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Development of Surfactant Coacervation in Aqueous Solution

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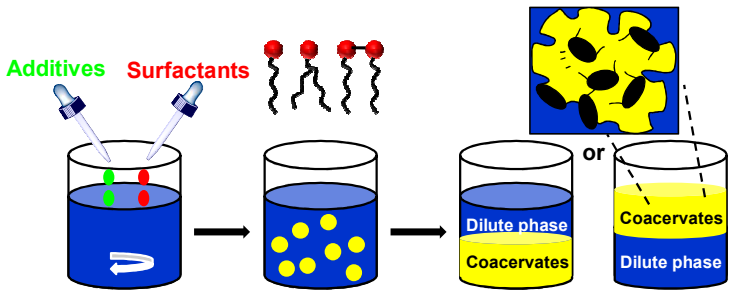

Through rational design of surfactant structure and utilization of additives, various surfactant coacervates can be constructed.

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Coacervation is a phenomenon in which a colloidal dispersion separates into two immiscible liquid phases, a liquid rich in colloidal phase in equilibrium with another diluted liquid phase. Surfactant coacervation here refers to coacervation whose main components are surfactants with low molecular weight. Over the past two decades, surfactants have been greatly developed and the studies on coacervation in the systems of novel surfactants have been reported. This review summarizes the development of coacervation occurring in monomeric surfactants, one-head and two-tail surfactants, gemini surfactants and their mixtures. The effects of surfactant molecular structures and external conditions on critical conditions for coacervation, structures of precursors and coacervates, and their relationships are described. Effects of inorganic salts, alcohols and organic salts on surfactant coacervation are also reviewed.

1. Introduction

Coacervation has attracted particular interest because of its widespread applications in water treatment,[1,2] cosmetic formulation,[3,4] protein purification,[5,6] tissue elasticity,[7] and pharmaceutical microencapsulation.[8-10] Coacervation is defined as a process in which a colloidal dispersion separates into two immiscible liquid phases in the same solvent medium. The dense phase rich in colloidal components is called as coacervate, in equilibrium with a relatively dilute liquid phase. Coacervate phase can remain as a turbid suspension of amorphous droplets or coalesce into a top or bottom liquid phase, depending on its density. Coacervation is a subtle balance of electrostatic interaction, hydrophobic association, hydrogen bond, van de waals' force and other weak interactions. When these weak interactions are reduced, coacervation is suppressed, and when these weak interactions are enhanced, precipitation may occur. Coacervation can be divided into simple and complex coacervation on the basis of coacervation mechanisms.[11] Simple coacervation only involves one colloid species such as macromolecules or surfactants, and can be generated by adding a dehydrating agent such as salts or alcohols, or by increasing temperature, which promotes inter-colloid interactions over the interaction of colloid species with solvent. Complex coacervation consists of at least two oppositely charged polyelectrolytes, biomacromolecules, surfactants and/or other colloid species, and is mainly driven by electrostatic attraction in the vicinity of electrical neutrality. Molecular structures, concentration, mixing ratio, ionic strength, pH, and temperature all affect the formation of complex coacervates. If classifying coacervation on the basis of the main components, coacervation can be divided into macromolecule coacervation and surfactant coacervation. Surfactant coacervation is the subject of this review.

Before reviewing surfactant coacervation, macromolecule coacervation will be briefly introduced because of its importance. Macromolecule-surfactant coacervation is a kind of complex coacervation and is placed in macromolecule coacervation here. Macromolecule coacervation was first investigated by Bungenberg de Jong for the system of gum arabic-gelatin in 1920-40s.[12] He coined the term "coacervation" and defined the phenomenon. Then Oparin popularized coacervates into life science and proposed that life was originated in coacervates.[13] Since then, macromolecule coacervation including synthesized polymers and natural biomacromolecules have been extensively studied, and experimental and theoretical investigations were well reviewed by Dubin,[14] Veis,[15] Bohidar,[16] Schmitt,[17] and so on. Moreover macromolecule coacervation applied in microcapsule formation was also reviewed.[18,19] The works from Dubin,[20-25] Burgess,[10] and the works cited in the references have greatly promoted advancements of complex macromolecule coacervation. Particularly several theoretical models have been proposed by Voorn and Overbeek,[26] Veis,[27] Nakajima and Sato,[28] and Tainaka[29] and have been compared in a review by Burgess.[19] These theoretical models addressed the phase separation kinetics and described the driving forces, specific conditions and formation process for coacervation. The Voorn-Overbeek theory described that coacervation was a spontaneous process driven by electrostatic interaction and interpreted coacervation as competition between electrostatic forces which tended to accumulate charged macromolecules and entropy effects which tended to disperse them.[26] Veis[27] modified the Voorn-Overbeek theory and attempted to explain complex coacervation between two oppositely charged gelatins. The Veis theory is limited to systems of low charge density and coacervation is thought to be driven by the gain in configurational entropy resulting from the formation of randomly mixed coacervate phase. The Tainaka

theory developed from the Veis theory is more general than the other theories and is applicable to both high and low charge density systems.[29] This theory thought that coacervation was driven by attractive forces among aggregates, which increased with the molecular weights and charge densities of macromolecules, and considered that the aggregates possibly became neutral prior to coacervation but without specific ion pairing.

