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The nature of the coacervate formed in the aqueous dodecyltrimethylammonium bromide–sodium 10-undecenoate mixtures

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Abstract

The formation of a coacervate in mixtures of dodecyltrimethylammonium bromide (DTAB)–sodium 10-undecenoate (SUD) aqueous mixtures was studied by light scattering, ζ potential measurements, and electronic microscopy. The coacervate appears when the ζ potential goes to zero, and the energy barrier against agglomeration disappears, promoting the agglomeration of micelles. Rod-like micelles agglomerate in bundles in the DTAB-rich side of the phase diagram, while spherical or globular micelles agglomerate in clusters in the SUD-rich side. This difference explains the differences in the transition micelles–coacervate in the opposite sides of the two-phase region.

Keywords: Coacervate; Dodecyltrimethylammonium bromide; Sodium 10-undecenoate; Catanionic mixtures; Mixed surfactants

1. Introduction

Research on surfactant mixtures is of considerable interest for numerous technical applications because surfactant mixtures enhance performance when compared to single surfactants. When mixing surfactants, specially oppositely charged ones, not only the properties of components are combined, but in many cases, new properties are found. These properties are of both fundamental and commercial interest, since surfactants used in industrial applications (e.g. detergents, tertiary oil recovery, drug carrier systems, flotation) are often mixtures. In spite of their widespread use, surfactant mixtures are not well understood at a fundamental level. It is important to have a general understanding of the mechanism of interactions between the surfactants in mixed systems and of the factors influencing various features of the phase equilibrium. Surfactant mixtures for specific applications are often chosen based on experience, empirical evidence, or trial and error research. To optimize the applications of surfactant mixtures, it is important to understand the interplay of forces that govern the phase behavior.

Aqueous mixtures of anionic and cationic surfactants exhibit many unique properties that arise from the strongly electrostatic interactions between the oppositely charged head groups. These systems have attracted the attention of numerous investigators [1–6].

There are theories that consider the influence of the structure of the micelle polar layer and electrostatic effects on micellization [7–10] and mixed micellization [8–10]. To improve these theories, it is necessary to have a good knowledge of the factors affecting the formation of micelles and their structure.

In general, the studied cationic–anionic surfactant mixtures are composed of strong electrolytes such as alkyltrimethylammonium halides and alkaline salts of alkylsulfonic acids. It is interesting to explore the effect of the mixed micellization on some properties such as hydrolysis when one of the components is a salt of a weak acid or a weak base. In a study on the effect of the presence of double bonds on the properties of a catanionic system, the aqueous dodecyltrimethylammonium bromide (DTAB)–sodium undecenoate (SUD) mixtures, we found that the system did not precipitate, even at 1:1 SUD:DTAB propor-

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tion, but showed the formation of a coacervate in a range of surfactant mixture composition. When SUD is added to DTAB micelles, the coacervate suddenly appeared at the mole fraction of SUD (without considering water) $\alpha_{SUD} = 0.44$. When $\alpha_{SUD} = 0.63$, the coacervate starts a gradual disappearing, and becomes a one-phase solution at $\alpha_{SUD} = 0.675$. Micelles have a preferential composition of 0.37 mol fraction of SUD. This behavior is attributed to the presence of the double bound at the distal extreme of the SUD molecule, which can form hydrogen bonds with water. In consequence, the $–CH{=}CH_2$ groups are situated at the interface between the hydrocarbon micelle core and water, reducing the interfacial free energy. Structural computations demonstrate that the mentioned SUD proportion produces complete coverage of the micelle surface by the double bonds [11]. This system also shows an unusual hydration behavior, and the partial molar volume of the mixtures is not ideal [12].

