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Recent Advances in Catanionic Mixtures

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Abstract

Most surfactant mixtures display synergistic physicochemical properties, which have led to their extensive application in various technologies. Aqueous mixtures of two oppositely charged surfactants, so-called catanionic surfactant mixtures, exhibit the strongest synergistic effect, which is manifested as high surface activity, enhanced adsorption and a low critical aggregation concentration. In addition, catanionic systems display rich phase behavior and a range of nano and microstructures, including small spherical micelles, rod-like micelles as well as open and closed bilayers (vesicles). The spontaneous formation of catanionic vesicles is of special interest due to their various applications in nanotechnology and pharmaceutical formulations. In this chapter, the properties of catanionic mixtures of amphiphilic molecules with advantageous properties are discussed. Since numerous papers dealing with catanionic mixtures of monomeric surfactants already exist, the aim of this chapter is to summarize recent progress in mixtures of structurally different surfactants. At the end of the chapter, special emphasis is placed on applications of catanionic mixtures.

Keywords: surfactants, catanionic mixtures, vesicles, phase behavior, application

1. Introduction

Due to their amphiphilic structure, surfactants exhibit unique physicochemical properties both in solutions and in solid state. Mixtures of two or more different surfactants often show improved properties compared to individual surfactant solutions. As a result, in household and industrial applications, surfactant mixtures are usually used [1, 2]. Aqueous mixtures of two oppositely charged surfactants, that is, catanionic surfactant mixtures, exhibit the strongest synergistic effect, which is manifested as high surface activity, enhanced adsorption and

low critical aggregation concentration [3–7]. In addition, catanionic mixtures display rich phase behavior governed by electrostatic and hydrophobic interactions, steric effects (geometric packing constraints) and hydrogen bonding. Therefore, such systems offer numerous possibilities in controlling molecular self-assembly by adjusting bulk properties and using appropriate surfactant molecules. Consequently, they are of special interest not only from fundamental point of view but also because of a wide range of industrial applications.

In this chapter, catanionic mixtures of amphiphilic molecules with advantageous properties are discussed. Since numerous papers dealing with catanionic mixtures of monomeric surfactants already exist, the aim of this chapter is to summarize recent year's progress in mixtures of structurally different surfactants. At the end of the chapter, special emphasis is placed on applications of catanionic mixtures. It should be pointed out that the field of catanionic mixtures investigation is vast and still expanding, so the present review can be neither fully comprehensive nor final.

2. Properties of catanionic mixtures

Catanionic mixtures can be prepared by mixing a cationic surfactant with an anionic one. Because two oppositely charged surfactants are present in the mixture, catanionic mixtures possess unique features, which can be summarized as follows [2–8]:

(1) strong electrostatic attractions between oppositely charged headgroups and ion pairing (**Figure 1**),

(2) pronounced synergism and solution behavior that considerably deviate from ideal mixing, that is, interfacial and aggregation properties of such systems are enhanced compared to those of single surfactants,

(3) strong dependence of the physicochemical properties, as well as the phase behavior, on the molar ratio and total concentration of the components,

(4) rich phase behavior and structural diversity where the size of aggregates ranges from the nano to micrometer scale (mixed micelles, vesicles, tubules, liquid crystalline phases, etc.),

(5) spontaneous formation of stable vesicles, including, in some cases, equilibrium vesicles and

(6) precipitation of catanionic surfactant (CA) at/or near equimolar bulk composition:

$$CX + YA \rightarrow CA + X^- + Y^+ \tag{1}$$

where CX and YA represent cationic and anionic surfactant, and X^- and Y^+ represent respective counterions.

Due to strong electrostatic attractions, addition of ionic surfactant to the solution of other, oppositely charged surfactants results in formation of tight ion pairs and removal of hydration water at the mixed aggregate/solution interface [8]. Thus, oppositely charged surfactant monomers form ion pairs, which can be described as pseudo double-tailed zwitterionic surfactants (**Figure 1**) [6].
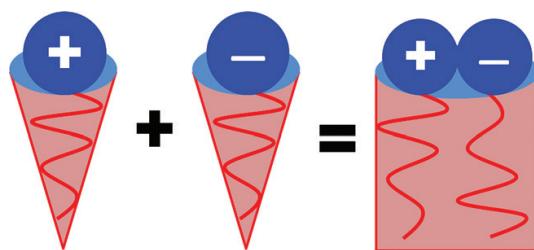
Figure 1. A schematic representation of ion pair formation in catanionic mixtures.

The formation of ion pairs has pronounced influence on the adsorption properties and self-assembly of catanionic mixtures. Unlike the solution of individual monomeric surfactants, in catanionic mixtures aggregates with minimal curvature, such as open and closed bilayers (vesicles), are spontaneously formed even at the low surfactant concentrations. For that reason, experimental investigations of dilute catanionic mixtures have made a key contribution to our understanding of the factors governing vesicle formation in surfactant systems [8, 9].

Spontaneous formation of stable vesicles in these systems can be explained by using packing parameter (P), which is defined with three nominal geometric parameters of surfactant molecules:

$$P = \frac{v_{hc}}{a_0 l_{hc}} \tag{2}$$

where a_0, v_{hc} and l_{hc} are the surface area per headgroup, the volume and fully extended length of the hydrophobic tail of the molecule, respectively [10]. The molecular shape and respective P will determine the type of preferred surfactants' aggregate: for $P = 0.33$, spherical micelles; for $P \approx 0.33$–0.5, cylindrical micelles; for $P \approx 0.5$–1, bilayer disks and vesicles; for cylinders (**Figure 1**) with $P \approx 1$ planar bilayers; and for $P > 1$, reverse structures. In other words, from the aspect of geometric constraints, the preferred structure of surfactant's aggregates, for a given hydrophobic tail size, strongly depends on the effective headgroup area. In general, the a_0 value depends on two opposite forces: (1) attractive hydrophobic interactions between hydrocarbon chains at the hydrocarbon-water interface and (2) repulsive electrostatic and/or steric interactions [8]. In the case of catanionic ion pairs, the effective headgroup area decreases, compared to the value of each of the surfactants individually, while the volume of the hydrophobic chain increases. As a result, the value of packing parameter approaches unity, which favors structures with low curvature like vesicles and flexible bilayers [10].

However, for better explanation of spontaneous vesicles' formation in catanionic mixtures, in addition to geometric parameters, the curvature free energy and its dependence on bilayer's composition should also be taken into account. In order for bilayer to have non-zero spontaneous curvature, its two individual leaflets should have equal and opposite spontaneous curvature (**Figure 2**). This is possible only when two leaflets have different compositions. Moreover, the composition should be such that average headgroup area in the outer leaflet is larger than the one in the inner. In catanionic mixtures, this is achieved by having higher molar ratio of the excess surfactant in the outer leaflet, resulting in larger headgroup spacing due to the electrostatic repulsions. In the inner leaflet, the higher fraction of paired surfactants reduces the headgroup area and results in positive curvature [5]. Therefore, spontaneously
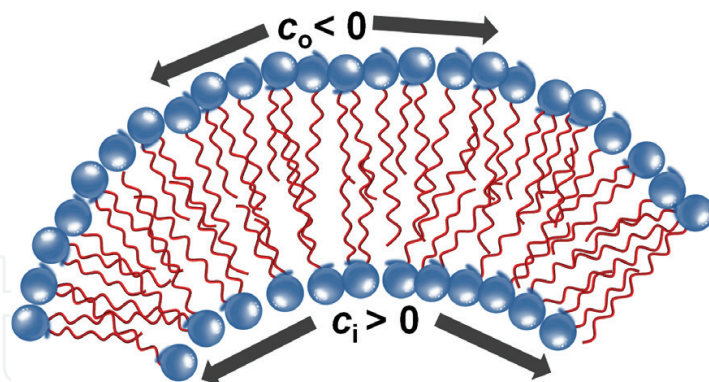
Figure 2. A schematic representation of catanionic bilayer with equal and opposite curvature of inner (c_i) and outer (c_o) leaflet (after [5]).

formed catanionic vesicles owe their stability to the non-ideal mixing of oppositely charged surfactants as well as to electrostatic effects.

The spontaneous formation of catanionic vesicles is of special interest due to their various applications in nanotechnology and pharmaceutical formulation, as will be discussed later in this chapter. Regarding the vesicle stability, different theoretical models have tried to rationalize why vesicles behave as true equilibrium aggregates rather than a dispersed form of a lamellar liquid crystal [11–13]. However, what is important for application purposes is that vesicles do readily form in catanionic mixtures and they appear to pose long-term stability. In addition, the low-cost and versatile physicochemical properties make them a good alternative to phospholipid vesicles, that is, liposomes [5].

A typical phase diagram for catanionic mixtures is schematically illustrated in **Figure 3**. However, there are numerous variations in the appearance of the catanionic phase diagram. The concentration regions in which vesicles form are represented by the lobes on both sides of the equimolar line. This indicates that vesicles are stabilized by the presence of excess surfactants. Catanionic vesicles usually have high degree of polydispersity, and their stability can be tailored by the choice of surfactant molecular structure, that is branched surfactants, and/ or those containing a bulky group in alkyl tail usually form more stable vesicles [6]. Likewise, in asymmetric surfactant mixtures, in terms of different alkyl chain numbers or length as well as different chain morphology, the vesicle phase is often considerably enlarged and found in a broad concentration range [14–16]. The size, surface charge density and permeability of catanionic vesicles can be tailored by varying temperature, concentration and molar ratio, as well as chain length of surfactants [17].

As the molar mixing ratio of the two surfactants or the total surfactant concentration is varied, different phase transitions involving vesicles are found: micelle-to-vesicle, vesicle-to-lamellar and vesicle-to-solid phase transitions (**Figure 3**). At the highest excess of the mixture components, mixed micelles of various sizes and shapes can be found, including globular, elongated (worm-like) and branched ones [7]. The size and shape of mixed micelles depend on bulk composition and total surfactant concentration as well as geometry of the surfactants, temperature, salt content, etc. In surfactant mixtures, micelle-to-vesicle transition has been broadly found to occur through two pathways [18]. One path involves limited micellar growth and
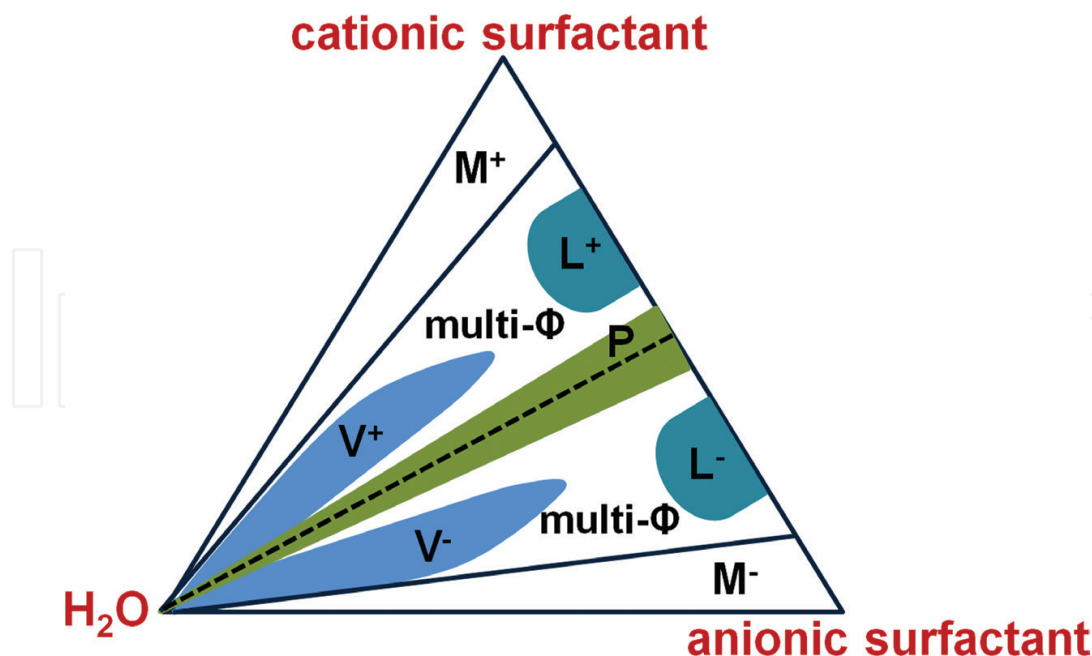
Figure 3. A schematic triangular phase diagram of symmetric catanionic mixture at constant temperature and pressure. The dashed line denotes the equimolar line dividing the diagram into the cationic-rich and the anionic-rich region. Close to the charge neutrality line, a solid precipitate (*P*) is usually formed, but excess charge in the system usually leads to vesicle stabilization (denoted as V⁺ and V⁻). Mixed micelles (denoted as M⁺ and M⁻) are usually formed at the highest excess of the mixture components. Multiphase regions (multi-Φ) often involve a lamellar phase occurring at higher concentrations (denoted as L⁺ and L⁻) (after [9]).

