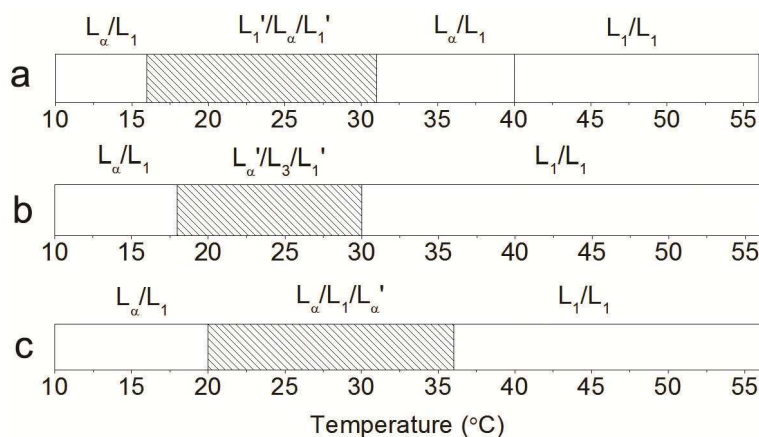
Figure 5. Observed phase region of surfactant mixtures as a function of temperature. The three-phase of the 100 mM C_{14}DMAO/26.5 mM Texapon N_{70}/26.5 mM HCOOH/H_2O system appears within 16 to 31 °C (a). In the LA/$C_{12}EO_4$/H_2O system (W_T = 23 wt.%; R_{LA} = 0.25) the three-phase region exists from 18 to 30 °C (b). The SL/TTABr/H_2O system (c_T = 100 mM; R_{SL} = 0.395) has a three-phase region existing from 20 to 36 °C (c). The L_α phase represents the planar lamellar phase, the L_1 represents the threadlike micelles phase, the $L_1{}'$ phase represents micelles phase disc like micelles phase and the L_3 phase represents sponge phase. Reprinted with permission from ref. 55 (copyright (2013) Nature).

The protonation of the molecules can be increased with the increase in temperature, causing the transition between self-assembles. A typical system formed by tetradecyldimethylamine oxide (C_{14}DMAO) with 4-phenylazo benzoic acid (AzoH) in aqueous solutions was reported by Hao et al.[56] C_{14}DMAO molecules can be protonized by AzoH molecules to form C_{14}DMAOH$^+$ species. The combination of C14DMAOH+ with Azo− through electrostatic interaction induces the decrease in the area of the head groups and the increase of packing parameter with the increase of

temperature, resulting in the structure transition from wormlike micelles to multilamellar vesicles (Figure 6). The small excess amount of protonized $C_{14}DMAOH^+$ species makes the bilayer membranes be positively charged, which sustains the stability of multilamellar vesicles.[57] According to previous work,[58] the balance between the edge energy and bending energy determined the shape of surfactant aggregates. Molecules with lager headgroups and short hydrophobic chains tended to gather on the edge of the aggregates because the curvature on the edge is bigger than in the bulk. The balance between edge energy and bending energy is sensitive to temperature, which is the possible reason for the microstructure transition.
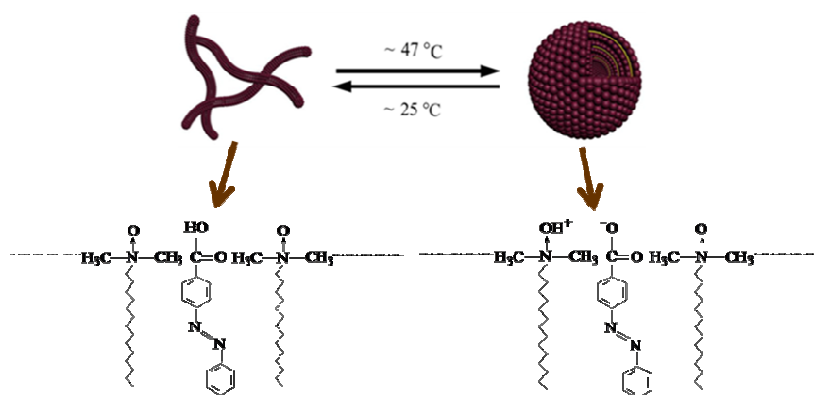
Figure 6. Schematic illustration of the structure transition from wormlike micelles to multilamellar vesicles. The $C_{14}DMAO$ molecules can be protonated by AzoH in the formation of multilamellar vesicles. Reprinted with permission from ref. 56 (copyright (2012) American Chemical Society).