Coacervate formation was also detected in the system sodium decanoate (SD)–dodecyltrimethylammonium chloride (DoTAC) by Sjöblom and Edlund [13] in the range $\alpha_{SD} = 0.44–0.58$. In this case, the formation of a coacervate was attributed to geometrical constraints caused by the difference in chain length. The systems DoTAC–sodium hexadecanoate [13], DoTAC–sodium octanoate [13] and DoTAC–sodium nonanoate (SN) [14] did not show formation of coacervate, whereas the system DoTAC–sodium dodecanoate (SDo) gives rise to precipitation [14]. The system didodecyldimethylammonium bromide (DDAB)–sodium taurodeoxycholate (STDC) also shows coacervate formation [15].

In this work, we studied the evolution of the surfactant aggregates in the aqueous DTAB–SUD mixtures when approaching to the two-phase region from both sides of the composition diagram.

2. Experimental

Sodium undecenoate (SUD, 99% Aldrich) and dodecyltrimethylammonium bromide (DTAB, 98% Aldrich) were employed as received.

To prepare the different samples, the appropriate amount of both surfactants was weighed and dissolved in double-distilled water to produce two concentrated solutions. Then the appropriate volume of each solution was poured into a volumetric flask to prepare mixtures with mole fraction of SUD (without considering water) $\alpha_{SUD} = 0$ (pure DTAB solution), 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1 (pure SUD solution).

Using the critical micelle concentrations (CMC) from literature [11] that are shown in Table 1, all solutions were prepared at concentrations above this concentration.

Table 1
Critical micelle concentration of DTAB–SUD mixtures obtained from reference [11]

α_{SUD}	CMC (mmol dm^{-3})
0	15.2
0.1	1.67
0.2	1.84
0.3	2.06
0.4	2.91
0.7	2.50
0.8	5.66
0.9	5.45
1	120

Light scattering measurements were made in Zetasizer 2700 Malvern 90 and 18 °C, $\lambda = 488.0$ nm, intensity 3.96, dispersant RI = 1.331.

Zeta potentials were obtained with a Zetamaster Model 5002 (Malvern Instruments, England) by taking the average of (at least) five measurements at stationary level. The cell used was a 5 mm × 2 mm rectangular quartz capillary.

To produce the uranyl staining of the different samples, 1 mL of each solution (with different α_{SUD} and $C = 2CMC$, 4CMC, and 10CMC) was mixed with 1 mL of 2% aqueous uranyl acetate and sonicated for ca. 20 s in an ultrasonic bath. The final concentration of samples was the CMC, 2CMC, and 5CMC, respectively. Then, the mixture was incubated in an ice-water bath for 30 min and applied to a carbon-coated Cu grid and then dried under vacuum.

The size of micelles and aggregates were determined by measurement on amplifications of the TEM photographs using a measurement microscope with 1/50 mm resolution.

A JEOL 100 CX II transmission electron microscope was used for the measurement, operating at 100 kV with a magnification of 100,000×.

To determine the composition of the two phases of the coacervate, samples of the upper and lower phases were studied. The density of the phases was obtained by weighing a known volume of the sample, and then it was dried to determine the water content. Another sample of the same phase was conductimetrically titrated with HCl to determine the SUD content, and the DTAB content was determined by subtraction of the quantity of SUD in the dry residue of the phase.

3. Theory

3.1. The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory

The theory of the stability of lyophobic colloids independently developed by Derjaguin and Landau [16] and Verwey and Overbeek [17] is known as the DLVO theory. This theory is based on the additivity of the attractive energy of interaction between two colloidal particles whose surface is separated by the distance D, caused by van der Waals forces, $W_{vdW}(D)$, and the repulsive electrostatic energy $W_E(D)$:

$$W_{DLVO}(D) = W_E(D) + W_{vdW}(D) \tag{1}$$

The electrostatic interaction energy between two spherical micelles was taken as [18]:

$$W_E(D) \approx 2\pi r_M \varepsilon\varepsilon_0 \psi_0^2 e^{-\kappa D} \tag{2}$$

where D is the closest distance between the surfaces of both micelles, r_M is the micelle radius, ε_0 is the vacuum permittivity, ε the dielectric constant of the medium (water), κ is the inverse of the Debye distance, and ψ_0 is the electric potential at