micelle/vesicle coexistence and is more common for systems with symmetric chain lengths [19]. Examples are dodecyltrimethylammonium bromide (C_{12}TAB)/sodium dodecyl sulfate (SDS) (**Figures 4** and **5**) [20], didodecyldimethylammonium bromide (DDAB, **Figure 6**)/SDS [21] mixtures and a few others involving amino acid-based surfactants [22, 23]. The second path involves strong micellar growth and is typical of highly asymmetric systems [19].
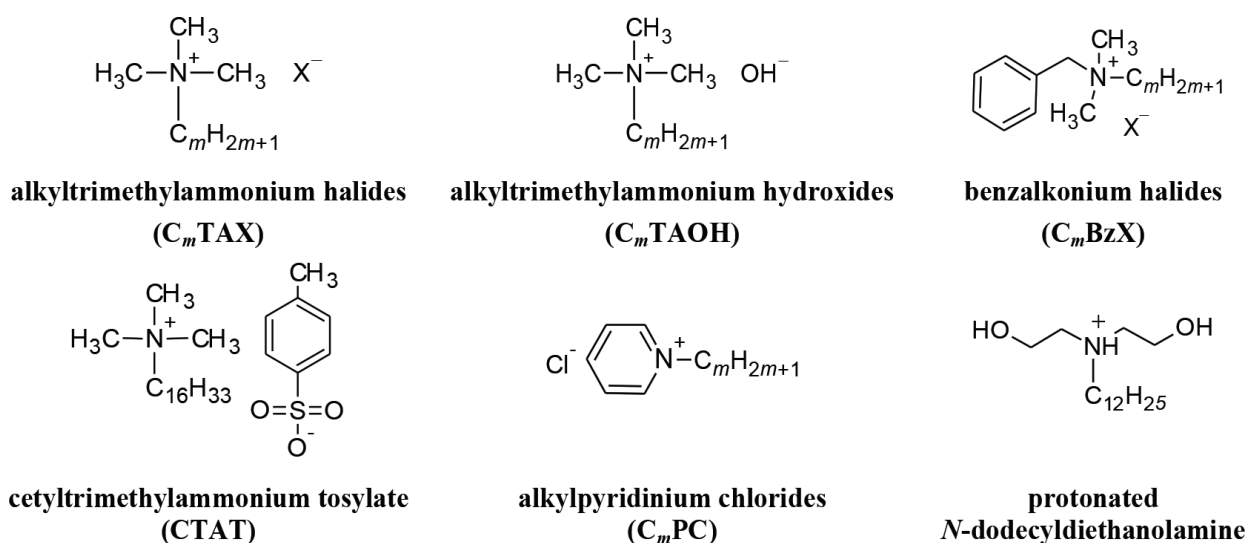

Figure 4. Molecular structures of monomeric cationic surfactants—quaternary alkyl ammonium salts. *m* = number of C atoms in alkyl chains and *s* = number of C atoms in spacer.
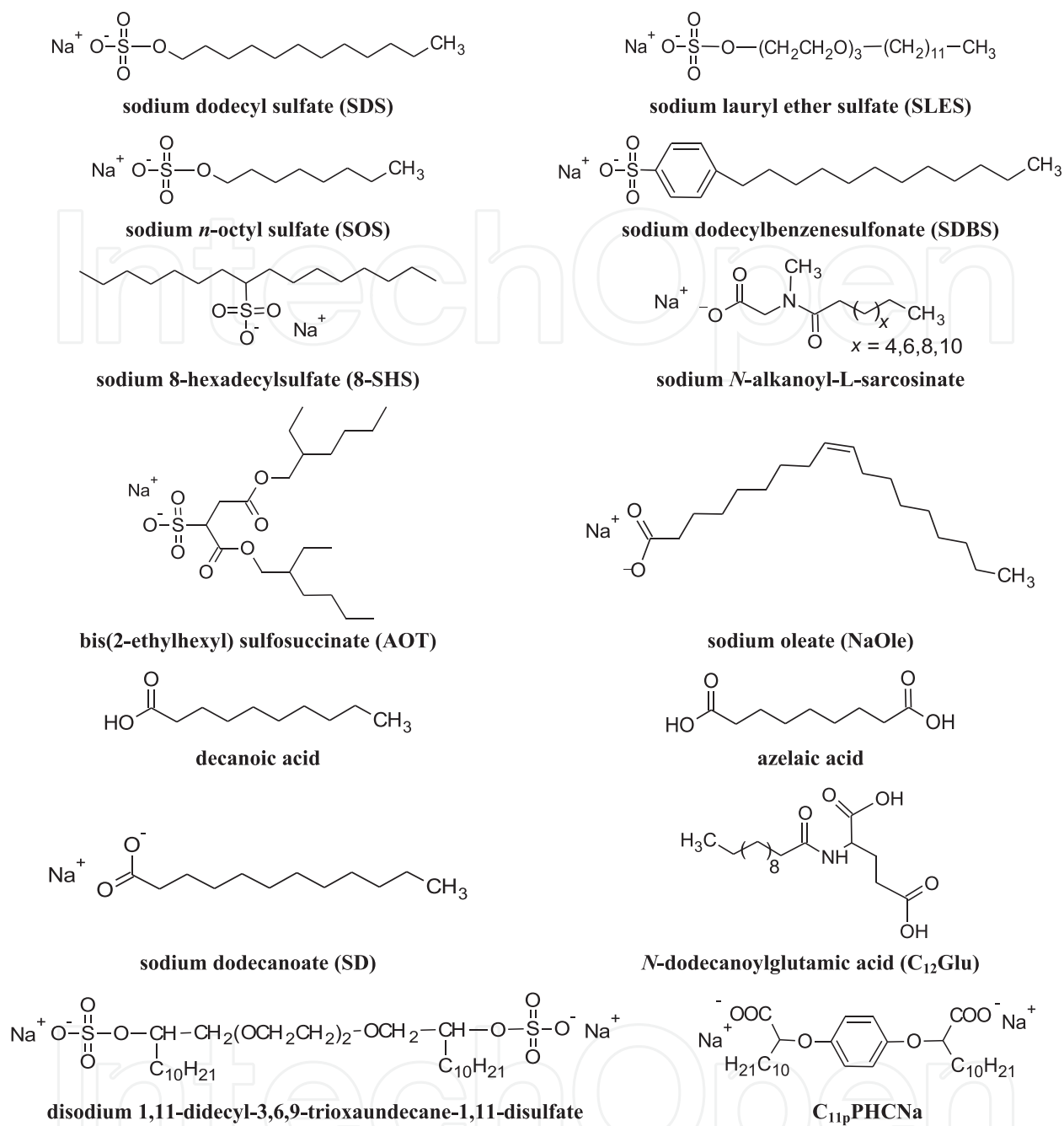
Figure 5. Molecular structures of various anionic amphiphiles.

In the majority of catanionic mixtures at equimolar concentrations precipitate, a new catanionic surfactant, which very often possesses lamellar structure, forms [2, 18]. It can form as only phase or in coexistence with (1) coacervates (small droplets in solution rich with surfactants) [6, 24] as well as (2) micelles or (3) lamellar phase, usually in asymmetric mixtures [14, 16, 22–28]. Formed precipitate can be redissolved by increasing concentration of one of the surfactants, leading to formation of micelles or vesicles. Although catanionic precipitate is generally found only near equimolar compositions or in samples below their Krafft temperature, it is
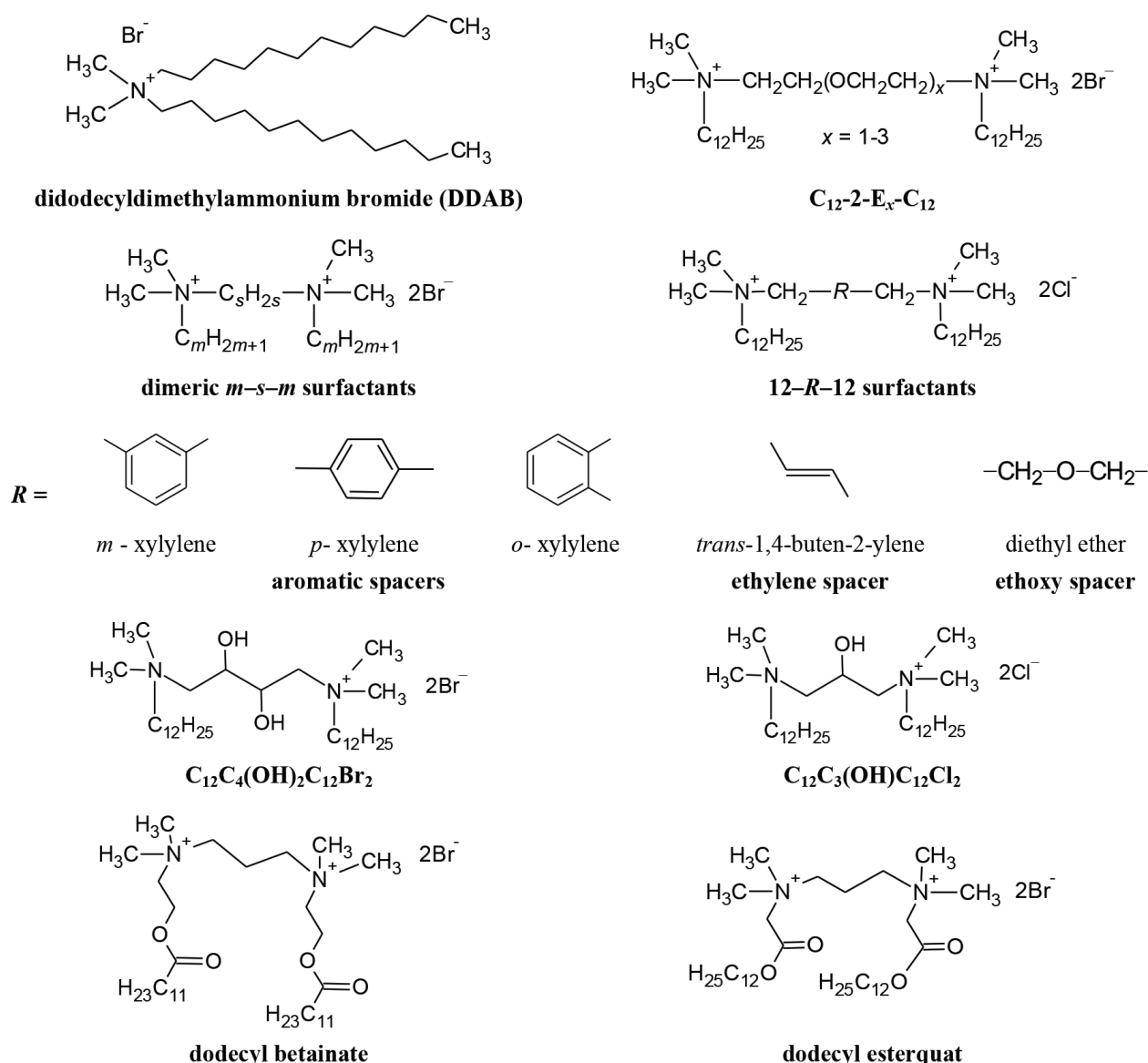
Figure 6. Molecular structures of double-tailed and dimeric cationic surfactants—quaternary alkyl ammonium salts. m = number of C atoms in alkyl chains and s = number of C atoms in spacer.

considered to be the main drawback for application of catanionic mixtures [3]. However, with the right selection of mixtures components, precipitation can be circumvented. Increased asymmetry in hydrophobic parts of surfactant molecules (different tail length or number, branched tails, rigid ring-based structures, etc.) weakens hydrophobic attractions among alkyl chains and prevents efficient packing into a crystalline lattice [14–16, 29]. As a result, precipitation does not occur and instead large micelles, vesicles or liquid crystalline phases can be formed.

Numerous studies showed that catanionic mixtures are characterized with solution behavior that considerably deviates from ideal mixing as well as pronounced synergism (high surface activity, enhanced adsorption, low critical micellization concentration (cmc), etc.) compared

to other types of surfactant mixtures [1, 3–7]. For example, the cmc values in catanionic mixtures can be several orders of magnitude lower than the ones of single surfactants. It is not surprising considering that molecular interactions between cationic and anionic surfactants are generally dominated by the attractive electrostatic forces. Additionally, driving force for the mixed aggregates formation is large increase in entropy, which is a consequence of counterion release from both surfactants. On the contrary, in the case of single surfactant aggregate, the entropy decreases due to the condensation of counterions [2].