As is well known, when samples are heated, the molecular thermal motion is intensified, weakening or breaking the hydrogen bonding, which modulates the balance of non-covalent interaction and causes the rearrangement of the surfactant molecules and the microstructure transition. Generally, the hydrogen bonding can be

reconstructed when samples are cooled to room temperature, inducing the recovery of

the microstructures. Thus, in temperature-sensitive systems, the self-assemblies can

be reversibly tuned by changing the temperature. The reversible transition between

helical fibrils and vesicles induced by temperature can be observed by mixtures of

alkyldimethylamine oxide (C_nDMAO) and lithocholic acid (LCA) in aqueous

solutions.[14] In this system, the breakage or reconstruction of the hydrogen bonds

produced by the temperature change leads to the aggregates transition, i.e., the

temperature change can modify the balance of weak interactions in the transition of

the self-assembly structures.

3.4. Light response

Light irradiation displays many advantages. Firstly, light-triggered biochemical

transformations represent sophisticated biological processes, in which optical signals

are recorded and transduced as physicochemical events. Secondly, light is an elegant

and non-invasive trigger, and can be operated in a clean environment, avoiding the

changes in compositions or thermodynamic conditions. Thirdly, light is a cheap and

readily available trigger to be used as a mild energy source. Fourthly, light can be

remotely and accurately controlled.[43] Amphiphilic molecules incorporated with some

photo-active groups, e.g., azobenzene, stilbene, and spiropyran, either in headgroups

or hydrophobic chains always undergoes reversible changes in conformation under

sequential illumination with UV and visible light. During the transition process, the

cis-trans isomerization, dissociation, intermolecular hydrogen transfer or group

transfers, and electron transfers usually occur.[59] The transformations can be classified

into two ways: one is thermally stable conversion, achieving under the change of

wavelength; the other undergoes a metastable state which responds only if light is continuously supplied.[23]

The occurrence of *cis-trans* isomerism for azobenzene and stilbene amphiphilic molecules depends on the incident wavelength. Thermodynamically stable, planar *trans* isomers are generally transformed into bent, less-hydrophobic *cis*-form under irradiation at around 360 nm and convert back at 460 nm.[23] In 1982, Shinkai et al. first reported the aggregation induced by photoinduced isomerism in the photo-responsive azobenzene amphiphiles systems.[60] Since then, many scientists devote themselves to the light-induced phase transition of aggregates. Reghavan et al. investigated the transition of wormlike micelles from long length to short length under light irradiation.[61] Our group studied the UV irradiation induced phase transition in aqueous solutions of $C_{14}DMAO$/*para*-coumaric acid (PCA), and observed the transition from vesicles to wormlike micelles, which was rarely reported.[62] As shown in Figure 7, the solution of *trans*-PCA (60 mM) mixed with 150 mM $C_{14}DMAO$ consists of vesicles with birefringence. When the solution underwent 60 min UV-irradiation in water bath at room temperature, the slightly turbid solution turned to transparent solution without birefringence. The viscosity of the solution sample exhibited obvious enhancement. This transition was attributed to the UV-induced *trans-cis* transition of PCA molecules. The $C_{14}DMAO$ molecules can be easily protonated by the weak acid, *trans*-PCA, in water, to form a catanionic surfactant system, for which the area of the hydrophilic headgroups, a_0, decreases, leading to the increase in packing parameter, P ($P = v/a_0 \cdot l_0$) and the formation of vesicles. After the