Relative to macromolecule coacervation, investigations on surfactant coacervation without macromolecules are much less. The main components of surfactant coacervation without macromolecules possess low molecular weights. Various surfactant systems generating coacervates have been reported. Although in principle coacervation can occur in other solvents, most of surfactant coacervations reported take place in water. Considering that surfactant coacervation is a liquid-liquid phase separation in surfactant systems, surfactant coacervation can be classified into three types. One type is clouding phenomenon or lower consolute behavior, that is phase separation upon heating for nonionic surfactants or certain zwitterionic and ionic surfactants at high concentration of inorganic and organic salts.[30-34] The main driving force for this kind of coacervation is the entropy of water release from the headgroups and alkyl chains of surfactants. Several excellent articles have reviewed the formation and applications of clouding phenomenon in surfactant systems.[35-37] The rest two types of surfactant coacervations are not risen upon the change of temperature. One of them usually takes place in mixtures of oppositely charged surfactants, and no droplets are observed but two liquid phases are formed upon quiescence.[38-40] This type of surfactant coacervation is normally called as an aqueous surfactant two-phase system (ASTP) instead of surfactant coacervation. Its main driving force is a combination of the entropy of counterion release and water release. In another situation, oily droplets are usually observed in phase separation and coacervate phase presents sponge-like structure. The term "coacervate" is also called as "L_3 phase", "anomalous phase", or "sponge phase". The last type of liquid-liquid phase separation in surfactant systems is the most characteristic surfactant coecervation and the term "surfactant coacervation" is most often used for it. Therefore, this review mainly summarizes the advances of the last type of surfactant coacervation over the past two decades, while the other two types of surfactant coacervations are only briefly introduced.

Early studies on surfactant coacervation were basically limited to the use of traditional monomeric surfactants and one-head and two-tail surfactants upon addition of different kinds of additives or oppositely charged surfactants. In recent years, along with the development of surfactants, novel surfactant coacervation has emerged and gemini surfactant coacervation becomes very attractive. In contrast to traditional surfactants, gemini surfactants can often generate coacervation by themselves without any additives. Thus, this review will include three sections: coacervation of single surfactants without additives; coacervation of surfactants with additives (alcohols, inorganic salts and organic salts); and coacervation of mixed surfactants. In each section, the studies on monomeric surfactants, one-head and two-tail surfactants, and gemini surfactants will be discussed. Main conclusions and brief prospective will be presented in the end. Although surfactant coacervation is a broad scope, the minireview is so limited. So we owe an apology for many contributors to the field whose works are not mentioned here.

2. Coacervation of single surfactants

Herein coacervation of single surfactants refers to the coacervation happening in a surfactant solution without the second component. Coacervation in aqueous solution is inherently associated with efficient dehydration in colloid self-assembly process. The dehydration extent of surfactants is dependent on their amphiphilic characteristic. Hydrophobic interaction among alkyl chains promotes intermolecular association of surfactants, enhancing the dehydration of surfactants. But polar and charged hydrophilic headgroups prefer to be hydrated at the interface of surfactant aggregates and water. Normally, surfactant coacervation should result from a combination of weak electrostatic repulsion among hydrophilic headgroups and strong hydrophobic attraction between alkyl chains, which leads to a condense aggregate as a consequence of efficient dehydration. However, if the dehydration is too strong, coacervation will be replaced by precipitation. A proper balance between dehydration and hydration is required to form coacervates.

2.1 Monomeric surfactants

Monomeric surfactants are most widely applied traditional surfactants. Each of them contains one hydrophilic moiety chemically attached to one hydrophobic alkyl chain. Monomeric surfactants can be subdivided into ionic, nonionic, and zwitterionic surfactants according to the charge properties of hydrophilic headgroups. Monomeric surfactant molecules usually aggregate into micelles when the concentration is above their critical micelle concentration. These micelles are homo-dispersed in aqueous solution stabilized by their surface charges and hydration shell. Thus normally a single monomeric surfactant cannot self-assemble into coacervates at room temperature.

Upon heating above a threshold temperature, aqueous solutions of nonionic or zwitterionic surfactant micelles exhibit clouding phenomena, forming two coexisting isotropic phases. The threshold temperature is termed as cloud point or lower consolute temperature, an important characteristic of nonionic or zwitterionic surfactants. Clouding phenomena are ascribed to efficient dehydration of hydrophilic portion of micelles at higher temperature. Early clouding phenomena were thought to be caused by micellar growth, micellar condensation, or the changes in the conformations of poly(oxyethylene) chain with an increase of temperature.[41-43] Another mechanism thought that the clouding phenomena are resulted from the formation of micelle clusters via an attractive inter-micellar interactions in nonionic micellar systems, which is enhanced with increasing temperature.[44] Recent evidences indicated that clouding phenomena can also be generated by the formation of connected micellar network or strongly orientation-dependent interactions between water and surfactants upon heating.[45] As described above, clouding phenomenon, by definition, falls into the category of surfactant coacervation. However, the term "clouding" is often used to name this kind of liquid-liquid phase separation instead of surfactant coacervation

2.2 Gemini surfactants

Gemini surfactants are made of two amphiphilic moieties connected by a spacer group at the level of the headgroups.[46-50] So far, most coacervations for single gemini surfactants reported took place in a series of zwitterionic gemini surfactants with different lengths of alkyl chains. The synthesis and characterization of these surfactants were performed by Menger group,[51-53] and their systematic works revealed that the formation of coacervates is mainly controlled by the length and symmetry of the two hydrophobic chains of the zwitterionic geminis. A "structural phase diagram" was constructed with the length values of the two hydrophobic chains (A and B) for 42 gemini surfactants at concentration of 5-50 mg/mL at 25 °C (Fig. 1a). Four main zones were identified as gels, micelles, coacervates, and vesicles. Coacervates form when the chain lengths are intermediate (8-12) and the two chains are identical or close to each other (e.g. A8B10, A10B10). For the surfactants with two alkyl chains of similar length, the shorter or longer chains (e.g. A8B8 or A14B16) lead to small micelles or vesicles. When the alkyl chains are quite dissymmetric (e.g. A18B8, A8B18), gels predominate with an interconnected network of vesicle-sized particles. Apparently the self-assembled aggregates are so sensitive to the chains that A8B10 and A10B8 form coacervates and micelles, respectively, only because the two chains exchange their locations. Remarkably, the images from cryogenic temperature high-resolution scanning electron microscopy (cryo-HRSEM) showed that the micron-sized spherical coacervate droplets in these systems exhibit a distinct sponge-like framework occupying the entire volume of the phase (Fig. 1b). This sponge-like structure is made of randomly connected bilayers, locally resembling the topology of a bicontinuous cubic phase, but displaying short-range order.[54-56] Moreover, the coacervate phase of surfactants, in equilibrium with a dilute surfactant phase, is enhanced by increasing the amount of surfactant but is insensitive to extra water. The two phases are in a thermodynamic equilibrium. In addition, the coacervate of the zwitterionic gemini surfactants shows salt tolerance because of their inner salt structure.