Synergism in catanionic mixtures can be quantitatively described using the regular solution theory (RST), which provides a thermodynamical approach to non-ideal mixing [1, 30–32]. Although frequently criticized on fundamental grounds, the RST still remains a helpful tool for description of the behavior of catanionic mixtures.

According to the RST and the standard state surface tension method, the mixed monolayer composition and the mixed monolayer interaction parameter can be calculated [1, 30–32]. The molar fraction of the cationic surfactant in the mixed monolayer (X_1) can be calculated according to the following equation:

$$\frac{X_1^2 \ln\left(\alpha_1 c_{1,2} / c_1 X_1\right)}{\left(1 - X_1\right)^2 \ln\left[\left(1 - \alpha_1\right) c_{1,2} / \left(1 - X_1\right) c_2\right]} = 1 \qquad (3)$$

where c_1, c_2 and $c_{1,2}$ are the molar concentrations in the solution phase of surfactant 1, surfactant 2 and their mixture, respectively, at the mole fraction α_1 of surfactant 1, required to produce a given surface tension (γ) value (see [31]).

The iterative solution of Eq. (3) gives X_1. The molecular interaction parameter in the mixed monolayer (β_{mon}) can be calculated according to the following equation:

$$\beta_{mon} = \frac{\ln\left(\alpha_1 c_{1,2} / c_1 X_1\right)}{\left(1 - X_1\right)^2} \qquad (4)$$

According to the RST, the deviation of experimentally obtained mixed micelle cmc value ($cmc_{1,2}$), from that calculated by assuming ideal mixing, can be represented by the molecular interaction parameter in the mixed micelle (β_{mic}). The molar fraction of the cationic surfactant in the mixed micelles (x_1) and β_{mic}, can be calculated according the following equations:

$$\frac{x_1^2 \ln\left(\alpha_1 cmc_{1,2} / cmc_1 x_1\right)}{\left(1 - x_1\right)^2 \ln\left[\left(1 - \alpha_1\right) cmc_{1,2} / \left(1 - x_1\right) cmc_2\right]} = 1 \qquad (5)$$

$$\beta_{mic} = \frac{\ln\left(\alpha_1 cmc_{1,2} / cmc_1 x_1\right)}{\left(1 - x_1\right)^2} \qquad (6)$$

where cmc_1, cmc_2 and $cmc_{1,2}$ are the critical micelle concentrations of surfactant 1, surfactant 2 and their mixture, respectively, at the mole fraction α_1 [31].

The β parameters measure attractive net interaction between different surfactants relative to the self-interaction of the two surfactants under the same conditions before mixing. In other words, the β parameters describe the extent of non-ideal mixing. When parameter β is negative, the interaction is attractive; however, when it is positive, the interaction between two different surfactants is repulsive. To obtain valid β parameters, several conditions must be met as pointed out by Zhou and Rosen [31].

By applying the RST, additional parameters can be calculated for catanionic systems, such as activity coefficients and free energy of mixing, but for the sake of brevity, only the main principles of the theory are mentioned. A detailed discussion of the RST is far beyond the scope of this chapter.

3. Phase behavior and physicochemical properties of catanionic mixtures containing structurally different surfactants

3.1. Catanionic mixtures of oligomeric and monomeric surfactants

Surfactants, which have attracted considerable interest in last three decades, are oligomeric surfactants. These compounds are made up of two (dimeric or gemini surfactants) or more (higher oligomeric surfactants) amphiphilic moieties covalently linked at the level of the headgroups, or very close to them, by a spacer group (**Figure 7**) [33, 34]. Large interest for the investigation and synthesis of oligomeric surfactants is a consequence of their superior properties in comparison to the conventional ones [33, 34]:

(1) their cmcs are one or two orders of magnitude lower than for the corresponding monomeric surfactants,

(2) they are more efficient in lowering surface tension,

(3) their aqueous solution can have a very high viscosity or even show viscoelastic properties at relatively low surfactant concentrations, whereas the solutions of corresponding monomers remain low viscous as water,

(4) also, they have better solubilizing, wetting and foaming properties and

(5) the increase of the number of alkyl chains within oligomeric series, that is, the degree of oligomerization, enhances the above characteristics although the changes are becoming less significant with increase of degree of oligomerization above (2) [33, 34].

Due to their enhanced properties, catanionic mixtures containing various dimeric surfactants have been subject of numerous papers [25, 35–46]. The most investigated are catanionic mixtures containing bis-quaternary ammonium salts with the alkyl spacers. This type of surfactants is usually denoted as m–s–m where m represents the number of carbon atoms in the hydrophobic chain and s is the number of carbon atoms in the spacer (**Figure 6**). The great
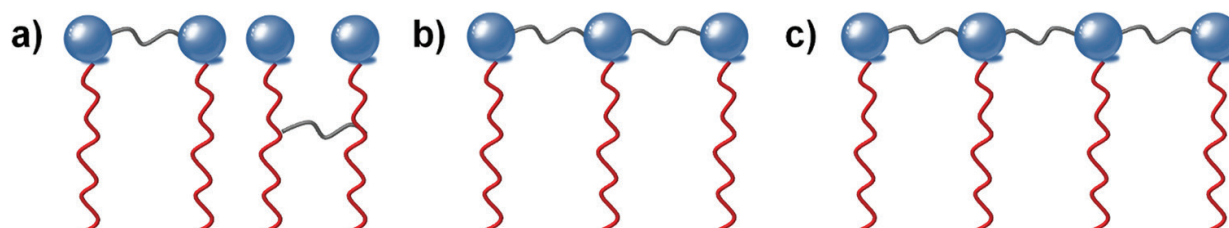

Figure 7. Schematic representations of (a) dimeric, (b) trimeric and (c) tetrameric surfactant molecule.

advantages of *m–s–m* surfactants are relative ease of their synthesis and possibility to tailor surfactant properties by changing spacer and chain length. Despite numerous papers dealing with catanionic mixtures containing dimeric surfactants, very few provide complete picture of the systems phase behavior.

Shang et al. determined the phase diagram for aqueous mixtures of 12–3–12 and SDS using freeze etching and negative staining on transmission electron microscope (TEM) [25]. Constructed phase diagram shows different phase regions in the majority of which coexistence of vesicles and micelles was found. As expected, the ratio of vesicles to micelles in diluted mixtures varies with bulk composition and total surfactant concentration. At higher surfactant concentrations, 12–3–12/SDS mixtures displayed very rich phase behavior, that is, regions of anisotropic phase, aqueous two-phase system (ATPS) as well as rod-like micelles and cylindrical clusters were detected. In order to corroborate experimental results, the authors used dissipative particle dynamics simulations. It was found that due to the finite size of the simulation box, results were somewhat different from that obtained by experiments [25].

Our group employed a variety of techniques: imaging by various microscopy techniques (light microscopy, confocal laser scanning microscopy (CLSM) and TEM) as well as dynamic (DLS) and electrophoretic light scattering (ELS) to determine phase diagram for 12–2–12/SDS system at the water-rich corner [35]. It was found that depending on bulk composition and total surfactant concentration in 12–2–12/SDS mixtures, various mixed nano and microaggregates form. The sequence of phases in the clear region in the SDS-rich side of the phase diagram is vesicles → the narrow coexistence region of vesicles and mixed micelles at the cmc_{SDS} → small mixed micelles. On the other hand, in the clear region in the 12–2–12-rich side, the sequence of phases is fragments of planar bilayers/lamellar sheets and vesicles → worm-like mixed micelles → transformation from worm-like to small mixed micelles above the $cmc_{12-2-12}$. In the precipitation region, two types of aggregates were detected, the tubules as prevailing aggregates on the 12–2–12-rich side and vesicles as prevailing aggregates on the SDS-rich side. The formation of tubules was ascribed to mutual influence of (1) specific molecular structure of 12–2–12 surfactant and (2) electrostatic interactions at the catanionic bilayer/solution interface. The microscopic observations indicated that tubular structures grow from rolled-up stacked catanionic bilayers [35].

Cheon et al. studied phase behavior in a very similar catanionic system, 12–2–12/sodium lauryl ether sulfate (SLES, **Figure 5**) by means of differential scanning calorimetry (DSC), UV-VIS spectroscopy, DLS, ELS and TEM [36]. These mixtures display less complex phase behavior compared to the 12–2–12/SDS system. In the phase diagram, isotropic molecular solution region, region of mixed micelles and vesicles formation as well as region of their coexistence were detected. Spontaneous vesicles formation has been attributed to electrostatic attractions and geometric packing constraints, that is formation of ion pair with "cuplike" structure that favors bilayer formation [36].

The phase behavior of 12–10–12/SDS system in diluted SDS-rich region using Langmuir trough, isothermal titration microcalorimetry (ITC), cryo-TEM and conductivity measurements has

been investigated by Bai et al. [37]. The phase diagram shows three regions with a single type of aggregate (spherical and non-spherical micelles and vesicles), separated by two regions where two types of aggregates coexist (spherical/non-spherical micelles and non-spherical micelles/vesicles) and finally one multiphase region. Authors have concluded that observed phase transitions are consequences of asymmetric and uneven distributions of oppositely charged surfactants in vesicles' bilayers and non-spherical micelles, respectively [37].

Wang et al. determined phase diagram for 12–6–12/SDS system at the water-rich corner by employing turbidity measurements, ITC and TEM [38]. At constant total surfactant concentration, as the molar fraction of SDS increased, the morphology of mixed aggregates gradually changed from 12–6–12-rich micelles, through multiphase regions containing a precipitate (catanionic surfactant) and vesicle region, to SDS-rich micelles. Both TEM and ITC allowed identification of stable vesicles' region in the SDS-rich side of the phase diagram. Authors have argued that spontaneously formed vesicles in investigated mixture are consequences of (1) non-ideal mixing of cationic and anionic surfactant in bilayers as well as (2) a mechanism which involves an entropic stabilization in cases where the spontaneous curvature is not favorable but the bending penalty is not too high (soft bilayers) [38].

The same group of authors investigated monolayers formed in mixtures of m–2–m (m = 12, 14, 16 and 18) surfactants with SDS using the Langmuir trough technique [39], as well as micellization in mixtures of 12–s–12 (s = 2, 6 and 10) with several common anionic surfactants (SDS, sodium taurodeoxycholate (NaTDC, **Figure 8**) and sodium dodecanoate (SD, **Figure 5**)) by conductivity [40].

In m–2–m/SDS systems, it was found, from pressure-area, pressure-temperature and compression-expansion curves, that all the equivalent mixtures form highly stable monolayers with rich phase behavior and different desorption mechanisms [39]. Furthermore, it was established that if excess of cationic dimeric surfactants is present in 12–2–12/SDS and 14–2–14/SDS mixtures, the molecules in excess desorb from the monolayer so that the electroneutral composition of adsorbed film is maintained.

Results obtained by conductivity method revealed that all investigated systems containing 12–s–12 dimers and anionic surfactants show synergistic effects and have negative values of the molecular interaction parameter [40]. For the mixtures with 12–2–12, the strength of interaction increases in the order SD > SDS > NaTDC, while for 12–6–12, the order was SD ≈ SDS > NaTDC. Additionally, for the same anionic surfactant, the interaction with 12–2–12 is always stronger than that with 12–6–12. It is known that short spacers (s < 10) tend to lie flat at the water-hydrocarbon interface, which can lead to unfavorable packing constraints at the mixed micelles. Since 12–2–12 has a shorter spacer than 12–6–12, the packing constraints are slightly weaker and, together with a higher charge density of the headgroup region, lead to more favorable attractive interactions with anionic surfactants. Results reported for mixtures with 12–10–12 suggest that a catanionic solid is largely stabilized compared to mixed micelles when the alkyl spacer is long and flexible enough [40].