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UV-light irradiation, the *trans*-PCA molecules turned to *cis*-form. The a_0 value increased significantly because the steric hindrance of *cis*-PCA is much larger than *trans*-PCA, which decreased the *P* value and resulted in the transition from vesicles to wormlike micelles.
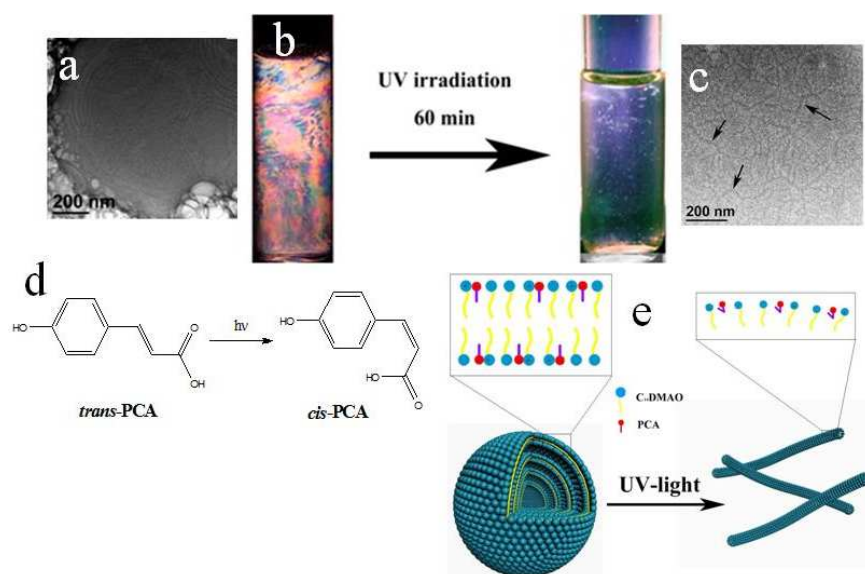
Figure 7. Cryogenic-transmission electron microscopy (Cryo-TEM) images of 60 mM *trans*-PCA and 150 mM $C_{14}DMAO$ aqueous solution before (a) and after UV-irradiation for 60 minutes (c); the change of birefringent patterns after UV-light irradiation (b); the schematic of photoisomerization of PCA molecule from *trans* to *cis* (d), and the microstructure transition mechanism from multilamellar vesicles to wormlike micelles induced by photo-irradiation (e). Reprinted with permission from ref. 62 (copyright (2011) Royal Society of Chemistry).

Recently, we observed the microstructure transition from wormlike micelles to vesicles triggered by irradiation of the mixtures of a nonionic surfactant, $C_{12}EO_4$, and sodium 4-phenylazobenzoic acid, AzoNa, in aqueous solutions.[63] The AzoNa molecules switch between their *cis*- and *trans*- forms under the transition between UV

and vis lights. The *trans-* and *cis-* forms have different solubility in water due to the different spatial structures and polarities, which changes the exchange kinetics of the surfactant molecules and results in a phase transition. The *cis*-form of AzoNa has higher polarity and solubility than the *trans*-form. When the transition from *trans-* to *cis-* is initiated under UV irradiation, there are more AzoNa monomers in *cis-* form than in *trans-* form, which reduces the number of AzoNa molecules in the bilayers due to the steric effect, resulting in a decrease in the interlamellar repulsive force and promotes bilayer formation. Furthermore, the increases in the volume of the hydrophobic chains also favored the formation of bilayers.

The spiropyran can switch between the energy stable, non-ionic hydrophobic form and the zwitterionic mercyanine form when being acted with the UV illumination.[64,65] The synthesis of spiropyran-modified surfactants was first reported in 1998.[66] In 2010,[65] Abe et al. reported the self-assembly of spiropyran-modified surfactants (SP-Me-6, Figure 8) on colloidal and fat silica tuned by the visible light irradiation. The MC form of SP-Me-6 produced disk-like or flattened spherical surface aggregates in the adsorption plateau region on a flat silica plate, whereas the SP form gave larger surface aggregates as a result of its greater hydrophobic/hydrophilic character. The difference in the hydrophobicity between the two isomers induced the reversible change, for which the dispersion stability of silica suspensions as well as in the surface force, were in response to the photoisomerization.
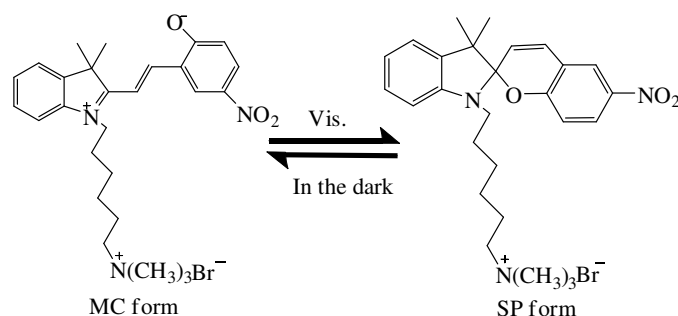
Figure 8. Chemical structures of two isomers of SP-Me-6. The MC form (left) is spontaneously formed in aqueous solution, while the visible light irradiation induces the photoisomerization to produce the SP form (right). The original MC form can reappear when the isomerized SP solution is stored in the dark.[65]

