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Thermotropic phase behavior of triple-chained catanionic surfactants with varying headgroup chemistry

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Abstract

Catanionic surfactants result from the pairing of oppositely charged amphiphilic molecules, forming a new class of surfactant molecules with various interesting lyotropic and thermotropic properties. With the aim of probing the role of both headgroup chemical nature/structure and molecular shape, a series of catanionic surfactants were synthesized. The cationic portion of the molecule is kept constant, being the dioctadecyldimethylammonium double chain. Different single-chained surfactants with varying headgroups and chain lengths are used as the anionic pair. The thermotropic behavior has been studied by DSC and the mesophase structural investigated by polarized light microscopy. The results indicate that, for a given chain length, parameters such as headgroup polarity and charge density, as well as volume, influence the catanionic surfactant behavior. The thermodynamic parameters are qualitatively evaluated, considering the headgroup chemical nature and the overall molecular structure.

Keywords: Catanionic surfactant; Thermotropic behavior; Liquid crystal; Charge density; Chain packing

1. Introduction

Ionic and neutral surfactants usually consist of a polar headgroup attached to a hydrophobic moiety of varying structure and size, most commonly a single or a double hydrocarbon chain. Catanionic surfactants are a relatively novel class of net neutral amphiphiles obtained by equimolar mixing of cationic and anionic surfactants with removal of the inorganic counterions. Due to the strong headgroup electrostatic interactions, one charged amphiphilic chain acts as counterion to the other one and the ion pair behaves as a single molecule, with multifaceted self-assembly properties in water [1–3]. For instance, at high concentration, they can form extensively swelling lamellar phases in binary systems [4,5] and microemulsions in ternary systems [6,7]. If instead of being double-chained, the catanionic is paired from a single- and a double-chained or from two double-chained surfactants, some important modifications of the lyotropic phase behavior occur. Thus, the catanionic obtained from sodium dodecyl sulfate and didodecyldimethylammonium bromide yields a bicontinuous cubic phase [8] and the one from the latter and the branched double-chained AOT yields a reverse hexagonal phase [9]. This effect can be understood, since as the number of chains increase from two to three and four, the effective surfactant parameter gradually becomes larger than unity; i.e., the spontaneous curvature of the catanionic film gradually becomes more negative.

The catanionic ion pair is also a Gibbs component present in nonequimolar catanionic mixtures, in addition to the simple salt, water, and the excess ionic surfactant [8]. These pseudo-ternary mixtures have the significant property of yielding, at low surfactant concentration, various mixed micelle geometries and spontaneously formed stable vesicles [8,10–14]. Several studies show that catanionic vesicles and bilayers possess a characteristic thermotropic gel-to-liquid crystal phase transition, similar to double-chained lipid vesicles [15–18]. Even some water-soluble catanionics (no salt

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present) form micellar and vesicular aggregates [1,2,19–21]. For instance, rigid nanodisks and catanionic vesicles, bearing a polyhedral shape, have recently been shown to form, under salt-free conditions, in aqueous mixtures of myristic acid and cetyltrimethylammonium hydroxide [18,22].

Despite this strong interest in the phase behavior of catanionic surfactants, several aspects deserve even further investigation, in particular the relation between geometry and self-assembly, with the goal of designing more efficient surfactants for vesiculation, viscosity control, and microemulsions, among other applications. Besides the lyotropic behavior, catanionics also display fairly interesting thermotropic behavior, exhibiting a stepwise melting from the solid crystalline to the liquid phase [8,23–25]. The formation of thermotropic liquid crystalline (lc) phases by certain classes of amphiphiles has been known and studied for some time, in particular for lipids [26–34] and metallic soaps [35,36]. Both the lyotropic and thermotropic behavior of amphiphiles are directly connected to molecular chemistry and geometric shape [31,37,38]. From the thermotropic viewpoint, catanionics appear to possess a greater number of lc phases than other mesogen-forming amphiphiles, owing to the more complex chain packing and headgroup interactions. When heated, catanionics often show polymorphism (as observed for lipids); moreover, several lc phases, mainly of the smectic type, have been observed [23–25]. With respect to chain length, the asymmetric catanionics have been pointed out to have richer behavior than the symmetric ones [24], probably due to the more unfavorable crystalline packing and hence the stabilization of liquid crystalline mesophases.