Aggregation behavior in mixtures of cationic dimeric surfactants derived from dodecyltri-methylammonium chloride (C_{12}TACl, **Figure 4**) and SDS by means of small-angle neutron
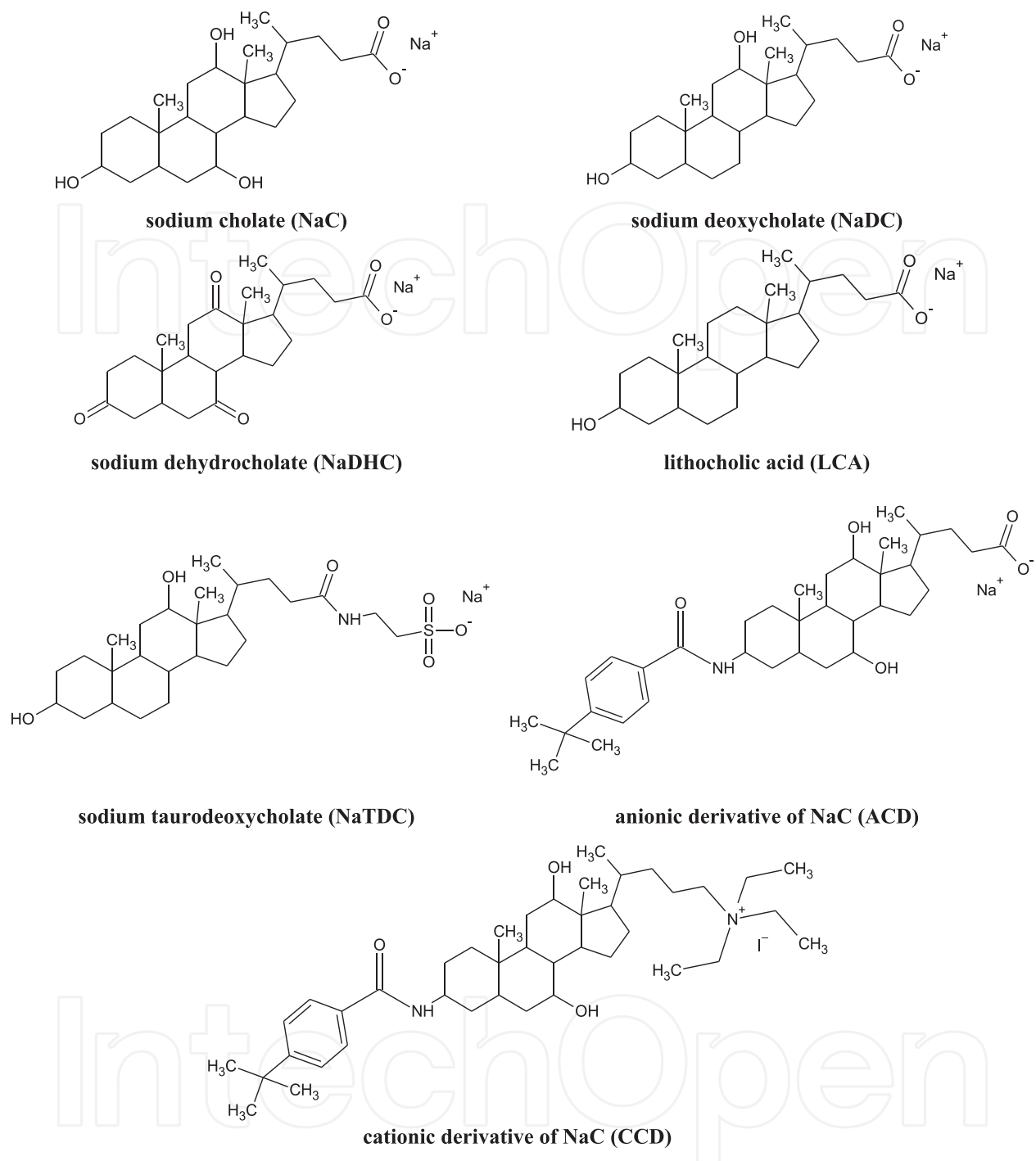
Figure 8. Molecular structures of bile salts.

scattering (SANS) and small-angle X-ray scattering (SAXS) was investigated by Prévost et al. [41]. Dimeric surfactants with spacers of different nature and geometry were used: *m*-, *p*- and *o*-xylylene (aromatic spacer), diethyl ether (ethoxy spacer) and trans-1,4-buten-2-ylene (ethylene spacer) (**Figure 6**). Authors concluded that among five spacers, due to their weak geometrical constraints and the ambivalent, hydrophilic and non-extensive lipophobic nature, ethoxy spacer is the most suitable for formation of vesicles in aqueous mixtures. On the contrary, the aromatic

spacers with their low flexibility and higher apolarity, compared to ethoxy spacer, generally led to precipitation in investigated mixtures. Furthermore, it was established that all mentioned dimeric surfactants form colloidally more stable mixtures with SDS than their monomeric counterpart $C_{12}TACl$ [41].

Ji et al. studied temperature induced phase transitions in aqueous mixtures of cationic dimeric surfactant, 1,4-bis(dodecyl-N,N-dimethylammonium bromide)-2,3-butane-diol ($C_{12}C_4(OH)_2C_{12}Br_2$, **Figure 6**), and anionic amino acid surfactant, N-dodecanoylglutamic acid ($C_{12}Glu$, **Figure 5**) at pH = 10.0 [42]. At 25 °C small spherical micelles, vesicles and entangled worm-like micelles were detected in the system. The main controlling factor for the aggregates transition at constant total surfactant concentration and varying molar ratio is strong electrostatic binding between oppositely charged surfactants which significantly reduces the headgroup area. Because both $C_{12}C_4(OH)_2C_{12}Br_2$ and $C_{12}Glu$ carry two charges, strong electrostatic interactions in these mixtures are not surprising. At higher temperatures, mixed aggregates formed at 25 °C experience different transitions, that is, the following phase transitions occur: (1) small spherical micelles → large vesicles, (2) large vesicles → solid spherical aggregates → larger irregular aggregates and (3) entangled worm-like micelles → branched worm-like micelles. The larger irregular aggregates and branched micelles ultimately lead to precipitation and clouding phenomenon, respectively. All described transitions are thermally reversible and transition temperatures can be tuned by varying the molar ratio and/or the total surfactant concentration [42].

Aghdastinat et al. investigated self-assembly in cation-rich mixtures of ester-containing cationic dimeric surfactants, named dodecyl esterquat and dodecyl betainate (**Figure 6**), with SDS in the presence of salt, KCl [43]. Obtained results show that the position of ester bonds in surfactants' tail plays an important role in physicochemical properties and aggregation behavior in their mixtures with SDS. After mixing with SDS morphology of dodecyl esterquat, aggregates change from cubic nanoparticles (cubosomes) to cylindrical nanoparticles which coexist with cubosomes. On the contrary, upon mixing with SDS, no significant structural change can be observed in dodecyl betainate aggregates, that is, vesicles are formed in both cases. Authors explained observed changes in morphology of mixed aggregates using RST [43].

Investigation of higher oligomeric surfactants and their mixtures is hindered by the more complex synthesis and purification compared to the dimeric molecules [33, 34]. Very few reports can be found on mixtures containing trimeric or tetrameric quaternary ammonium surfactants [47–49].

Chen et al. studied self-assembly in mixtures of trimeric cationic surfactants, tri-(N-dodecyldimethylhydroxypropylammonium chloride) phosphate (PTA, **Figure 9**) and double-tailed anionic surfactant, bis(2-ethylhexyl) sulfosuccinate (AOT, **Figure 5**) by means of DLS and TEM [47]. Obtained results demonstrated that PTA/AOT vesicles are stable and can be found in a broad concentration range. The TEM micrographs revealed that at high surfactant concentrations, tubular microstructures, vesicle fusion and vesicle-tubular microstructure transition occurred. In addition, it was found that formation of tubular structures is more pronounced in aged samples. Authors have discussed the mechanism of vesicles and tubules formation from the viewpoint of molecular geometry and electrostatic interaction between oppositely charged surfactants [47].
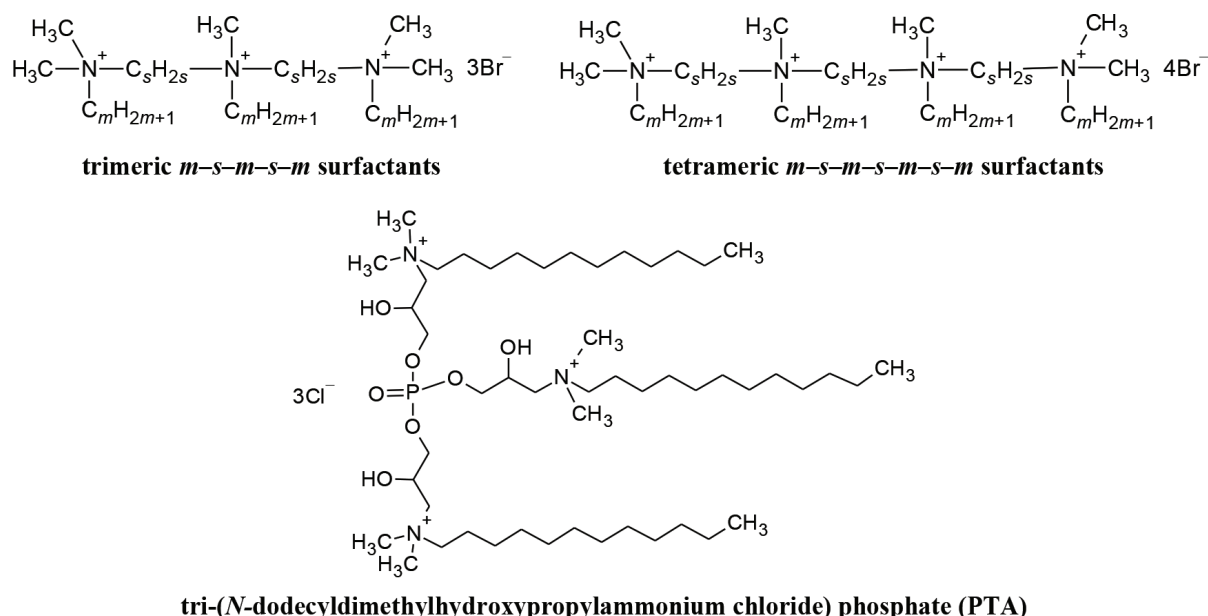
Figure 9. Molecular structures of higher oligomeric surfactants—quaternary alkyl ammonium salts. m = number of C atoms in alkyl chains and s = number of C atoms in spacer.

Yoshimura et al. investigated mixtures of trimeric cationic surfactants, m–2–m–2–m (m = 8, 10 and 12, **Figure 9**), and sodium n-octyl sulfate (SOS, **Figure 5**), employing several techniques such as static surface tension, fluorescence spectroscopy and DLS [48]. As expected, m–2–m–2–m/SOS mixtures show stronger micellization ability and lower cmc values compared with pure trimeric surfactants. In addition, the chain length of trimeric surfactants significantly influenced mixtures' properties at the air/water interface and in the solution. For example, m–2–m–2–m/SOS mixtures show a linear decrease in the cmc values with increasing alkyl chain length. Furthermore, the 8–2–8–2–8/SOS system exhibited a smaller surface area occupied by a surfactant molecule (a_{min}) compared to 10–2–10–2–10/SOS and 12–2–12–2–12/SOS mixtures [48].

Our group studied a series of quaternary ammonium bromide oligomers (from dimer to tetramer, **Figures 6** and **9**) with dodecyl chains connected at the level of headgroups by a short ethylene spacer and their mixtures with SDS [49]. In high excess of SDS (cationic surfactant: SDS = 1:9), negatively charged vesicles form in all mixtures regardless of the number of dodecyl chains in cationic surfactant. Contrary to vesicles, the mixed monolayer is enriched with cationic surfactant. Moreover, the increase in the number of dodecyl chains decreases the molar fraction of SDS in the mixed monolayer. Observed results can be explained by strong electrostatic headgroup interactions modulated by packing constraints imposed by the geometry of oligomeric surfactants [49].

Since anionic dimeric surfactants attract much less attention than cationic, there are only few reports describing catanionic mixtures containing dimeric surfactants as anionic components [44–46]. Back in 1996, Zana et al. investigated mixtures of disodium1,11-didecyl-3,6,9-trioxaundecane-1, 11-disulfate (**Figure 5**) and C_{16}TAB, in the presence of NaBr, employing conductivity, spectrofluorometry, time-resolved fluorescence quenching and cryo-TEM [44]. Obtained results proved that the aggregation numbers of the mixed micelles are larger than

those of pure $C_{16}TAB$ micelles even at very low molar ratio of dimeric surfactants. Apart from micelles, TEM micrographs revealed the presence of vesicles and very large aggregates which looked like distorted multi-bilayered vesicles with many defects [44].

Luo et al. and Zhao et al. studied interactions in catanionic mixtures containing anionic dimeric surfactant: O,O-bis(sodium 2-lauricate)-*p*-benzenediol ($C_{11p}PHCNa$, **Figure 5**) [45, 46]. It was found that large spherical aggregates form in $C_{12}TAB/C_{11p}PHCNa$ mixtures and transform into branched and worm-like micelles with increasing NaBr concentration. In addition, authors established that due to the changes in morphology of mixed aggregates, viscosity of the $C_{12}TAB/C_{11p}PHCNa$ mixtures gradually increases. Furthermore, it was reported that adsorption behavior in mixtures of two dimeric surfactants, $C_{11p}PHCNa$ and (oligoona) alkanediyl-α,ω-bis(dimethyldodecylammonium bromide) (C_{12}-2-E_x-C_{12}, **Figure 6**), strongly depends on the molar ratio, that is, strong adsorption at the air/water interface is present in excess of cationic surfactant while in excess of anionic surfactant premicellization occurs.