Utilizing the photoisomerization of azobenzene to control the host-guest interaction between azobenzene based surfactants and cyclodextrin (CD) and to adjust the self-assembly is very interesting. Driven by hydrophobic and van der Waals interactions, the *trans*-azobenzene can be well-recognized by α-cyclodextrin (α-CD).[66] When *trans*-azobenzene is changed to *cis*-azobenzene, α-CD can not include the bulky *cis*- form anymore due to the mismatch between the host and guest. Therefore, the host-guest assembly and disassembly between azobenzene and α-CD by external photostimulation can act as a driving force to build molecular shuttles, motors, and machines.[67] Photocontrol inclusion and exclusion reactions of an azobenzene-contained surfactant with α-CD can undergo reversible assembly and disassembly, as shown in Figure 9.[68] Zhang et al. synthesized azobenzene-surfactant (AzoC$_{10}$) and tuned its assembly via introducing UV light to regulate the host-guest interaction between AzoC$_{10}$ and α-CD.[68] AzoC$_{10}$ molecules formed vesicles in aqueous solutions. When α-CD was added, the vesicles were disrupted owing to the

binding of α-CD to the azobenzene. However, after the photoirradiation under UV-light, α-CD could not bind with the azobenzene any more, resulting in the re-formation of vesicles. This process was reversible by applying visible light and recovering azobenzene to *trans-* form. This research provided a model stimuli-responsive vesicle system to combine photochemistry and host-guest chemistry.
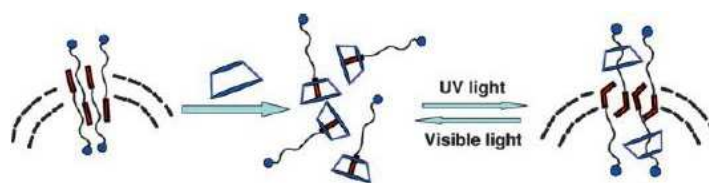
Figure 9. Illustration of the photo-controlling reversible assembly and disassembly of AzoC10 modulated by α-CD and light illumination; red bar: azobenzene moiety, blue spot: pyridinium group. Reprinted with permission from ref. 68 (copyright (2007) John Wiley and Sons).

3.5. Redox response

The hydrophilic-hydrophobic balance of amphiphilic molecules containing redox-active functional groups such as ferrocene, viologen, and N-alkylated nicotinamides can be facilely manipulated by controlling the number of positive charges on the surfactants.[69] These amphiphilic molecules are considered as promising systems to trigger reversible changes in self-organization. In 1985, Saji et al. reported the first ferrocene-based surfactant, for which the critical micelles concentration (*cmc*) and micellization behavior modulated by electron transfer was investigated.[70,71] Through spectroscopic studies, they found that the micelles could be broken up into monomers by oxidation and re-formed by reduction.

For the ferrocene-based surfactants, transitions between the oxidation and reduction states of ferrocenyl surfactants can lead to substantial changes in the charge and amphiphilic nature of the surfactants. The terminal ferrocene group is electrically neutral and sparingly soluble in water. When being oxidized, the hydrophilic cationic ferricenium ions can be formed. The change in charge and the balance of hydrophilicity/hydrophobicity can induce the variation in the microstructures of aggregates. Based on this consideration, Abe and co-workers used a ferrocenyl surfactant, (11-ferrocenylundecyl) trimethyl-ammonium bromide (FTMA), to be mixed with sodium salicylate to regulate the aggregation between wormlike and elliptical micelles *via* redox reaction.[72] FTMA had a redox-active ferrocenyl group at the end of its alkyl chain, allowing the electronic control of its chemical structure between reduced and oxidized states: the ferrocenyl group in reduced form was hydrophobic, while the ferricinium cation in oxidized form showed hydrophilicity. The remarkable change in hydrophilic-lipophilic balance of FTMA through the redox reaction induced its aggregation behavior transforming between the wormlike and elliptical micelles.