Thereafter, Menger group[57] further synthesized a family of branched-chain zwitterionic geminis with different carbon numbers of main alkyl chains (n = 9, 10, 18), and found that coacervation takes place in aqueous solution of the geminis with the intermediate main alkyl chain (n = 10) (Fig. 1c). Slightly decreasing the main hydrophobic chain length by only one ethylene (n = 9) suppresses coacervates and generates vesicles, while increasing n to 18 induces gels. Menger proposed that such sensitivity of zwitterionic gemini surfactant coacervation to the length and symmetry of the two hydrophobic chains can be understood in terms of the negative Gaussian curvature of the monolayers forming bilayers. The Gaussian curvature (H_0) of monolayers forming bilayers is defined by $H_0 = 1/R_0$, where R_0 is the spontaneous radius of curvature. When H_0 is close to zero, surfactants self-assemble into a lamellar structure. When H_0 is positive, surfactant monolayers show a curve to water, and the monolayers prefer to break into micelles. When H_0 is slightly negative, surfactant bilayers fuse with each other and transfer to a disordered sponge-like phase, i.e., coacervates (Fig. 1d). Hyde et al.[58] expressed if a negative Gaussian curvature is desirable for surfactant bilayer, the critical packing parameter of the surfactant should be larger than 1, which means that the hydrophobic domain of the surfactant must be bulky compared with its hydrophilic headgroups. This is a necessary requirement on molecular shape for surfactants to form coacervates. Dozens of the zwitterionic gemini surfactants can self-assemble into coacervates without variation of environmental conditions just because they meet the requirement of coacervation on molecular shape. In addition, for the zwitterionic gemini surfactants, the hydrophilic part probably adopts an alternating "(+–)(+–)(+–)" arrangement in the adsorbed monolayer of aggregates triggered by electrostatic attraction between oppositely charges. The efficient packing of hydrophilic parts endows the zwitterionic surfactants with the ability of self-assembling into bilayers. The two alkyl chains with intermediate or identical length yield proper hydrophobic interaction and flexibility in the bilayers which induce coacervates instead of micelles and vesicles.

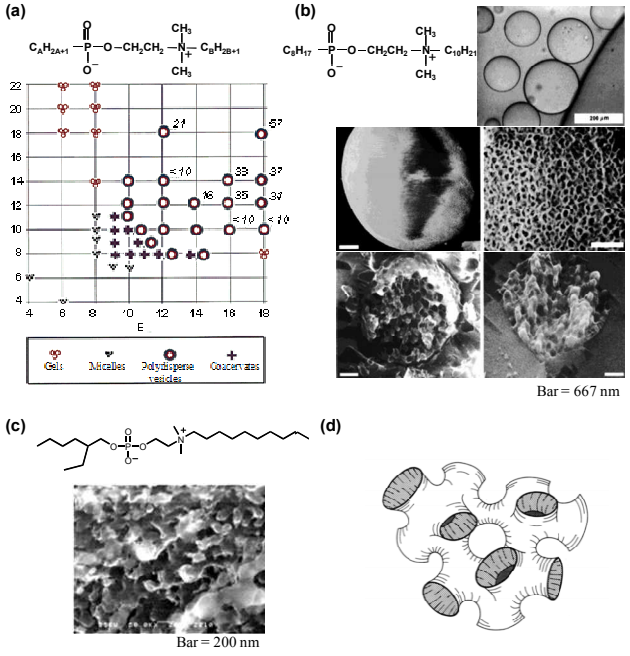

Fig. 1 Coacervation of zwitterionic gemini surfactants. (a) Structural phase diagram of 42 zwitterionic geminis; (b) light microscopy image (top) and cryo-HRSEM images (middle) of A8B10 coacervate droplets, cryo-HRSEM images of fractured A8B10 coacervate droplets (bottom); (c) cryo-HRSEM image of branched zwitterionic geminis; (d) proposed schematic illustrations of zwitterionic surfactant coacervates. Adapted from refs. 51, 53, 56 and 57. Copyright: American Chemical Society.

Besides zwitterionic surfactants, some nonionic gemini surfactants also exhibit coacervation phenomenon without increasing temperature. Whether nonionic gemini surfactants can form coacervates depends on the nature of hydrophilic headgroups. Imura et al.[59] reported an occurrence of simple coacervation in a single "natural" glycolipid biosurfactant, 4-*O*-(4′,6′-di-*O*-acetyl-2′,3′-di-*O*-alkanoyl-*β*-D-mannopyranosyl)-D-Erythritol (MEL-A), and found that the absence of 4′-O-acetyl group leads to a slight decrease in spontaneous curvature and induces a drastic aggregate transition from coacervates to vesicles (Fig. 2a).

Our group[60] reported that a pH-sensitive carboxylic gemini surfactant (SDUC) forms oily phase (coacervate) in aqueous solution at pH around 4.0, while forms vesicles at higher pH. The decreased electrostatic repulsion and increased hydrogen bond among the carboxylic groups of SDUC at lower pH are responsible for the coacervation from the fusion of vesicles. Therefore strong electrostatic repulsion between the headgroups of ionic gemini surfactants is against coacervation. However, Niu group[61] found that cationic gemini surfactants with diethylammonium headgroups and diamido spacers form vesicles at lower concentration, and the vesicles aggregate into coacervates with increasing concentration (Fig. 2b). Transmission electron micrographs (TEM) indicate that the coacervates exhibit both sponge and vesicle-like structures. The formation of coacervates is probably caused by the adhesion and fusion of vesicles at high concentration through hydrogen-bonding between the diamido spacers of the surfactants. Therefore, introducing additional weak attractive interactions such as hydrogen bond and π-π stacking can assist coacervation in single surfactant systems.