In addition to properties which can be found in traditional catanionic systems, common features that can be drawn for catanionic mixtures of oligomeric and monomeric surfactants are:

(1) both physicochemical properties and phase behavior strongly depend on the length of the spacer (*s*) and alkyl chains (*m*) as well as the nature of the spacer (aromatic, hydrophilic, hydrophobic, etc.) in the oligomeric molecule,

(2) in general, all mixtures exhibit a strong synergistic effect which is manifested as high surface activity, enhanced adsorption and low cmc values but usually to a lesser extent than traditional mixtures of corresponding monomeric surfactants,

(3) due to high asymmetry between surfactant molecules in mixtures, in terms of different alkyl chains number or length, vesicle phase is often found in a very broad concentration range. Although this phenomenon was observed in mixtures of monomeric surfactants as well, it is more pronounced in oligomeric/monomeric surfactant mixtures due to increased asymmetry in molecular structures of components and

(4) in mixtures with dimeric surfactants, very often, elongated (cylindrical) and tubular aggregates can be found which were ascribed to a specific structure of dimeric molecules and electrostatic interactions in the catanionic micelles and bilayers. For example, it is well known that pure 12–2–12 in solutions forms structures with relatively less curvature, such as cylindrical and elongated worm-like micelles even at very low concentrations.

3.2. Catanionic mixtures of surface active ionic liquids (SAILs) and surfactants

In recent years, surface active ionic liquids (SAILs) have emerged as fascinating compounds due to their dual nature as well as unique and tunable physicochemical properties [50]. With combined properties of ionic liquids (ILs) and amphiphiles, SAILs represent a novel class of surfactants. The term ionic liquids refers to a class of substances formed by a poorly coordinated large organic cation with delocalized charge and either a small anion, such as Br⁻, or relatively large one, such as $[(CF_3SO_2)N_2]^-$ [51]. Consequently, ILs possess melting points

under 100 °C, often even lower than room temperature. Due to their unique characteristics such as high thermal stability, negligible vapor pressure, high conductivity and great ability to dissolve inorganic/organic compounds, ILs have attracted much interest for a variety of applications [52, 53].

Among different classes of SAILs, imidazolium-based compounds composed of the 1-alkyl-3-methylimidazolium cation ([C$_n$mim]$^+$, where n = number of carbon atoms in the hydrophobic chain, **Figure 10**) and their mixtures have been most extensively studied. Compared to the conventional alkyltrimethylammonium surfactants, imidazolium-based SAILs exhibit a stronger tendency to self-assemble and slightly better surface activity [50, 54]. Imidazol ring, which can be found, for example, in amino acid histidine, makes them also biologically interesting. Furthermore, it is known that SAILs exhibit low toxicity so their use as drug-delivery agents can represent a step forward in medicinal chemistry [50]. Recently, Sharma and Mahajan published a comprehensive review summarizing influence of various additives, including surfactants, on the physicochemical properties of imidazolium-based ILs [50]. Due to the large amount of published data, the aim of this section is to discuss only aqueous cat-anionic mixtures containing SAIL, although numerous reports of systems in which ILs acted as self-assembly media exist.

Zhao et al. reported the phase diagram of catanionic system composed by cationic SAILs, [C$_{16}$mim]Cl and SDS [55]. Results from rheology and polarized optical microscopy observations demonstrated that a gel phase with quite high water content is formed in the [C$_{16}$mim]Cl-rich side of the phase diagram. On the contrary, in the SDS-rich side, lamellar phases were detected. The [C$_{16}$mim]Cl/SDS gel phase showed low ordering and similar rheological properties to vesicles usually formed in traditional catanionic systems [55].

Formation of gel phase was observed in a very similar system, [C$_{14}$mim]Cl/SDS mixtures, by Zhao et al. as well [56]. The SEM micrographs showed that gel phase is structured as a complex three-dimensional network. Authors argued that hydrophobic and electrostatic interactions present in the system are essential for gel-phase formation. In order to prove this thesis, mixtures in which [C$_{14}$mim]Cl was replaced with [C$_4$mim]Cl and SDS with SOS were also studied. In both of these systems, gel phase was not found. Performed control experiments demonstrated a key role of hydrophobic interactions in gel formation. In additional control experiments, 1-dodecanol was used instead of SDS to confirm the crucial role of electrostatic interactions in gel formation. In this case, the gel phase was also not found [56].

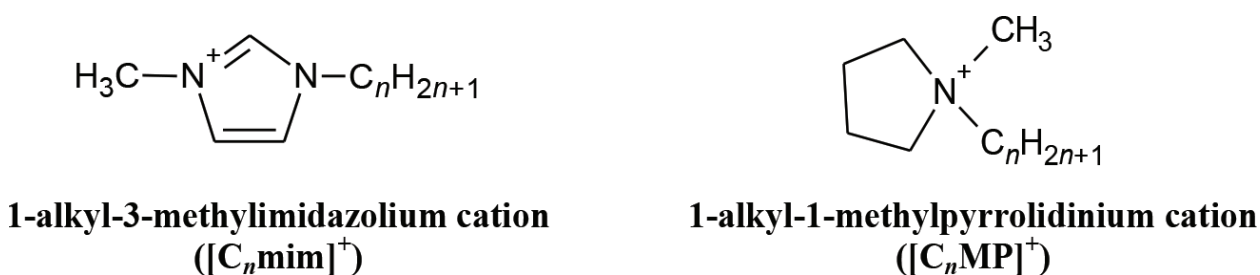**1-alkyl-3-methylimidazolium cation**
([C$_n$mim]$^+$)

1-alkyl-1-methylpyrrolidinium cation
([C$_n$MP]$^+$)

Figure 10. Molecular structures of cations in surface active ionic liquids (SAILs). n = number of C atoms in alkyl chains.

The group of the same author also studied phase behavior in mixtures of *N*-dodecyl-*N*-methylpyrrolidinium bromide ([C$_{12}$MP]Br, **Figure 10**) and SDS by employing TEM, conductivity and rheological measurements [57]. It was found that at constant [C$_{12}$MP]Br concentration, as the molar fraction of SDS increases, the morphology of mixed aggregates changes as follows: mixed micelles → vesicles → coexistence of catanionic precipitate and vesicles → coexistence of catanionic precipitate and mixed micelles. Spontaneous vesicles formation was discussed in terms of packing parameter [57].

Micelle-to-vesicle transition induced by *β*-cyclodextrin (*β*-CD) in mixtures of [C$_{16}$mim]Cl and sodium oleate (NaOle, **Figure 5**) has been investigated by Dai et al. [58]. Cyclodextrins are structurally related cyclic oligosaccharides formed during bacterial digestion of cellulose [59]. It is known that the interior environment of *β*-CD is hydrophobic and its outer surface is hydrophilic. Authors established that in [C$_{16}$mim]Cl-rich mixtures, micelle-to-vesicle transition can be triggered by addition of sufficiently high *β*-CD concentration. The main factor governing this phase transition is formation of inclusion complexes in the system [58].

Chabba et al. employed various techniques such as tensiometry, steady-state fluorescence, DLS and SANS to study interactions of cationic SAILs, [C$_n$mim]Cl (*n* = 8, 10 and 12), with sodium dodecylbenzenesulfonate (SDBS, **Figure 5**) [60]. Results obtained by tensiometric and steady-state fluorescence measurements revealed strong synergism in the system. As well as in the classic catanionic mixtures, strong synergism between the cationic SAIL and anionic SDBS can be attributed to the strong electrostatic interaction between oppositely charged headgroups along with the hydrophobic interactions between the alkyl chains. However, authors argued that in addition to these forces, *π*–*π* and cation–*π* interactions between the imidazolium cation and the benzene ring of SDBS, as well as hydrogen bonding, between most acidic proton of imidazolium ring and sulfonate group of SDBS, also come into play. In general, ionic liquid cations frequently contain multiple donor sites able to participate in hydrogen bonding, resulting in H-bonds of varying strength and type [61]. Within an imidazolium cation, the H-bond donor is the C—H unit, the C2—H proton being the most acidic, followed by the other two hydrogens on the aromatic ring (C4—H and C5—H) and alkyl chain methyl hydrogens. The H atoms on imidazolium ring all participate in the formation of H-bonds with water molecules and in the ubiquitous H-bonds among the highly hydrated imidazolium cations even in very diluted IL solutions [62]. Similar increase in synergistic behavior due to additional non-covalent interaction was found in [C$_{12}$mim]Br/AOT, [C$_{12}$mim]Cl/ibuprofen (**Figure 11**) and [C$_8$mim]Br/SDBS mixtures [16, 63, 64]. Furthermore, as observed from DLS and SANS, the [C$_n$mim]Cl/SDBS mixtures exhibit micelle-to-vesicle transition dependent on the alkyl chain length and the molar ratio of the surfactants. It was found that vesicle region prevails in a broad range of concentrations and that mixtures show high stability towards precipitation [60].

Gehlot et al. studied mixtures of [C$_8$mim]Br and SDBS by employing a variety of techniques such as tensiometry, conductometry, UV-VIS spectroscopy, cryo-TEM, AFM, DLS, ELS, ITC, steady-state fluorescence and ^{1}H NMR measurements [64]. Based on the results obtained from these various physicochemical and imaging techniques, authors have concluded that: (1) spontaneously formed and differently shaped [C$_8$mim]Br/SDBS vesicles (sphere, tubes and ribbons) exist in a broad range of concentrations, (2) a negative value of interaction parameter and lower experimental cmc values, compared to the theoretically determined values,

diclofenac sodium (DFNa)   **ibuprofen**   **camptothecin**

trifluoperazine dihydrochloride (TFP)   **tetracaine hydrochloride (TC)**

cytarabine hydrochloride (CH)   **lidocaine**

diphenhydramine   **orphenadrine**   **amitriptyline**

alprenolol   **naproxen**   **propranolol**

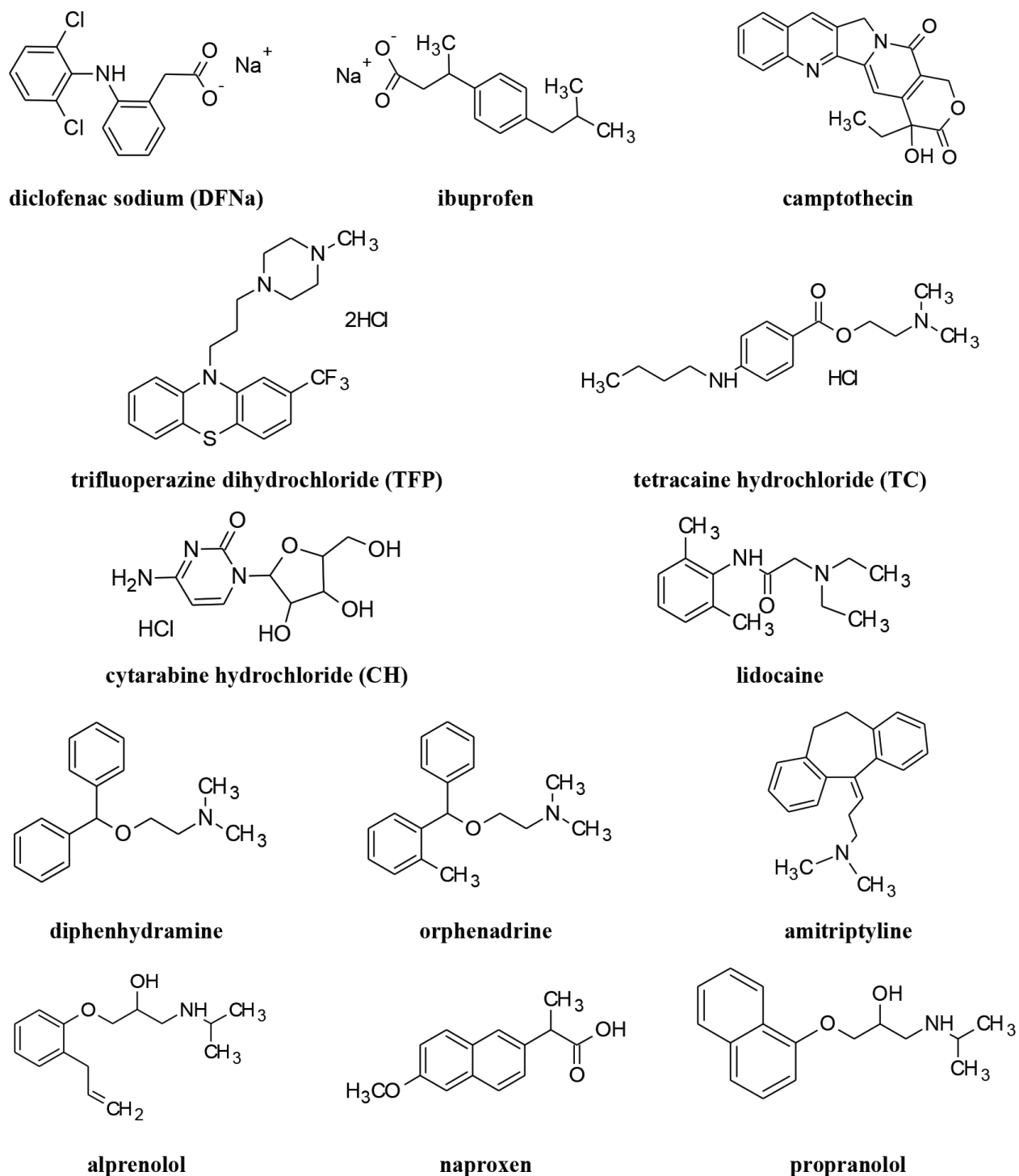**Figure 11.** Molecular structures of amphiphilic drugs.

indicate high synergism in the system, (3) major forces responsible for synergism are electro-static and hydrophobic interactions as well as π-π stacking of aromatic rings and (4) Br$^-$ as a counterion in palisade layer assists in compact packing of ions, which leads to the formation of vesicles [64].