3.6. Shearing response

Shear flow has a strong influence on complex fluids, especially the self-assembled structures of amphiphilic molecules in solutions. Because the introduction of mechanical force can alter the microstructures of aggregates,[73] the effect of shear force on aggregation behavior of amphiphiles has attracted growing interest over last decades both in theoretical and experimental viewpoints. Shear forces can influence many types of aggregates in solutions, e.g., the microstructure transition among

wormlike micelles,[74] sponge phase,[75] hexagonal liquid crystalline phase,[76] and lamellar structures (planar lamellar phase and vesicles).[77] Among the extensive researches, the effect of shear force on the transition of lamellar phase, sponge phase to lamellar phase, lamellae-to-vesicles, and multilamellar-to-unilamellar vesicles has attracted intensive attention.[77]

The lamellar structure usually contains many defects, especially in the vicinity of the phase transition boundaries, in the dislocation loops or thermodynamically stable defects where the lamellar bilayers are highly curved with the most common defects of edge dislocation.[78,79] When exposed to higher shear rates, the defective lamellar structures exhibit the trend to reorient and form multilamellar vesicles (MLVs). Zilman and Granek[80] proposed the mechanism of the MLVs formation under shear based on the undulation instability. They suggested that the shear flow generates an effective force that acted on the excess area and thereby exerted an effective pressure. At a low shear rate (typically below $\dot{r} = 1$ s^{-1}), the bilayers are mainly parallel to the flow with defects (dislocations) in other two directions. Above a critical shear rate, the defects in the flow direction are completely suppressed, inducing the lamellar bilayers buckles into harmonic shape modulation and then breaks up into MLVs. Many techniques such as rheometer-small angle neutron scattering (rheo-SANS), rheometer-small angle light scattering (rheo-SALS), deuterium nuclear magnetic resonance (^{2}H NMR), cryo-TEM and FF-TEM can be used to monitor the transition processes. The formation of MLVs can be characterized by a butterfly-type scattering pattern in SANS and a four-lobe pattern in depolarized SALS. The transition from

planar lamellar structures to vesicles can also be characterized by the variation from the double peak to a single peak and a decrease of quadrupole splitting in ^{2}H NMR spectra. It should be pointed that for the more dilute solutions of those aggregates with hydrophilic layers in large thickness, the quadrupole splitting may be very small due to the less anisotropic environment of the water molecules. FF-TEM and cryo-TEM observations can give visual images of the structure transition. In addition, rheological measurements reflect the variation of macroscopic properties under shearing and are useful to monitor the structure transition process, which can provide important information to practical applications. The shear-induced transition from planar lamellar structures to MLVs has been studied extensively in systems of sodium salt of bis(2-ethylhexyl) sulfosuccinate (AOT)/brine,[81] sodium dodecyl sulfate (SDS)/alcohol/water,[82] and aqueous of ethylene oxide surfactants C_nE_m/water.[83] The features of MLVs formed *via* shearing are summarized as follows:[83] 1) The shape of MLVs are not spherical but polyhedral; 2) The MLVs have a narrow size distribution, which can be tuned from a few to a tenth of micrometers depending on the applied shear rate;[84] 3) When shear is removed, the recovery of the planar lamellar structure requires a rather long time, usually days to months;[85] 4) The formation time of MLVs depends on the shear rate.[83]

The reported work mainly focused on semidilute or concentrated surfactant solutions. Recently, Hao and co-workers utilized FF-TEM, cryo-TEM, and rheological measurements to investigate the shear-induced structure transition and recovery in dilute solutions of tetradecyltrimethylammonium hydroxide

(TTAOH)/lauric acid (LA)/deoxycholic acid (DeCA)/H_2O system with the mass concentration of total surfactants being about 4.7 ~ 4.9 %.[73] The molar concentration of TTAOH was equal to that of the mixed acids (LA and DeCA). When x ($x = n_{DeCA}/(n_{DeCA}+n_{LA})$) was within 0.3 - 0.2, the structure transition from planar lamella to MLVs induced by shear was observed. The transition of a typical sample of $x =$ 0.25 was shown in Figure 10. With the increase in shear rate, the shear viscosity increased first, exhibiting a shear thickening property due to the formation of vesicles, and then decreased because of the shear thinning character of vesicles under high shear rates. The cryo-TEM images in Figure 10 clearly showed the planar lamellar structures and MLVs before and after shearing, respectively. The MLVs were found closely packed with diameters within 500 - 1000 nm. Due to the extruding of each other, the shapes of most MLVs were deformed. This research enriches the results of shear effect on the self-assembly in salt-free catanionic surfactant solutions and provides important information to the practical applications.
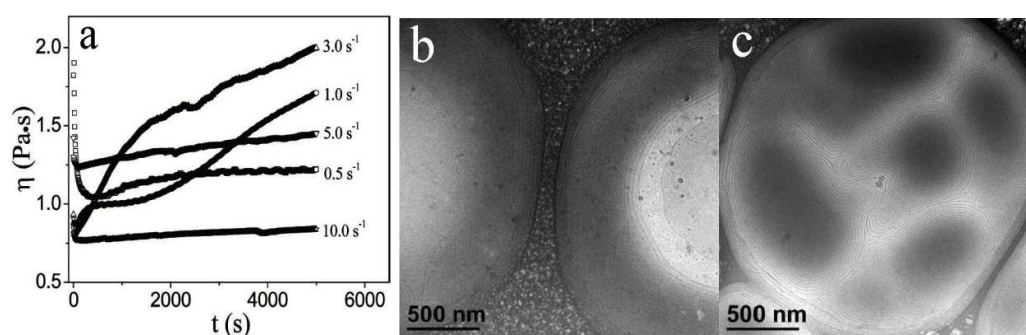