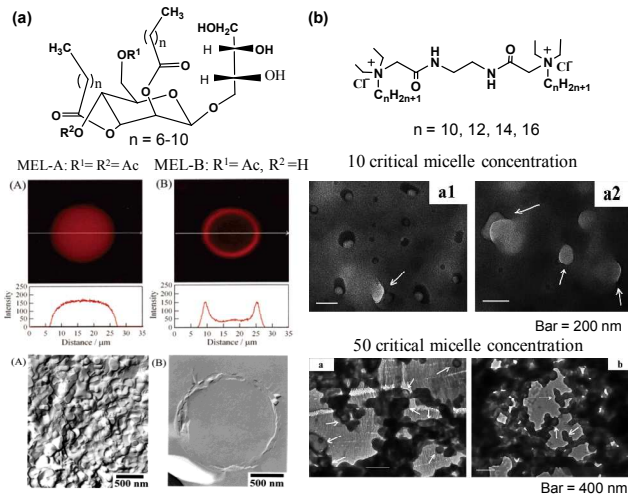

Fig. 2 Aggregate transition from vesicles to coacervates induced by variation of gemini surfactant structure and concentration. (a) Fluorescence intensity distributions (top) and freeze-fracture transmission electron micrographs (bottom) of colloidal dispersions formed from Mel-A and MEL-B, (b) TEM images of the gemini surfactants of aqueous solutions with 10 times (top) and 50 times (bottom) the critical micelle concentration. Adapted from refs. 59 and 61. Copyright: American Chemical Society.

As described above, the structure natures of hydrophobic chains and hydrophilic headgroups of surfactants are the key controlling factors to surfactant coacervation. Besides, the formation of single surfactant coacervation is also affected by counterions. Jaeger et al.[62] observed coacervation in a shamrock surfactant with iodide counterions $(CH_3)_3N^+(CH_2)_{12}N^+(CH_3)_2$-$(CH_2)_{12}N^+(CH_3)_3 3I^-$ rather than chloride counterions $(CH_3)_3N^+$-$(CH_2)_{12}N^+(CH_3)_2(CH_2)_{12}N^+(CH_3)_3 3Cl^-$. This was attributed that iodide ions bind more effectively than chloride ions to the cationic surfactant headgroups.

3. Coacervation of surfactants with additives

Although some single surfactants can generate coacervation, the prevalent cases of surfactant coacervation are with the aid of additives. Inorganic salts, alcohols and organic salts are the most often used additives to help the formation of coacervates.

3.1 Coacervation of surfactants with inorganic salts

3.1.1 Monomeric surfactants

Surfactant coacervation with inorganic salts was first observed in mixtures of a long chain cationic surfactant Hyamine 1622 with different kinds of monovalent or polyvalent inorganic salts .[63-65] It was found that the surfactant coacervation depends on the concentration, hydrated radii, and valency of salts. There is a critical salt concentration above which coacervation can occur, while below which the surfactant solution is homogeneous. The critical salt concentrations in a 3% Hyamine 1622 solution were found to be 0.027 M for KSCN, 0.059 M for $KClO_3$, 0.064 M for NaBr, 0.067 M for $NaNO_3$, 0.320 M for NaCl, 0.079 M for $Cu(NO_3)_2$, and 0.430 M for $CuCl_2$. The binding of salts with ionic surfactants induces growth and fusion of surfactant aggregates through screening electrostatic repulsion between the ionic headgroups of the surfactant. A small increment of salts induces tremendous growth of micelles before coacervation. As reported, above the critical salt concentration, the homogeneous solution of Hyamine 1622 separates into two liquid phases over a wide range of concentration. The volume of coacervate phase decreases with increasing the concentration of salts and is proportional to $A + B/C^{1/2} + D/C^{3/2}$, where A, B and D are constants and C is the concentration of added salts. At very high salt concentrations of several moles, the surfactant colloidal species start to precipitate instead of coacervate.

Surfactant coacervations show a characteristic specificity to the counterions of added salts. The cationic Hyamine 1622 systems described above are sensitive to anions, while surfactant coacervations of anionic soap systems including alkali oleates, stearates and palmitates[11] are sensitive to cations. The effectiveness of surfactant coacervation follows a Hofmeister series or lyotropic series for monovalent counterions and is enhanced with an increase of the valency.[66] The stronger the binding of counterions to ionic surfactants, the more effective the shielding of the electrostatic repulsion among the ionic headgroups, and then coacervation is more preferred.

3.1.2 One-head and two-tail surfactants

The microstructures of coacervates and the aggregates prior to coacervation are associative with the nature of surfactants. For one-head and two-tail negatively charged surfactant Aerosol OT (AOT) reported by Menger et al.,[67] AOT in aqueous solution self-assembles into vesicles and the vesicles transit into coacervates by introducing alkali metals (Li^+, Na^+, K^+, Rb^+, Cs^+). Although the AOT coacervate was previously observed by Acharya et al.,[68] Menger did more thorough work on the system. The coacervate was rationalized in terms of positive-to-negative changes in the spontaneous mean curvature (H_0) of the AOT bilayers, which was caused by decreased electrostatic repulsion among the AOT headgroups. The critical parameters of the AOT coacervation in the presence of the alkali metal salts were determined. At a fixed salt concentration, the coacervate volume increases linearly with the AOT concentration. Moreover, the coacervate phase contains

high content of water but is immiscible with the dilute aqueous phase. It was found that a coacervate of 0.2 M AOT and 0.3 M NaCl in water is immiscible with 0.3 M NaCl in water. This is attributed to the enthalpic requirements for breaking up three dimensional sponge-like AOT structure of coacervates. Similar microstructure of surfactant aggregates prior to coacervates was also observed by Giokas group.[2] Polymerized vesicle coacervates were achieved in a cationic ammonium one-head and two-tail bromide surfactant (4-carboxybenzyl)bis[2-(10-undecenoy-loxy)ethyl]methylammonium bromide by UV excitation in a wide range of potassium chlorate levels.