Our group studied phase transitions in mixtures of $[C_{12}mim]Br$ and AOT using a multi-technique approach [16]. Depending on the bulk composition and total surfactant concentration, mixed micelles, coacervates, lamellar and inverse bicontinuous cubic liquid crystalline phase were observed. At stoichiometric conditions, coexistence of coacervates and vesicles was found at lower and bicontinuous cubic phase and vesicles at higher total surfactant concentrations. A mechanism was proposed in which phase transitions from a dispersed lamellar to inverse cubic bicontinuous phase occur as a consequence of charge shielding and closer packing of oppositely charged headgroups followed by a change in bilayers curvature. Additionally, along with electrostatic attractions and geometric packing constraints, additional non-covalent interactions in the system (hydrogen bonding, π-π stacking) enhanced attractive interactions and stabilized low curvature aggregates [16]. In the ternary diagram of the system similar to $[C_{12}mim]$/AOT, 1-butyl-3-methylimidazolium tetrafluoborate $([bmim]BF_4)$/AOT, different phase behavior was observed. In the water-rich corner of the phase diagram, regions of isotropic fluid and lamellar phase were found [65]. In addition, substitution of BF_4 anion with Br^- causes the collapse of lamellar phase [66]. Murgia and co-workers employed a variety of techniques such as conductivity, optical microscopy, SAXS and NMR self-diffusion experiments to detect modifications on macro- and micro-scales within the systems upon the substitution of ILs counterion BF_4 with Br^-. Thus, the remarkable differences observed between the two systems appear to be mainly due to a specific counterion effect [65, 66].

Singh et al. reported structural changes induced by composition and dilution in aqueous catanionic mixtures containing SAILs ($[C_{12}mim]Br$ and $[C_{14}mim]Br$) and a drug, diclofenac sodium (DFNa, **Figure 11**), as the anionic component [29]. The observed phase transitions were probed by SANS, DLS and ELS. The SAIL/DFNa systems display rich phase behavior and structural diversity of mixed aggregates, that is, depending on the bulk composition and total surfactant concentration, spherical and small micelles with prolate ellipsoidal shape as well as rod-shaped micelles and vesicles were detected. The ^{1}H NMR measurements revealed that DFNa intercalated into SAIL micelles via cation-π and π-π interaction in addition to hydrophobic interaction. It was found that increase in DFNa molar ratio increases aggregates curvature. Unlike conventional linear chain surfactants, a specific structure of DFNa does not allow effective packing of cationic-anionic pairs which prevented precipitation in equimolar mixtures [29].

Catanionic systems also containing a drug, ibuprofen and $[C_{12}mim]Cl$ have been investigated by Sanan et al. [63]. Various techniques such as surface tension, steady-state fluorescence, UV-VIS spectroscopy, DLS and ^{1}H NMR measurements were used to provide a comprehensive knowledge about $[C_{12}mim]Cl$-ibuprofen interactions. The interactions between the SAIL and drug molecules are found to be highly synergistic both in the mixed micelles and in the mixed monolayer. The formation of highly surface active catanionic complexes of 1:1 stoichiometry ($[C_{12}mim]Cl^+$ibuprofen$^-$), stabilized largely by a combination of electrostatic, hydrophobic, cation-π and π-π interactions, was established through spectroscopic investigations. Depending on the bulk composition and total surfactant concentration of mixed micelles, unilamellar and multi-lamellar vesicles were detected in the system [63].

Vashishat et al. investigated mixtures of bile salts (sodium cholate (NaC) and sodium deoxycholate ((NaDC), **Figure 8**) with $[C_{12}mim]Br$ [67]. From a biochemical point of view, bile salts

play a vital role in many physiological processes, and more will be said about their catanionic mixtures in the next section. In order to obtain detailed information about interactions between [C$_{12}$mim]Br and bile salts in the mixed monolayer and in the mixed micelles, surface tension and steady-state fluorescence measurements were conducted. Various micellar and interfacial parameters, including cmc, β_{mic}, a_{min}, surface excess concentration (π_{max}) and surface pressure at cmc (π_{cmc}), were estimated. It was found that investigated mixtures exhibit pronounced synergism in mixed monolayer formation as well as micellization. Due to the more hydrophobic nature of NaDC, which allows its molecules to get deeply intercalated in the mixed micelles compared to NaC, mixture with NaDC showed stronger synergistic effect. In addition, this study aimed to determine the solubilization capacity of the poorly soluble drug, phenothiazine, in micellar media. It was found that solubility of phenothiazine is dependent on the hydrophobicity and the size of the micelles, with solubility increasing in the order: NaC < NaDC < [C$_{12}$mim]Br/NaC < [C$_{12}$mim]Br/NaDC [67].

Along with the properties of traditional catanionic mixtures, in systems containing SAIL, the following characteristics can be found:

(1) variation in the alkyl chain length of both SAIL (*n*) and surfactant (*m*) causes a significant change in the physicochemical properties and phase behavior of the systems,

(2) the magnitude of SAIL-surfactant interactions is larger for surfactants with aromatic moiety in their structure, for example, SDBS. The reason behind this is the involvement of cation-π and π-π interactions due to the π-electron cloud of the benzene ring in SDBS and the imidazolium ring in [C$_n$mim]$^+$ cation,

(3) along with electrostatic and hydrophobic interactions, additional non-covalent interactions (hydrogen bonding, π-π stacking) (1) enhance attractive interactions and (2) increase synergistic effect as well as (3) stabilize low curvature structures in SAIL-surfactant systems and

(4) apart from self-assembled aggregates commonly found in catanionic mixtures, formation of gel phase was observed in some SAIL-surfactant systems.

3.3. Catanionic mixtures of biologically active molecules and surfactants

Due to their important roles in various physiological processes and pharmaceutical applications amphiphilic biologically active molecules, as well as their catanionic mixtures, have been the subject of numerous papers. Historically, the most-studied catanionic mixtures of this type as biologically active molecules contain either (1) amphiphilic drug or (2) bile salt. Therefore, aqueous catanionic mixtures of such molecules are mostly summarized and discussed in this section.

In addition to [C$_n$mim]Br/DFNa and [C$_{12}$mim]Cl/ibuprofen systems [29, 63], mentioned in the previous section, Mahajan's group recently reported on: (1) interactions between the cationic drug, trifluoperazine dihydrochloride (TFP, **Figure 11**) and anionic surfactants, SDS and AOT [68] as well as (2) interactions prevailing in catanionic mixtures containing cationic drug,

tetracaine hydrochloride (TC, **Figure 11**) and anionic surfactants, SDBS and sodium lauroyl sarcosinate (SLS, **Figure 5**) [69]. In all investigated mixtures, various micellar and interfacial parameters were determined from surface tension measurements and by applying the RST. Obtained results revealed strong synergism in systems' bulk and surface properties such as high surface activity and low cmcs. As expected, it was established that TC interacts more strongly with SDBS and that TC-SDBS complex possesses higher binding constant, as compared to TC/SLS mixture, due to the additional non-covalent interactions in the system (π-π stacking). Furthermore, Jiang et al. investigated aggregation behavior of vesicles formed by TC and AOT using conductivity, turbidity measurements, TEM, DLS and ELS [70]. The TC/AOT aggregates exhibited different morphology, charge properties, interaction enthalpies and drug release behaviors depending on the mixtures' bulk composition. Obtained drug release profiles indicated that investigated drug-containing vesicles have promising applications in drug delivery systems.

Zhao et al. determined various physicochemical parameters (cmc, Γ_{max}, a_{min}, surface tension at the cmc (γ_{cmc}), degree of counterion binding, etc.) from the surface tension and electrical conductivity measurements in mixtures of DFNa and DDAB [71]. The cmc and γ_{cmc} of mixed DDAB/DFNa systems were found to have values between that of pure DFNa and DDAB solutions. In addition, (1) the in vitro release results demonstrated that DDAB/DFNa vesicles exhibit good sustained drug release properties while (2) the hemolytic toxicity studies show that vesicles in mixtures with high DFNa molar ratio are safe for intravenous administration within the effective concentration [71].

Bile salts are well known and important biologically active surfactants, produced in the liver from cholesterol, which play an important role in emulsification of lipids, fats, fat soluble vitamins, etc. [67]. Due to their great importance in metabolism of insoluble molecules, such as phospholipids and monoglycerides, they have been extensively studied. They possess a unique molecular structure when compared with typical surfactant molecules, like the steroids, they have a nucleus composed of four fused rings, three cyclohexane rings and one cyclopentane ring as well as hydrophilic hydroxyl groups (**Figure 8**). Bile acids are favorable compounds for construction of supramolecular structures because of their biocompatibility, high structural rigidity, amphiphilicity and chirality [72].

Our group investigated 12–6–12/NaC and C_mTACl (m = 12, 14 and 16)/NaC mixtures employing a combination of techniques such as surface tension, conductometry, light microscopy, DLS and ELS [24, 73]. In all investigated systems, synergism in micellization and adsorption was observed. With increasing total surfactant concentration, in equivalent 12–6–12/NaC mixtures, morphology of mixed aggregates changes as follows: complexes $\rightarrow$ flexible cylindrical mixed micelles $\rightarrow$ coexistence of vesicles, coacervates and solid crystalline phase. In the high excess of cationic surfactant, the small 12–6–12 micelles are prevailing structures while with an increasing content of NaC, the long flexible mixed micelles are dominant. Obtained results demonstrated that interplay between (1) electrostatic effects, (2) geometry of molecules as well as (3) dissimilar separation of the hydrophobic and hydrophilic moieties in the surfactants dictates phase behavior of these systems [24].

The most interesting discovery in C_mTACl/NaC systems was that catanionic surfactants, precipitated in/or close to equimolar region, show a variety of morphologies including twisted ribbons and crystalline tubules, which are not commonly found in this kind of systems [73]. The three-dimensional structures that are yielded by the self-assembly of lipids and surfactants have recently drawn much research interest due to their applications in nanotechnology [74]. Formation of tubules in C_mTACl/NaC mixtures can be attributed to several factors: (1) chiral packing of NaC molecule in a bilayer, (2) strong attractive interactions between oppositely charged headgroups at the bilayer/solution interface and (3) hydrogen bonding at the bilayer surfaces, which enhance formation of multilayer sheets and their twisting and/or rolling up [73].

Long, fiber-like tubular structures instead of crystalline tubules were observed in the cationic-rich dilute region of DDAB/NaTDC system by Marques and Khan [75]. Authors suggested that formation of long tubular structures is a consequence of specific NaTDC's rigid ring-based structure with hydroxyl groups. Previously, Marques's group studied the phase behavior of the same catanionic pair but in the bile salt-rich area [26]. It was reported that the system displays coacervation instead of precipitation at equimolarity, consisting of a viscous isotropic solution in equilibrium with a very dilute solution. Formation of tubular structures was not detected in this part of the phase diagram.

Liu et al. reported that in lithocholic acid (LCA, **Figure 8**)/tetradecyltrimethylammonium hydroxide ($C_{14}TAOH$, **Figure 4**) system transition from vesicles to tubules was observed, while in mixtures of LCA with cetyltrimethylammonium hydroxide ($C_{16}TAOH$), transition from vesicles to helical ribbons occurred [72]. Thus, despite a difference of only two methylene groups in the alkyl chain of $C_{14}TAOH$ and $C_{16}TAOH$, morphology of mixed aggregates in these two systems is largely different. In addition, it was found that time required for the phase transition depends on alkyl chain length as well. In the $C_{14}TAOH/LCA$ systems, the transition from vesicles to tubules was completed within several hours, while in the $C_{16}TAOH/LCA$ system, the vesicles were converted to helical ribbons after more than 4 days, depending on the concentration and temperature [72].