Figure 10. The variation of shear viscosity with time at different shear rates for sample of x = 0.25 at 100 mM TTAOH/(DeCA+LA) (a); Cryo-TEM images before (b) and after (c) shearing at 20 s^{-1} for 5000 s.[73]

The sponge phase is free flowing and optically isotropic, and does not present the long-range order and the birefringence at static state.[86] It consists of the infinite membrane bilayers in a convoluted morphology, which are randomly interconnected, dividing the sample volume into two equivalent strongly interwoven parts. The relative stability of the sponge and lamellar structures depends critically on the membrane curvature and flexibility. The transition between the two phases can be readily achieved by changing membrane properties. Cates and Milner[84,85] proved that the isotropic sponge phase could transform to lamellar phase under shearing. The transition is dependent on several experimentally observable parameters: a) On increasing solvent volume fraction, the transition becomes more feasible; b) The transition occurs more readily with time over a certain shear rate being applied to the sample; c) For the fixed shear time and sequence of shear rate, the critical shear rate for phase transition increases as the relaxation time increases; d) For a given value of shear time and relaxation time, the critical shear rate for phase transition decreases as the initial shear rate decreases. During shearing, the lamellar phase is stabilized over sponge phase. However, the sponge phase is recovered as the true equilibrium state within several hours after the removal of shearing.[75,86,87] The transition from bicontinous sponge structure to lamellar structure induced by shearing has been studied in detail by Yamamoto and Hao.[75,88-90]

3.7. Salinity response

Molecular self-assembly in surfactant systems is largely dependent on the number of water molecules surrounding the headgroups. When salts are added to surfactant solutions, the surfactant headgroups are dehydrated, which causes a decrease in a_0

value (the effective area per molecule at the interface) and consequently an increase in the packing parameter P, resulting in the aggregate transition.[91,92] At the same ionic strength, different salts have different effect on the surfactant aggregation behavior. Base on the ability to precipitate hen egg-white protein, Hofmeister[93] proposed a particular order of inorganic salts, which was the well-known Hofmeister series. He explained that the different effects of salts with the same ionic strength were the results of the difference of their water withdrawing power. In 1997, Collins et al. put forward the law of matching water affinities, indicating that the oppositely charged ions with approximately equal free energy of hydration preferred to form ion pairs.[94-96] To a large extent, the variation of aggregates both in biological systems and catanionic systems is dominated by the electrostatic interaction among the charged headgroups intra- and inter-aggregates, which means that the systems are highly sensitive to salts.[97] Thus, to study the influence of salts on surfactant self-assembly is useful to investigate the specific salts effect in biological systems and to design particular surfactant systems to meet the demand in academic research and practical applications.

  Much work of salts effect on the catanionic surfactant systems has been performed. Kunz observed a salt induced micelle-to-vesicle transition in a catanionic system composed of sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB) with an excess of SDS.[92,98] They demonstrated that the transition was dependent on the excessive surfactant and its headgroup feature. When the anionic surfactant was in excess, only the cation specificity could be found; on the contrary,

the anion specificity was just observed in the catanionic surfactant system with excessive cationic surfactants. When SDS was replaced by SL, the cation order of an excess of SDS, which followed the Hofmeister series, was completely opposite to that of an excess of SL because of different nature of their headgroups.