3.2 Coacervation of surfactants with alcohols.

3.2.1 Monomeric surfactants

Surfactant coacervates induced by alcohols are commonly L_3 or sponge phase, and are directly related to their concentration and molar ratio. Alcohols in surfactant coacervation were usually pentanol or hexanol. When alcohols were added to surfactant solutions, coacervation has been found in nonionic surfactants,[69] zwitterionic surfactants,[70] and ionic surfactants with excess salt.[71,72] In surfactant/alcohol/water ternary phase diagrams, the two-phase region is usually observed on either side of L_3 phase: L_3/L_α (lamellar phase) region and L_3/L_1 (isotropic phase) region. In Fig. 3, Hoffmann et al.[70] mapped out the phase diagrams of the ternary system, zwitterionic surfactant tetradecyldimethylamine oxide C_{14}DMAO, heptanol and water. The two-phase $L_3/L_{\alpha h}$ region is defined between the L_3 phase and the lamellar $L_{\alpha h}$ phase, and covers a large surfactant and alcohol concentration range but only over an extremely narrow alcohol/surfactant ratio. The freeze fracture transmission electron images (FF-TEM) of L_3 phase showed sponge-like structure with more or less a network of ordered curved bilayers.

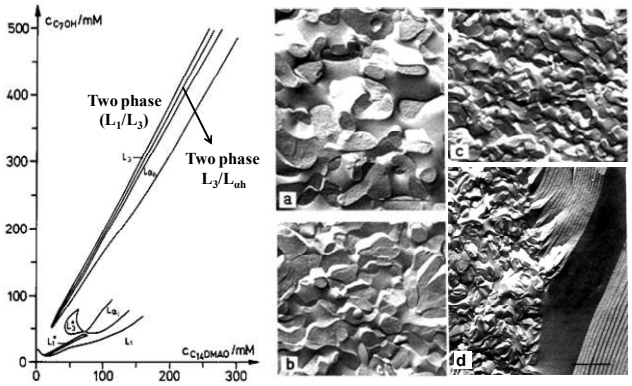

Fig. 3 Phase diagram of C_{14}DMAO/heptanol/water at 25 °C (left); FF-TEM images of L_3 phase at different C_{14}DMAO/heptanol concentrations (right): (a) 50 mM/110 mM, (b) 70 mM/135 mM, (c) 100 mM/185 mM, and (d) 70 mM/135 mM in which L_α phase exists. Adapted from ref. 70. Copyright: American Chemical Society.

The formation of coacervate phase (L_3) is dependent on the alkyl chain length of alcohols. A previous work of Hoffmann et al.[73] demonstrated the higher homologue alcohols than hexanol cannot cause L_3 phase. In a chapter about L_3 phase, Hoffmann et al,[74], pointed out that L_3 phase is very sensitive to ionic charges, and it becomes unstable when a few percent of neutral surfactants are replaced by ionic surfactants in surfactant/alcohol systems. For most ionic surfactant/alcohol systems, L_3 phase may form when the headgroup charges of surfactant molecules are sufficiently shielded by excess salt. For examples, Strey et al.[71] observed L_3 phase in a ternary system of cetylpyridinium chloride/hexanol/NaCl in water. Hoffmann et al.[72] found L_3 phase in the system of calcium dodecyl sulfate CDS/alcohol in water where CDS behaves like a nonionic or double-chain surfactant because the binding of calcium ions with dodecyl sulfate ions.

Compared with the hydrocarbon alcohols above, perfluorinated alcohols are much more effective in inducing surfactant coacervation. Khaledi et al.[75] showed that a small percentage of a perfluorinated alcohol induces coacervation in aqueous media for a broad range of surfactants with diverse molecular structures and compositions (Table 1).

Table 1 Perfluoro-Alcohol/Acid Induced Surfactant Coacervation Systems. TFE: trifluoroethanol; HFIP: hexafluoroisopropanol; TFA: trifluoroacetic acid; PFPA: pentafluoropropionic acid; HFBA: heptafluorobutyric acid. Adapted from ref. [75]. Copyright 2013 American Chemical Society.

Table 1A Complex perfluoro-Alcohol/Acid Induced Coacrvates

Group	Anionic amphiphile	Cationic surfactant	Coacervator
1	Sodium alkane sulfates: SDS, SHS, SOS, DBSA	DTAB, CTAB, OTAB	TFE, HFIP, TFA, PFPA, HFBA
2	Phospholipids: DPPG	DTAB, CTAB	HFIP
3	Bile acid salts: SC, SDC	DTAB, CTAB	TFE, HFIP, TFA,
4	Perfluorinated surfactant: PFOA	CTAB	HFIP

Table 1B Simple perfluoro-Alcohol Induced Coacrvates

5	Zwitterionic surfactant: DMMAPS	TFE, HFIP
6	Zwitterionic phospholipid: DPPC	HFIP
7	Anionic phospholipid: DPPG	HFIP
8	Cationic surfactants: DTAB, CTAB	HFIP
9	Anionic surfactants: SDS + HCl	HFIP
10	Nonionic surfactants: Triton X-100, Triton X-114	HFIP

3.2.2 One-head and two-tail surfactants

Phospholipid is a typical one-head and two-tail surfactant. If alcohols are used as its solvent while water or electrolyte solutions are used as its poor solvent, mixing phospholipid/alcohol solutions with water can yield coacervation. Ishii et al.[76,77] pointed out it is important to simple coacervation of phospholipid that solvent and nonsolvent are mutually miscible. Batzri et al.[78] applied coacervation to prepare single-bilayer liposomes by injecting an ethanolic solution of phospholipid into water. Ishii et al.[77] investigated effects of alcohols (methanol, ethanol, and 1-propanol) and salts (sodium chloride and calcium

chloride) on simple coacervation in the system of phospholipid/alcohol/water, and found that phospholipid forms coacervates when ethanol is used as a solvent, but forms a transparent highly viscous gel when methanol or 1-propanol is used instead. Moreover, a larger volume of water phase is required to induce the phospholipid coacervation with 1-propanol in comparison with methanol or ethanol.