Motivated by their numerous potential applications in nanotechnology, Manghisi et al. prepared and characterized tubules in mixtures of anionic (ACD) and cationic (CCD) derivatives of NaC (**Figure 8**) [74]. It was found that charge of synthesized CCD/ACD tubules ranges from negative to positive values depending on the surfactant molar ratio in the mixtures. Analysis of the TEM micrographs revealed a correlation between the diameter and the composition of the tubules [74].

Bhattacharjee et al. investigated mixtures of cetylpyridinium chloride ($C_{16}PC$, **Figure 4**) and NaDC using DLS, SANS and SAXS [76]. It was shown that phase separation, i.e. coacervate phase, occurs near the equimolar composition at low surfactant concentrations and, contrary to expectations, disappears at higher concentrations. This associative phase separation has been explained on the basis of competition between electrostatic attraction and entropy of the components mixing. Additionally, based on the obtained results, authors suggested that structural features of bile salts are not favorable for formation of catanionic vesicles when

combined with $C_{16}PC$. However, stable mixed micelles of widely differing morphologies were formed in a broad concentration range [76].

Fernández-Leyes et al. reported on physicochemical properties and phase behavior of DDAB/ sodium dehydrocholate (NaDHC, **Figure 8**) and DDAB/NaDC mixtures using surface tension measurements, conductivity, DLS, ELS and TEM [77, 78]. The RST was applied for evaluating the non-ideal interactions between molecules in adsorbed monolayer and mixed micelles. All systems exhibited synergism in mixed monolayer formation as well as micellization. The obtained pC_{20} values, negative logarithms of the surfactant concentrations at which the surface tension of water is reduced by 20 mN m^{-1}, demonstrated that both mixed systems have analogous adsorption efficiencies, which are similar to the pure DDAB solutions and superior to that obtained for both bile salts. Nevertheless, difference in their adsorption effectiveness was observed: NaDC causes an increase of surface excess concentration, while NaDHC produces the opposite effect. The lower Γ_{max} values obtained for DDAB/NaDHC system are related to the deep penetration of the hydrophobic steroid backbone of NaDHC molecules that cause a great disturbance of DDAB hydrocarbon tails, that is larger a_{min} [77]. Furthermore, it was found that mixed aggregates in DDAB/NaDHC system are mainly composed of DDAB, regardless of the NaDHC solution molar fraction. Nevertheless, the gradual inclusion of NaDHC molecules leads to structural transformations in the system. The incorporation of NaDHC into DDAB bilayers had two effects: (1) the DHC$^-$ and DDA$^+$ ions form ion pairs that are much less hydrated than separate ion headgroups, which consequently reduce the effective headgroup area and (2) the intercalation of the rigid ring-based structure of bile salts between DDAB chains causes an increase of chain repulsion due to steric effects [78].

Pereyra et al. analyzed $C_{16}TAB$/NaDHC system with two procedures: (1) the RST and (2) the EOMMM (Equation Oriented Mixed Micellization Modeling) [79]. Investigated system showed a non-ideal and asymmetric behavior with attractive interaction between the components, as reflected by the obtained interaction parameters. Moreover, it was established that the affinity of DHC$^-$ ions for $C_{16}TAB$ micelles is stronger than that of $C_{16}TA^+$ ions for NaDHC ones [79].

Apart from the properties which can be found in traditional catanionic systems, common features of catanionic mixtures with biologically active molecules are:

(1) the rigid ring-based structure of amphiphilic drugs and especially, bile salts, as well as high asymmetry between surfactant molecules in mixtures, does not allow effective packing of cationic-anionic pairs and often prevents precipitation in equimolar mixtures. Instead, coacervates or vesicles can be found,

(2) for the same reason, synergism observed in these systems is less pronounced compared to traditional mixtures of monomeric surfactants,

(3) most catanionic mixtures containing bile salts revealed that apart from electrostatic interactions, the geometry and planar distribution of hydrophobic and hydrophilic properties of bile salts play a marked role in the construction of various mixed aggregates and

(4) frequent occurrence of tubules in catanionic mixtures containing bile salts can be attributed to several factors: (1) chiral packing of bile salt molecule in a bilayer, (2) strong attractive interactions between oppositely charged headgroups at the bilayer/solution interface and (3) hydrogen bonding at the bilayer surfaces, which enhance formation of multilayer sheets and their twisting and/or rolling up.

4. Applications of catanionic mixtures

In the past decades, a large number of systems for the controlled and targeted delivery of pharmaceutical compounds have been designed based on various self-assembled aggregates such as micelles, vesicles, liquid crystalline phases, tubules, etc. [80–82]. Catanionic systems, due to their rich phase behavior and numerous possibilities in mediating molecular self-assembly, by adjusting the mixing molar ratio and using appropriate geometry of surfactant molecules, offer considerable advantages in delivering biomolecules. For example, catanionic mixtures easily and spontaneously form vesicles at non-stoichiometric molar ratios. Vesicles are not only significant because they mimic biological membranes, but also due to their utility as drug carriers and targeted drug delivery systems.

As already mentioned, precipitation is considered to be the main drawback for application of catanionic mixtures [3]. However, as it can be seen from preceding sections, this drawback can be circumvented by using surfactants of largely different molecular structures. In addition, biologically active molecules, such as amphiphilic drugs, can be used as one of the mixtures' components, which provide a whole range of possibilities for designing novel drug delivery systems.

In addition to drug delivery applications, catanionic mixtures are drawing attention in the synthesis of novel materials, development of novel analytical methods and corrosion protection. As in drug delivery systems, vesicles play the most prominent role in these applications. However, other types of catanionic aggregates are becoming increasingly of more interest as structure-directing templates.

4.1. Pharmaceutical applications: drug delivery systems

Among different types of self-assembled drug delivery systems, vesicles remain one of the most common strategies for the delivery of drugs and genetic material in the human body [80, 83]. In general, vesicles can adsorb considerable amount of species needed to be transferred and efficiently bind to the cells. Also, it is possible to tune their physical state (gel, liquid, liquid crystalline) and in that way additionally control the release [83]. By far, most used vesicles are those composed of natural polar lipids—so-called liposomes. Liposomes possess excellent biocompatibility and biodegradability but often exhibit low stability, as they are susceptible to chemical degradation by hydrolysis and peroxidation. This is the key reason why catanionic vesicles, with their relative ease of preparation and long-term stability, attract attention

as possible alternatives. In addition, catanionic vesicles can be made of biocompatible surfactants as well, such as amino acid-derived surfactants [19, 22, 23, 84].

However, despite the positive outlook for catanionic vesicles, the first studies have shown that they display number of problems such as (1) low encapsulation efficiency, both initial and long-term efficiency were not as high as for liposomes and (2) permeability, that is, occurrence of leakage due to the poor bilayers tightness [5, 7, 85]. Kaler et al. were the first to report spontaneous vesicles' formation from mixed cationic and anionic single-chain surfactants, that is, cetyltrimethylammonium tosylate (CTAT, **Figure 4**) and SDBS, as well as their potential to load glucose [86], while Caillet et al. investigated the encapsulation of anionic dye carboxyfluorescein (CF), riboflavine and glucose in C_{16}TAB/SOS vesicles [87]. These studies have shown that the permeability of vesicle membranes can be tailored by choosing appropriate surfactants' tail length. Surfactants with short alkyl chain enable higher permeability of amphiphilic films which in turn enable rapid and complete release, while longer tails increase vesicles' stability. These studies have also shown that expected specific interactions of ionic compounds with the surface of the vesicles can improve the entrapment efficiency [7]. Additionally, Wang et al. reported that CF can be encapsulated in the inner water pool as well as electrostatically adsorbed to the oppositely charged bilayers of CTAT-rich vesicles formed in CTAT/SDBS mixtures [88]. Moreover, achieved loading capacity was 10 times greater compared to phosphatidylcholine liposomes. However, no entrapment of CF was observed in SDBS-rich vesicles.

One way to overcome drawbacks of catanionic vesicles as drug delivery systems is preparation of mixtures in which one of the components is amphiphilic drug. For example, problem with permeability, that is integrity and tightness of the vesicles, is then reduced since drug molecule is incorporated into the catanionic bilayers. This approach also enables usage of the mixed micelles as self-assembled delivery systems [7].

As already discussed in the previous section, regarding the physicochemical properties and phase behavior of drug-surfactant mixtures, most of the recent research was done by Mahajan's group [29, 63, 68, 69]. Catanionic systems containing (1) anti-inflammatory drug for pain control and treatment of rheumatic diseases, diclofenac sodium [29, 71], (2) non-steroidal anti-inflammatory drug, ibuprofen [63], (3) antidepressant and antipsychotic drug, trifluoperazine dihydrochloride [68], as well as (4) tetracaine hydrochloride [69, 70], an anesthetic used in topical ophthalmic solutions, were investigated by a number of groups. In addition, Liu et al. established that amphiphilic anticancer drug, cytarabine hydrochloride (CH, **Figure 11**), and AOT can self-assemble into vesicles in the aqueous solution [89]. The parallel artificial membrane permeability assay (PAMPA) and hemolytic toxicity studies were carried out to evaluate the potential use of CH/AOT vesicles in drug delivery. The results indicate that catanionic vesicles can improve the permeability of CH about 160 times in PAMPA model and markedly decrease the hemolytic toxicity of both CH and AOT compared with their respective solutions. In addition, in vitro drug release behavior results for both CH/AOT vesicles and CH/AOT vesicles incorporated into the thermosensitive PLGA-PEG-PLGA hydrogel revealed them as good sustained drug release systems [89].

In most cases, two main strategies to improve release properties of catanionic vesicles are employed which are (1) incorporation of vesicles into the gels and (2) preparation of environment sensitive vesicles. Catanionic aggregates formed from drug and oppositely charged surfactant and then incorporated into the gel have been extensively studied by Edsman's group with the objective to utilize them for prolonged release [90–96]:

(1) Catanionic aggregates containing various drug compounds, diphenhydramine, lidocaine, ibuprofen, naproxen, alprenolol, propranolol or orphenadrine (**Figure 11**), and ionic surfactants, SDS, $C_{14}TACl$, $C_{12}PC$ or benzalkonium chloride (C_mBzCl, **Figure 4**) incorporated in Carbopol® 940 or agar-agar gels, were studied. Obtained results demonstrated that both micelles and vesicles from the three systems examined in the release studies (lidocain/SDS, orphenadrine/SDS, ibuprofen/$C_{14}TACl$) helped to prolong the release between 10 and 100 times compared to the release of the pure drug from the gel [90].

(2) Constructed phase diagrams of the mixtures of three different cationic drug compounds, diphenhydramine, tetracaine and amitriptyline (**Figure 11**), with SDS, showed that although the diagrams may differ in some parts, vesicles and branched micelles are present in all three cases on the SDS-rich side. Drug release from Carbopol® 940 and agar gels revealed that sustained drug release may be accomplished by incorporation of investigated catanionic vesicles and micelles into the gels [91].

(3) Investigation of pH and ionic strength influence on the phase behavior of diphenhydramine/SDS and tetracaine/SDS mixtures, as well as study of drug release from drug/surfactant aggregates in Carbopol® gels, demonstrated that drug release in both systems was somewhat affected by changes in both pH and ionic strength but remained in all cases significantly prolonged compared to the release of the free drug [92].

(4) A study of controlled release of charged drugs from five different types of gels by adding surfactants (SDS, Brij 58, $C_{12}BzBr$) that can interact with the drug and polymer matrix demonstrated that interactions between the surfactant aggregates and the polymer can be used to further modify the drug release [93].

(5) When drug/SDS vesicles, drug substance being alprenolol or tetracaine, were mixed with polymers, one bearing hydrophobic modifications, one positively charged and one positively charged bearing hydrophobic modification, gels were form only in the case when negatively charge catanionic vesicles were mixed with positively charged polymer-bearing hydrophobic modification. In addition, the release of drug substance from these systems, where the vesicles are not trapped within the gel but constitute a founding part of it, could be significantly prolonged. The release rate was affected to a greater extent by variation of vesicles' concentrations than by variation in polymer concentration [94].

(6) Release profiles of (1) alprenolol/SDS aggregates incorporated into the SoftCAT and Carbopol® gels [95] and (2) tetracaine/SDS or capric acid aggregates incorporated into the SoftCAT and carbomer gels [96] have shown that prolonged drug release from this system enables prolonged skin penetration.

Regarding the preparation of environment-sensitive vesicles, Ghosh et al. [97] investigated pH-induced release of model drug (calcein, fluorescent dye) as well as hemocompatibility and cytotoxicity of catanionic vesicles containing anionic amino acid-based carboxylate surfactants, sodium N-alkanoyl-L-sarcosinate with varying chain length (**Figure 5**) and C_{12}TAOH or C_{16}TAOH. Obtained results demonstrated that with pH decrease (pH ≤ 5), vesicles are transformed into small mixed micelles. It can be concluded that investigated vesicles are sensitive to pH change of the environment and interesting as drug delivery systems in which drug release is triggered by pH change. The hemocompatibility and cytotoxicity evaluation revealed that vesicles are hemocompatible and nontoxic.