In salt-free catanionic surfactant systems, our group demonstrated that the addition of salts could induce abundant aggregation behaviors.[99,100] A transition from uni- and multilamellar vesicles to densely packed multilamellar vesicles by adding salts was obtained.[100] This transition was brought by the reduction of the repulsion between the bilayers induced by the excess salt. In addition, the transition was a reversible process. The densely packed multilamellar vesicles can turn back to uni- and multilamellar vesicles by removing the salts. In the anionic–nonionic mixtures, the introduction of electrolytes can induce the transition from micelles/vesicles two-phase to a homogeneous onion-like phase, and can also lead to expansion of the lamellar phase region.[101] The reason might be that the electrolyte added shield the electrostatic repulsion between the micelles, causing a decrease in the a_0 value and an increase in the packing parameter, P, which is favorable for the formation of lamellar structures. For the lamellar phase, the electrolytes can shield the electrostatic repulsion between the bilayers, resulting in more flexible membranes and a decrease of the viscoelasticity of the solutions. Thus, we conclude that the charge and ionic strength facilitate the flexibility of membrane in anionic-nonionic mixtures. Thus, the phase transition in the complex fluids can be tuned by altering charge and ionic strength.

4. Conclusions and perspectives

Growing research interest is focused on tailoring the self-assembled structures and realizing the switching between diverse amphiphilic supramolecules. These smart systems, dramatically responding to environmental stimuli, can be used in a number of processes, e.g., regulating the transportation of molecules near oil/water interface,[44] changing wettability,[102,103] or converting electrical,[102] optical,[104] thermal[105] or pH[106] signals to chemical, biochemical or physicochemical ones. They are playing increasingly important roles in a wide range of areas, such as nanotechnology, biological engineering, and material science.

Lately, the field of stimuli-responsive materials has been growing considerably since the past decade. Plenty of "intelligent" nanostructured systems have emerged and been proposed for wide applications, for instance, in electronic devices, as 'smart' optical systems,[61,107] in micro-electromechanical systems, in coating, and quite significant in biomedical field for drug delivery,[108] diagnostics, biosensors,[109] artificial organs, and tissues engineering.[110] The self-assembled structures that response to external stimuli, as shown in section 3, are envisaging candidates for smart material systems. They show excellent controllability, which provides an opportunity for capture and release and can be used for the controllable drug delivery. It should be pointed out that although the responsive systems have many potential applications, few of them have been developed into commercialization, for which the efforts should be focused on in future investigations.

Amphiphiles self-assembled structures can be manipulated by altering the external conditions, such as pH, temperature, light, solvent polarity, ionic strength, shear force,

oxidation/reduction reactions, etc. This review systematically explains how to speculate the self-assembled structures and reversibly tune the aggregate transition without change the compositions. The fabrication of a stimuli-responsive system relies on the introduction of a stimuli-sensitive unit, either by attachment of a responsive group or, more simply, by the introduction of a responser into the surfactant solutions. The responsive surfactants or additives acts by modulating the critical packing parameter when triggered by external stimuli, leading to the reorganization and the structure transition of the aggregates.

It is anticipated that the intelligent systems will have significant influence on advance applications. Reversible and delicate control of the aggregate transition by imparting stimuli may find niches in smart materials, such as intelligent switches, gas or humidity sensors, and smart fluids, etc., and in controlled-release systems, nanotechnology and tissue engineering field. This ambitious goal to be undertaken in the future will bring the rapid development of new multi-responsive amphiphilic systems in practical applications.

Acknowledgements

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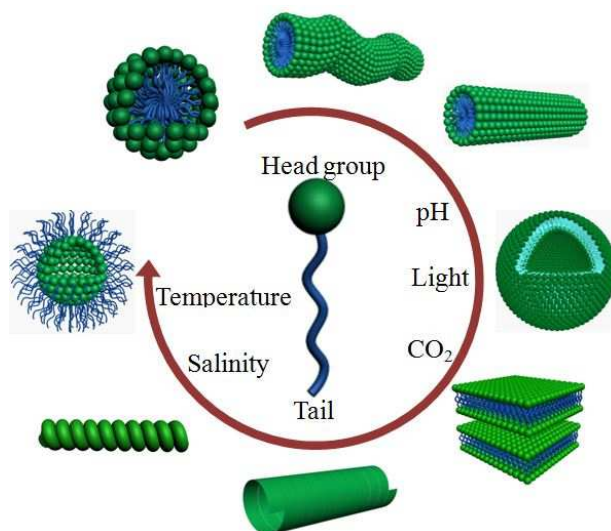
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This review article has summarized recent achievements of manipulating amphiphilic molecules and their self-assembled structures via different external stimuli.