3.3 Coacervation of surfactants with organic salts

Unlike inorganic salts or alcohols, organic salts simultaneously display electrostatic and hydrophobic interactions with oppositely charged surfactants. The occurrence of coacervation in surfactant/organic salt systems not only depends on the nature of hydrophobic groups of organic salts but also relies on the geometry of organic salts.

3.3.1 Monomeric surfactants

Jiang et al.[79] studied the phase behaviors of aqueous mixtures of dodecyltrimethylammonium bromide (DTAB) with a series of sodium oligoarene sulphonates (POSn) where n is the number of charges on the sulphonate, and observed coacervates with green fluorescence in the mixtures of DTAB with POS4 or POS6 at charge neutralization point (Fig. 4). The coacervates are suppressed when POS4 or POS6 are replaced by less charged POS2 or POS3. The surface tension and small angle neutron scattering results indicated that POS4 and POS6 show the feature of polyelectrolytes while interacting with DTAB. The formation of coacervates can be understood in terms of the construction of zwitterionic oligomeric surfactant analogues through electrostatic and hydrophobic interaction between DTAB and the oligomeric salts. When mixing DTAB with other dyes including tartrazine, amaranth, carmosine, or erthrosine, coacervation also takes place.[80]

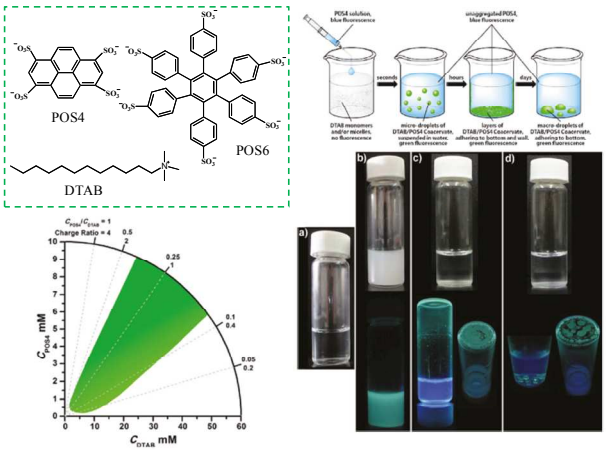

Fig. 4 Phase separation (right) and phase diagram (left) in aqueous mixtures of DTAB and sodium oligoarene sulphonates POS4 at room temperature. Adapted from ref. 79. Copyright: American Chemical Society.

Bendito et al.[81] reported that tetrabutylammonium ions (Bu_4N^+) lead to surfactant coacervation in vesicular solutions of ionic surfactants alkanoic (alkyl = octyl, decyl, dodecyl, and tetradecyl) and oleic acids. These alkyl carboxylic acids form vesicles at pH near their apparent pK_a where the deprotonated/protonated species are at stoichiometric molar ratio. With increasing the Bu_4N^+ concentration, the vesicles form coacervates and the coacervation region is very wide (carboxylic acid/Bu_4N^+ molar ratio from 0.3 to 10). In the coacervation, Bu_4N^+ accelerates the suspensions of alkyl carboxylic acid/carboxylate mixtures due to its salting-in feature. Electrostatic attraction and hydrogen bonds are established in addition to hydrophobic interaction in the hydrocarbon region. Particularly, one or two butyl groups of each Bu_4N^+ may stretch outside the polar shell of the alkyl carboxylic acid vesicles because of the steric restriction, while the rest butyl groups of Bu_4N^+ may connect with the butyl groups of other Bu_4N^+ molecules in the same or different vesicles. The continuous cross-linking among the Bu_4N^+ molecules bridges the vesicles. As the Bu_4N^+ concentration increases, more and more vesicles are connected, finally leading to the occurrence of coacervation. Similar to Bu_4N^+, cationic organic salt benzyltriphenylphosphonium chloride with four benzene rings at a very low concentration of 1 mM can also induce coacervation in 0.1-0.5 mM sodium dodecyl sulfate (SDS) aqueous solution.[82] In addition to the interactions mentioned above, in this system π-π interaction plays an important role of connecting different surfactant aggregates in coacervation.

Considering practical applications of surfactant coacervation in food and life science, biocompatible bile salts have been widely used.[83-87] Almgren et al.[83] reported the phase behavior of cetytrimethylammonium bromide (CTAB) with bile salt sodium desoxycholate (NaDOC), and found that a coacervation region (Fig. 5a) exists in the L_1 phase (micelle phase) opposed to the Lα (lamellar phase) phase in the dilute surfactant area. The area of two L_1-type fluid phases is elongated and almost symmetrically located near the equimolar ratio of the two oppositely charged compounds. The charged neutralized coacervates are proved to be built up by a three-dimensional network of interwoven tread-like aggregates. The interwoven tread-like microstructure instead of sponge structure is probably resulted from the rigid steroid skeleton of NaDOC. The polar face of NaDOC is oriented toward bulk solution, but its nonpolar face is placed toward the micelle core, and the NaDOC molecules incorporate in the CTAB aggregates and force the headgroups of CTAB apart. This situation favors the formation of highly curved aggregates. Replacing CTAB by other alkyltrimethylammonium bromides (C_{18}TAB, C_{14}ATB, and C_{12}TAB), the aggregation and phase separation of the mixtures with NaDOC display similar situations.

Panda et al.[86] investigated the effect of the nature of bile salts on the phase behavior of alkyltrimethylammonium bromides (C_nTAB) with different alkyl chain length (n = 12, 14, 16). All the C_nTAB/sodium cholate (NaC) mixtures only form clear isotropic phase, while all the C_nTAB/NaDOC mixtures can form coacervates. Among them, the mixtures of C_nTAB (n = 14, 16) with NaDOC exhibit a transition from rodlike micelles to coacervates, but the C_{12}TAB/NaDOC mixture does not form rodlike micelles before coacervation. The different phase behavior of C_nTAB with NaC and NaDOC can be understood from the location of bile salts at micelle/water interface where NaC with one more hydroxyl group is much closer to the bulk solution.