Motivated with known antibacterial activity of anionic and cationic surfactants, Chaouat et al. prepared three component vesicles consisting of N-dodecyldiethanolamine, decanoic acid and azelaic acid (**Figures 4** and **5**) and evaluated their antimicrobial activity against different strains of bacteria [98]. Obtained results revealed that antimicrobial activity of catanionic vesicles displays synergistic effect compared with the activity of individual components.

Not only catanionic vesicles are considered of interest for designing drug delivery systems. The 1D structures, such as tubules, that are yielded by the self-assembly of lipids and surfactants are of particular interest for their applications in nanotechnology and pharmaceutical applications [74]. Lin et al. prepared multi-walled nanotubes using two anticancer drug amphiphiles in which drug camptothecin (CPT, **Figure 11**) was loaded [99]. Used amphiphiles contained one, two or four hydrophobic CPTs conjugated to a β-sheet-forming peptide sequence through a reducible disulfylbutyrate linker. The authors proposed that nanotubules were formed by combination of three occurrences: (1) 1D elongation, (2) formation of multilayers and (3) bilayer extension from helical ribbons due to mixing of oppositely charged drug amphiphiles.

The interaction between amphiphiles and DNA was studied over a long period of time in the area of gene therapy [7]. Likewise, due to their features, catanionic vesicles are of potential interest as non-viral gene carriers. Interactions of DNA and cationic vesicles result in complexes in which DNA molecule adopts more compact conformation and has reduced charge, facilitating its uptake through cell membranes. The fundamental framework for DNA/catanionic vesicles application has been established by Lindman's group [100–103]. In a number of studies, they have shown that:

(1) Positively charged C_{16}TAB/SOS vesicles can induce folding transition in large single linear DNA molecules, as well as adsorption of globular DNA. No such effects were observed in the presence of negatively charged vesicles. Most importantly, it was shown that the folding transition is reversible and that change in surfactants molar ratio results in DNA unfolding and release [100].

(2) Longer chain anionic surfactant (SDS vs. SOS) was more efficient in releasing DNA into the solution from catanionic vesicles [101], which was explained in terms of chain length dependence of surfactant self-assembly [102]. However, no influence of hydrophobicity of the cationic surfactant (C_{12}TAB, C_{14}TAB, C_{16}TAB) was observed.

(3) Interactions between DNA and positively charged vesicles are strong. Formed complexes withstand dilution or addition of excess surfactant or DNA and do not dissolve. Their structure resembled to other systems previously described, that is DNA molecules were packed between surfactant bilayers [103].

La Mesa's group [104] has shown that interaction with C_{16}TAB/SDS vesicles can protect a sensitive molecule, exogenous RNA, from RNase, resulting in efficient delivery of RNA across the cell membrane. The efficiency of delivery increases when vesicles are formed in the presence of RNA. In a recent study [105] of DDAB/8-hexadecyl sulfate (8-SHS, **Figure 5**) vesicles interaction with calf thymus DNA, it was shown that strongly associating complexes are formed. Results revealed that their structure depended on DNA content. At low concentration, formed complexes resemble to bare vesicles, while at higher concentrations, multi-lamellar entities are formed in which adsorbed amount of DNA increases with its concentration. Further increasing DNA concentration leads first to formation of large clusters of vesicles and then to precipitation. DNA molecules undergo compaction process, which facilitates penetration into cell and at the same time protects it from nucelases action. The compaction process is reversible as addition of anionic surfactant induces DNA release [105].

4.2. Synthesis of advanced materials

Surfactants' role in the synthesis of nanomaterials renewed interest of research community for applying surfactants and self-assembled aggregates in the preparation of new materials. Surfactants have been used in the synthesis of inorganic materials, either as soft templates or in the surfactant-mediated synthesis [106]. Despite wide-ranging structural diversity of surfactants' aggregates, vesicles, and thus catanionic vesicles, are still frequently the template of choice. Due to the special structure of vesicles, inorganic material can be formed in different reaction environments: (1) the "bulk" solution outside the vesicles, (2) the inner chamber, (3) the outside surface or (4) the hydrophobic palisade layer of the vesicles [107, 108]. Different reaction environments enable formation of material of vastly different morphologies.

Recently, vesicles formed by SAIL, [C_{12}MP]Br (**Figure 10**), and a divalent metal surfactant, copper dodecyl sulfate (Cu(DS)$_2$·4H$_2$O), were used for preparation of leaf-like CuO nanosheets [108].

Using vesicles composed of imidazolium-based SAIL, [C_{12}mim]Br (**Figure 10**) and SDS as structure-directing templates, Yuan et al. synthesized silica hollow spheres [107]. Silica hollow spheres of controlled size were previously synthesized in C_{12}TAB/SDBS mixtures by Kepczynski et al. [109]. Furthermore, catanionic vesicles formed in C_{16}TAOH/Mg(DS)$_2$ mixture were used for preparation of Mg(OH)$_2$ hollow nanospheres [110]. Interestingly, it was observed that encapsulation of Mg(OH)$_2$ particles, followed by crystal fusion, can induce the size and shape change of catanionic vesicles under non-equilibrium conditions. This phenomenon facilitated the direct observation of hydrophobic membrane fusion by means of TEM microscopy [110].

Not only inorganic hollowspheres were synthesized in the presence of catanionic vesicles. Morgan et al. developed the method for preparation of polymeric spheres by introducing polymerizable monomer into the vesicle's bilayer [111]. This method was later used for

synthesis of polydisperse hollow polystyrene spheres in CTAT/SDBS and C_{16}TAB/SOS mixtures [112]. Additionally, a lot of research work employing the different preparation methods with polymerized ion pair amphiphile vesicles was done by Chung's group [113–117]. Recently, hollow microspheres of poly(3,4-ethylenedioxythiophene (PEDOT), ranging from 0.5 to 10 mm, were synthesized by oxidative polymerization in the presence of C_{16}TAB/SDBS vesicles. It was established that formation and size of microspheres were influenced by surfactant molar ratio. Moreover, it was shown that SDBS was incorporated in the polymer chain as dopant [118].

In addition to vesicles, catanionic micelles can be also effective templates for preparation of nanoparticles (NPs). For example, C_{16}TAB/SDS micelles were used in synthesis of mesoporous γ-Al_2O_3 NPs [119]. Authors demonstrated that the choice of the surfactant is important for the synthesis of organized mesoporous aluminas with a well-defined porosity, although it is unclear how the presence of micellar aggregates affects the final architecture in cationic-anionic double hydrolysis method [119].

Short-chain catanionic mixtures composed of C_{10}TAB and SOS were used in synthesis of highly ordered supermicroporous silica [120]. Pore size in the range 1–2 nm had hexagonal structure which was strongly dependent on the surfactants molar ratio. Previously, Ohkubo et al. reported synthesis of silica particles in which precise control of both, the pore size and the structure of pores, was achieved by changing C_{16}TAB/SOS mixing ratio [121]. Moreover, use of the cationic surfactant with longer alkyl chain, C_{18}TAB, shifted the point of phase transition from hexagonal phase to lamellar phase to lower concentration of SOS. Lind et al. reported on vesicle-like patterned, mesoscopically ordered silica synthesized in C_{16}TAB/decanoic acid mixtures with toluene used as the swelling agent [122]. Obtained results demonstrated that lower interfacial charge density of the mixed aggregates stabilizes structures of lower interfacial curvature and therefore facilitates a more controlled solubilization of toluene. In addition, it was shown that the pore size of the hexagonal phase could be controlled by changing the C_{16}TAB/decanoic acid and the C_{16}TAB/toluene molar ratios [122].

Using surfactants' aggregates as structure-directing templates in the synthesis of new materials is essentially a biomimetic approach [106]. Hard tissues in organisms, such as bones and teeth, are formed in the processes in which organic matrix (composed of surface active proteins, lipids, etc.) has a role of the template which determines morphology, size and orientation of inorganic phase. Therefore, it is not surprising that several attempts of biomineral synthesis in the presence of catanionic mixtures have been reported.

Prelote and Zemb used catanionic aggregates with hexagonal structures formed in mixtures of polyoxyethyleneoleyl ether phosphate (POEPO$_4$) and C_{14}TAB as structure-directing templates for synthesis of mesoporous hydroxapatite (HAP) with high surface area [123]. HAP is thermodynamically the most stable calcium phosphate phase which attracts attention due to its similarity to bone mineral. It is widely used as biomaterial for bone and dental tissue regeneration in the form of different ceramics formulations and as coating. In that sense, mesoporous HAP is of special interest as a 3D scaffold. Hexagonal network of cylindrical micelles formed in the C_{14}TAB/POEPO$_4$ mixture was preserved during the synthesis of HAP, which enabled formation of the precipitates with the structural characteristic of the hexagonal

network. However, the repetition distance was low and obtained precipitates were not truly mesoporous material. In addition, the precipitates were not able to withstand calcification.

Tari et al. have shown that the morphology of HAP NPs in C_{16}TAB/SDS solution depends on surfactant molar ratio [124]. In the SDS-rich region, rod-like HAP NPs were obtained, while in C_{16}TAB-rich region, HAP nanosheets were formed.

Control of polymorphism and crystal morphology is not only important in the biomineral synthesis but also for fundamental understanding of biomineralization processes in vivo. Chen and Nang have shown that surfactants molar ratio in C_{16}TAB/SDS mixtures can be used to control both the morphology and polymorphism of $CaCO_3$ crystals [125]. Furthermore, Dong et al. obtained brick-like (dodecahedrons) and star-like (icositetrahedrons) calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) crystals, not observed before, in mixtures of calcium dodecyl sulfate and C_{14}TAB with excess $CaBr_2$ [126].

4.3. Novel analytical methods

Several research groups investigated the use of catanionic aggregates in the development of new analytical and detection methods.

CTAT/SDBS vesicles, both positively and negatively charged, were used for highly efficient electrostatic sequestration of small molecules of similar weight but opposite charge, that is CF, lucifer yellow, sulforhodamine 101, doxorubicin and rhodamine 6G [127]. Authors have established that charge-dependent effect enables use of CTAT/SDBS vesicles for selective capture and separation of oppositely charged solute from a mixture of solutes.

Kahe et al. used C_{16}TAB/SDS mixtures in propanol water as a novel microextraction system for the preconcentration and determination of trace amounts of lead in (1) saline solutions and (2) food samples [128]. Since only small amount of propanol in water was used, both hydrophilic and hydrophobic sites in extraction solvent were available for interaction with analytes of various polarities enabling good efficacy. Obtained results confirm that the catanionic aggregate dispersive microextraction method can be used as a simple, safe, fast and low-cost technique for the microextraction of various organic and inorganic compounds from real samples [128].

Chen et al. employed coacervates formed by addition of hexafluoroisopropanol (HFIP) to C_{12}TAB/SDS mixtures for extraction of strongly polar sulphonamides (SAs) from environmental water samples [129]. Results demonstrated that even small amount of HFIP can induce coacervation and two-phase separation in a broad concentration range in C_{12}TAB/SDS system. In addition, analysis of real water samples confirmed that investigated method can be efficiently used for the preconcentration and determination of SAs traces.

With an aim to improve methods for Au(III) extraction, Wang et al. used $C_{12}C_3(OH)C_{12}Cl_2$ (**Figure 6**)/NaDC vesicles [130]. Through stepwise extraction and ligand-modified vesicles system, separation of Au (III), Cu (II) and Fe (III) from mixed solution was successfully achieved. The results collected in this study revealed great potential of catanionic aggregates in development of environmental friendly Au recovery method [130].

Gao et al. proposed a new method for determination of anionic surfactants based on in situ formation of catanionic aggregates in the presence of amphiphilic 2-(2-hydroxyphenyl) benzothiazolefluorogen probe [131]. Described approach enables quantitative determination of low anionic surfactant concentrations and can be extended to wash-free imaging of bacteria.

The role that carbohydrate-protein interactions have in biological processes and difficulties in their evaluation motivates development of novel analytical methods. Pond et al. applied CTAT/SDBS vesicles with incorporated glycans in the outer surface to form glycan array for investigating carbohydrate-lecitin interactions. The method proved to be facile and opens possibilities for characterizing unknown lecitins [132].

4.4. Corrosion protection

Catanionic mixtures also proved to be efficient in corrosion protection of mild steel. C_{16}TAB/SDS mixtures demonstrated better protective efficiency than the individual surfactants. This was explained by strong adsorption on the metal surface and formation of protective surfactant film. The strong adsorption was evidenced by more negative values of the adsorption free energy of C_{16}TAB/SDS mixtures compared to the individual surfactants [133].

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