In a previous paper, it has been seen for a series of double-chained catanionics that headgroup chemistry and volume constraints play a determinant role in the melting behavior [25]. In this work, we extend to the study of the thermal behavior of catanionics to a series of triple-chained catanionics, formed by the pairing of a dioctadecylammonium chain and an anionic single chain. The synthesized compounds bear an even higher degree of asymmetry as compared to double-chained catanionics, due to the unequal number of chains in each ionic part and the unequal chain length. Based on the obtained results, some conclusions as to the chemical nature of the surfactant (charge density of the headgroups, symmetry and length of the hydrophobic chains) and mesophase formation will be presented.

2. Materials and methods

Catanionic surfactants were synthesized by the direct mixture of equimolar solutions of the sodium salts of the anionic surfactant and the cationic surfactant, according to previously reported procedures [1,4,5]. A small excess of the anionic surfactant was used in order to facilitate the solid purification. The catanionic precipitate was washed several times with cold high-purity Millipore water to remove the resulting NaBr and traces of coprecipitated ionic surfactant. The following anionic surfactants were used: sodium octylsulfate (99% from Merck), sodium octylsulfonate (99% from Sigma), and sodium benzenesulfonate (99%, from Merck), sodium decylsulfate (99%, from Sigma), and sodium decylcarboxylate and sodium dodecylsulfate (99%, from Sigma). The cationic surfactant dioctadecyldimethylammonium bromide (>99%) was purchased from TCI, Tokyo. The synthesized compounds are depicted in Fig. 1. Elemental analysis shows, as expected from previous work [4,25], that all the compounds are in good purity without traces of salt or excess surfactant.

DSC scans were made using a Setaram DSC141 calorimeter. Samples were weighed to aluminum crucibles, and an empty crucible was used as a reference. Heating–cooling–

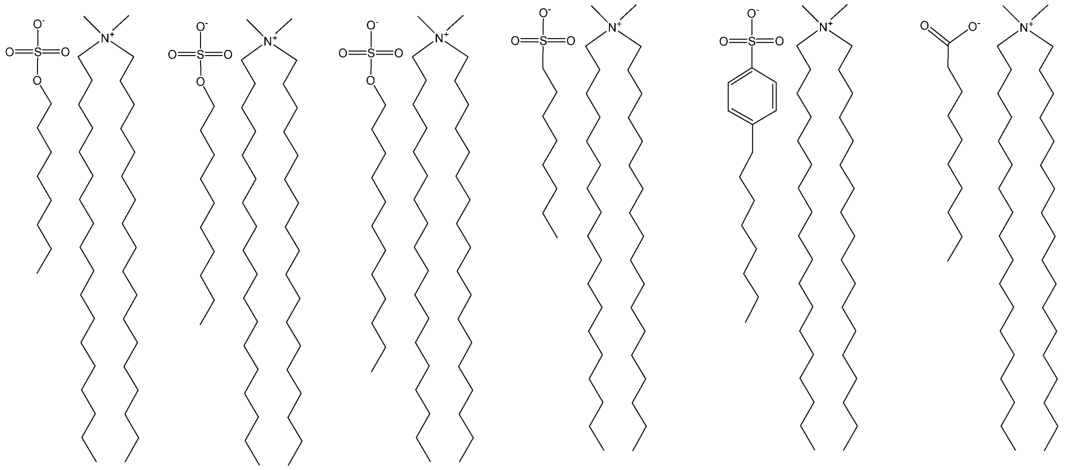
$2C_{18}C_8(S)$ $2C_{18}C_{10}(S)$ $2C_{18}C_{12}(S)$ $2C_{18}C_8(So)$ $2C_{18}C_8(BzSo)$ $2C_{18}C_{10}(Cx)$

Fig. 1. The molecular structure of the catanionic surfactants $2C_{18}C_8(S)$, dioctadecyldimethylammonium octylsulfate; $2C_{18}C_{10}(S)$, dioctadecyldimethylammonium decylsulfate; $2C_{18}C_{12}(S)$, dioctadecyldimethylammonium dodecylsulfate; $2C_{18}C_8(So)$, dioctadecyldimethylammonium octylsulfonate; $2C_{18}C_8(BzSo)$, dioctadecyldimethylammonium benzenesulfonate; $2C_{18}C_{10}(Cx)$ dioctadecyldimethylammonium decylcarboxylate.