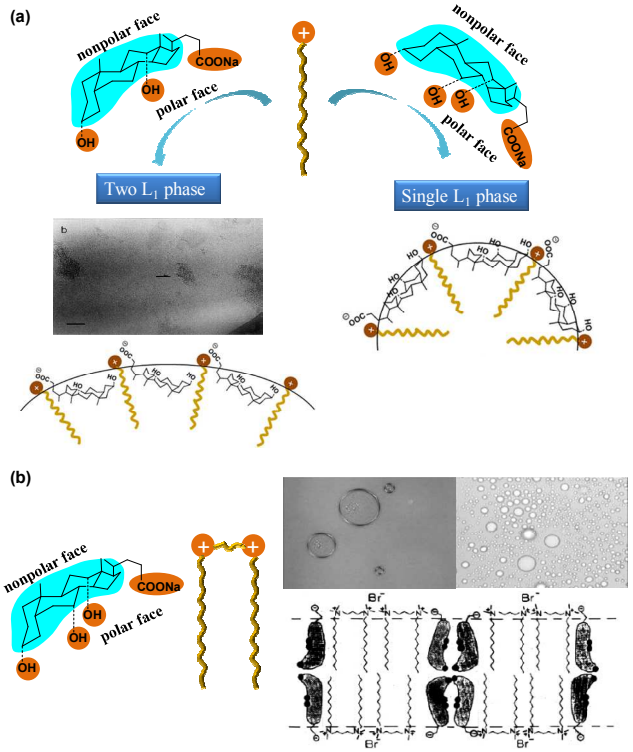

Fig. 5 Illustrations of effects of surfactant and bile salt structure on coacervation. (a) Two L_1 phases for C_nTAB/NaDOC mixtures and the coacervates show interwoven tread-like structure; single L_1 phase for C_nTAB/NaC mixtures. (b) L_α phase and coacervates of $C_{12}C_6C_{12}Br_2$/NaC mixtures. (a) Adapted from refs. 83 and 86. Copyright: Elsevier. (b) Adapted from ref. 88. Copyright: Taylor & Francis LLC.

3.3.2 Gemini surfactants

Gemini surfactants possess much stronger ability to form coacervates due to the dimeric amphiphilic structure. The investigation on the phase behavior of cationic gemini surfactant hexamethylene 1,6-bis(dodecyldimethylammonium bromide) ($C_{12}C_6C_{12}Br_2$) with bile salt sodium cholate (NaC) in dilute solution[88] indicated that coacervate phase coexists with L_α or crystal phase in the equivalent mixture (Fig. 5b). The NaC molecules inserted in the surfactant aggregates were demonstrated to exist as dimers through hydrogen bond among the three hydroxyl groups. Compared with monomeric surfactant, the coacervation in the mixture of gemini surfactant with NaC is probably promoted by stronger electrostatic and hydrophobic interactions in the NaC dimers and the dimeric structures of gemini surfactants. However, the coacervates cannot be separated from lamellas and crystals in the whole concentration range studied.

Our groups[89] achieved separate coacervate phase through the interaction of the same cationic ammonium gemini surfactant with sodium benzoate (NaBz) in aqueous solution. The formation of coacervates was found to mainly depend on the NaBz and $C_{12}C_6C_{12}Br_2$ concentrations and their molar ratio (Fig. 6). A critical NaBz concentration of at least 0.10 M is required to form coacervates. The amount of $C_{12}C_6C_{12}Br_2$ required for coacervates is very small and covered a very wide concentration region. The phase boundaries of coacervation shift to higher $C_{12}C_6C_{12}Br_2$ concentration with increasing NaBz concentration. The Cryo-TEM and SEM results showed that the precursors of coacervation are long, dense and almost uncharged threadlike micelles, and the coacervates are a three-dimensional layer-layer stacking network structure formed by the assembly of threadlike micelles. The formation of coacervates can be rationalized from the variations of the electrostatic and hydrophobic interactions of $C_{12}C_6C_{12}Br_2$ with NaBz and the resultant aggregate changes upon the increase of the $C_{12}C_6C_{12}Br_2$ concentration. The enhanced electrostatic and hydrophobic interactions between NaBz and $C_{12}C_6C_{12}Br_2$ bring about the micellar growth from small spherical to threadlike, and finally the interlacing of threadlike micelles leads to the three-dimensional dense network, that is coacervate.

By changing the hydrophilic part of organic salt, our group[90] constructed another coacervation system in which a pH-sensitive *N*-benzoylglutamic acid (H_2Bzglu) and $C_{12}C_6C_{12}Br_2$ were used. Besides the H_2Bzglu and $C_{12}C_6C_{12}Br_2$ concentrations and their molar ratio, pH significantly impacts the formation of coacervates. The coacervates are formed when the H_2Bzglu species with one negative charge are dominated. A lower critical H_2Bzglu concentration of 0.03 M was required to form coacervates than that for NaBz. Herein H_2Bzglu molecules not only display electrostatic and hydrophobic interactions with $C_{12}C_6C_{12}Br_2$ like NaBz, but also have hydrogen bonds between their carboxylic acids. The hydrogen bonds lead to the formation of H_2Bzglu oligomers. The double chains of $C_{12}C_6C_{12}Br_2$ and the H_2Bzglu oligomers play the roles of connecting aggregates through multiple binding sites. These factors endow the mixture with a very high efficiency in generating coacervation.

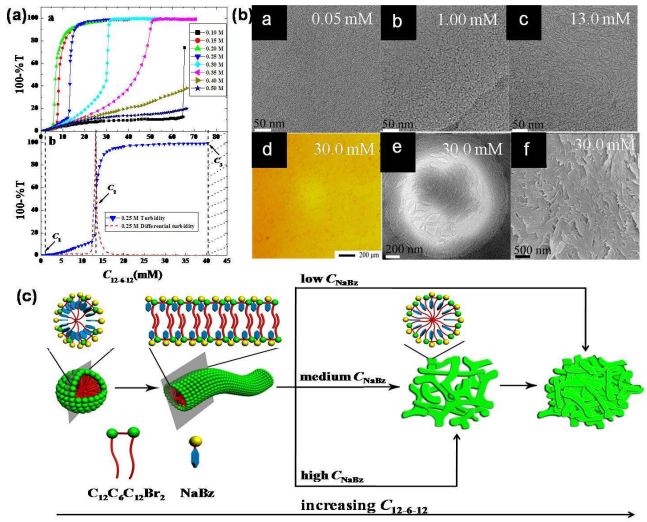

Fig. 6 (a) Determination of coacervation region with turbitidy by titrating $C_{12}C_6C_{12}Br_2$ solution into NaBz solutions of different concentrations; (b) Cryo-TEM images (a, b, c, e), light microscopy image (d), SEM image (f) of the aggregates at different $C_{12}C_6C_{12}Br_2$ concentrations and 0.25 M NaBz; (c) Proposed schematic illustrations of the variations of the aggregate morphologies. Adapted from ref. 89. Copyright: The Royal Society of Chemistry.

4. Coacervation of mixed surfactants

Aqueous mixtures of oppositely charged surfactants have been widely employed to fabricate coacervates because of their strong electrostatic and hydrophobic interactions. As pointed out by Filipović-Vinceković[91] and Panda et al.,[92] coacervates in catanionic surfactant mixtures are normally generated at charge neutralization point in the transition region from precipitates to micelles. Dey et al.[93] proved that the coacervates are 1:1 complexes in the mixture of sodium N-lauroylsarcosinate (SLS) and N-cetylpyridinium chloride (CPC). The surfactants were thought to form ion pairs in the coacervates. In each ion pair, two non-covalently attached alkyl chains are connected to a common pair of headgroups bound through electrostatic interaction. The structure of the surfactant ion-pairs is similar to that of zwitterionic gemini surfactants.

The coacervate structures of mixed surfactants are significantly affected by the compositions of mixtures. Schulz et al.[94,95] found that the dilute aqueous mixture of sodium 10-undecenoate (SUD)–DTAB has different precursors of coacervation in the opposite sides of the two-phase region. Rod-like micelles agglomerate into bundles in the DTAB-rich side of the region, while globular micelles agglomerate into clusters in the SUD-rich side.

However, when coacervation takes place in many cases of oppositely charged surfactants, no droplets were observed, but two liquid phases were observed upon quiescence. The surfactants are usually richer in one phase than in another phase, but both phases are dilute. The two phases are formed by different kinds of aggregates. This type of coacervation is commonly termed as an aqueous surfactant two-phase system (ASTP) as described in the introduction. The formation of ASTP in catanionic surfactant systems is strongly dependent on surfactant aggregates. On the basis of the aggregate structures formed in surfactant-rich phase, ASTP can be separately induced by entanglement of rod-like micelles, formation of lamellar phase, or dense packing of vesicles.[38-40,96-100] Kaler et al.[96] observed the entanglement of rod-like micelles in surfactant-rich phase in catanonic mixtures of CTAB and sodium octyl sulfate (SOS). Huang et al.[97] reported the microstructures of ASTP in the mixtures of dodecyl-pyridinium chloride (DPCl)/sodium laurate (SL) and DTAB/SL. The FF-TEM images proved that the upper and bottom phases are dense and sparse vesicles, respectively. Moreover Huang's group[98] investigated the effects of surfactant concentration, temperature, salt concentration and additives (octanol, toluene) on ASTP in DTAB/SL. They found that the addition of salt, octanol and toluene induces the phase separation whereas increasing the temperature inhibits the phase separation. Furthermore, Huang et al.[99] studied the ASTP behavior in an aqueous mixture of cationic gemini surfactant hexamethylene 1,6-bis(dodecyldiethylammonium bromide) ($C_{12}C_6C_{12}Br_2$(Et)) with SL, and revealed that the surfactant aggregates in the upper and bottom phases are lamellar structure and vesicles, respectively, and the aggregate structures are influenced by temperature and shearing. Similarly, lamellar structure was also observed by Hao et al.[40] in the upper phase of the ASTP systems consisting of SL with tetradecyltrimethylammonium bromide (TTAB) or tetradecyltrimethylammonium hydroxide (TTAOH).

5. Conclusions and perspectives

This short review summarizes the development of coacervation occurring in single surfactants, surfactants with inorganic salts, alcohols or organic salts, and surfactant mixtures. The involved surfactants include monomeric surfactants, one-head and two-tail surfactants, and gemini surfactants. The effects of surfactant molecular structures and external conditions on critical conditions for coacervation, structures of precursors and coacervates, and their relationships have been described. Surfactant coacervation requires that surfactant aggregates are close to electrically neutrality prior to coacervation. Surfactant coacervation can be controlled by charge density, alkyl chain length and number, concentration of surfactants, and mixing molar ratio of surfactants to additives or oppositely charged surfactants. Surfactant coacervation can be induced by the entanglement of wormlike micelles, the cross-linkage of vesicles, the fusion of bilayers, and so on. Surfactant coacervates exhibit sponge structure in most of cases.

Even though a larger number of surfactant coacervation have been studied over the past few decades, further development of more efficient surfactant coacervation is expected because of enormous practical needs in drug encapsulation, cosmetics, detergents, protein separation and so on. On the basis of the conclusions from literatures, introducing a larger number of intermolecular interaction types and sites will greatly improve the ability of surfactants to generate coacervation at lower concentration and with fewer components. Therefore, with the development of surfactants, gemini surfactants and the extended oligomeric surfactants provide tremendous potential for coacervation because of their structural diversity and more interacting groups. So far the reports on coacervation of gemini and oligomeric surfactants are still quite scarce. Thus the coacervations produced by these novel surfactants deserve to be explored in the future. Searching more efficient and functional organic additives to induce surfactant coacervation is another fascinating aspect in this field. Endowing additives with functions (such as drug and pigments) and multi-interacting sites will expand the applications and reduce the cost of surfactant coacervation.

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Notes and references

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