



Effect of alkyl chain asymmetry on catanionic mixtures of hydrogenated and fluorinated surfactants

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ARTICLE INFO

Article history:

Received 1 July 2009

Accepted 5 September 2009

Available online 2 October 2009

Keywords:

Fluorinated
Hydrogenated
Catanionics
Rheology
Mixed

ABSTRACT

In this work we studied and compared the physicochemical properties of the catanionic mixtures cetyltrimethyl-ammonium bromide–sodium dodecanoate, cetyltrimethyl-ammonium bromide–sodium perfluorodacanoate, octyltrimethylammonium bromide–sodium perfluorodacanoate and cetyltrimethyl-ammonium bromide–sodium octanoate by a combination of rheological, transmission electron microscopy (TEM) and polarized optical microscopy measurements. The binary mixtures of the surfactants have been analyzed at different mixed ratios and total concentration of the mixture. Mixtures containing a perfluorinated surfactant are able to form lamellar liquid crystals and stable spontaneous vesicles. Meanwhile, system containing just hydrogenated surfactants form hexagonal phases or they are arranged in elongated aggregates.

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1. Introduction

The study of mixtures of surfactants is a subject of great interest both from practical and theoretical points of view. In the first case a fundamental understanding of these systems is required for different industrial and daily applications such as detergents, cosmetics or pharmaceutical and petroleum industry. The second case is focused on the variety of behaviors that the mixtures can show as compared to those showed by pure surfactant systems. In this sense, many scientists have devoted particular attention to mixtures of cationic and anionic surfactants. In 1987, P. Jokela, B. Jönsson and A. Khan introduced the term “catanionic” to designate an equimolar mixture of two oppositely charged surfactants (the parent surfactants) from which the inorganic counterions are completely removed. The catanionic surfactant thus has no net charge, and one long alkyl chain organic ion acts as a counterion of the other [1–3]. These systems have allowed cheap and good-quality samples to be manufactured for the development of nanotechnology due to the wide range of aggregate microstructures by adjusting composition and packing parameters. The range of different structures observed in these systems is largely a result of electrostatic interactions between charged heads. As a general tendency, spontaneous formation of thermodynamically stable vesicles appears to be a feature of these mixtures [4]. Kaler et al. proposed that highly nonideal mixing of the two kinds of surfactants groups was held responsible for the stability [5]. Zemb

et al. have shown that can form hollow aggregates with a regular icosahedral shape, which are stabilized by the presence of pores located at the vertices of the icosahedra [6a,b]. Recently Rico-Lattes and co-workers have demonstrated the role of the cohesive energy parameter on catanionic systems [7a,b].

In the last years there was an increasing interest in mixtures of fluorocarbon- and hydrocarbon-based surfactants that have been reported to have a limited mutual solubility. Initially, the coexistence of two types of micelles, one fluorocarbon-rich and another hydrocarbon-rich was postulated on the basis of the mutual repulsion of surfactant alkyl moieties [8,9]. However, based on ¹⁹F and ¹H chemical shift data, Nordstierna et al. [10] have recently proposed a single type of micelles within which fluorinated surfactants are preferentially coordinated by fluorinated ones and hydrogenated surfactants by hydrogenated ones.

It is not straightforward to find experimental studies dealing with the effect of the symmetry, or asymmetry, between both alkyl chains. In the first case the lattice of liquid crystal energy is lower and the system can precipitate or form packed vesicles in equimolar ratio. For the second case due to the different alkyl chain length, a dense packing is sterically unfavorable and instead of precipitates or vesicles, elongated micelles are formed due to favorable packing. Thus, precipitation can be avoided if surfactants contain one long and one short alkyl chain [11–13]. However, it is important to take into account that some irregular behavior could be related to the even alkyl chain carbon numbers of the tail [14,15].

In this work, we extend our earlier studies on diluted mixtures of hydrogenated and fluorinated mixtures [16–18] to obtain highly viscous fluids or liquid crystals at low total surfactant con-

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centration, focusing on the effect of the alkyl chain length, mixed ratio and the substitution of H by F atoms. The hydrogenated cationic surfactants chosen were octyltrimethylammonium and cetyltrimethyl-ammonium bromide. The anionic hydrogenated surfactants were: sodium octanoate and dodecanoate, and the fluorinated ones were sodium perfluorooctanoate and sodium perfluorodecanoate. Rheology, transmission electron microscopy and polarized optical microscopy were used to track the behavior of the different systems.

2. Experimental

2.1. Materials

Octyltrimethylammonium bromide (C8TAB), cetyltrimethylammonium bromide (CTAB), sodium octanoate (C8HONa), sodium perfluorooctanoate (C8FONa) and sodium perfluorodecanoate (C10FONa) of at least 97% purity were obtained from Lancaster Synthesis Ltd. Sodium dodecanoate (C12HONa) with purity over 99%, were obtained from Sigma Chemical Co. All materials were of analytical grade, and solutions were made using doubly distilled and degassed water.

2.2. Rheology

Rheological experiments were performed on a Bohlin CS-10 stress-controlled rheometer. A Couette geometry with a cup of 27.5 mm diameter and a bob type Mooney cell was used. The cell was heated by a reservoir of fluid circulating from a Julabo thermostated bath. The sample was equilibrated for at least 20 min at each temperature prior to each experiment. Both steady and dynamic rheological experiments were performed at each temperature. Dynamic frequency sweep measurements were performed in the linear viscoelastic regime of the samples, as determined previously by dynamic stress sweep measurements. For the steady-shear experiments, an equilibration time of 90 s was given at each shear stress.

2.3. Transmission electron microscopy (TEM)

The morphological examination of the structures was performed by transmission electron microscopy (CM-12 Philips). Samples for TEM were prepared by the negative-staining technique with a 2% (w/v) phosphotungstic acid. A carbon Formvar-coated copper grid was put into the solution for 1 min and then into the sodium phosphotungstate for another 1 min. Then the grids are dried. In between and thereafter, excess liquid was sucked away with filter paper. For each system, at least two TEM samples were prepared and observed independently.

2.4. Polarized optical microscopy

Samples were placed between two glass slides and observed between crossed polarizers in a Nikon Eclipse E20 polarizing microscope with a COPLIX 54 electronic camera. The samples were then left to evaporate to detect the phases formed as a function of decreasing peripherally water content. The peripheral evaporation technique consists of letting the samples to slowly evaporate through the limits of the cover slide, thus creating a concentration gradient from dry crystals outside to the original solution at the center of the sample. Subsequently, a drop of water was added to produce peripheral dilution and observe the formation of hydrated phases.

3. Results and discussion

3.1. CTAB-C12HONa system

At the beginning of this study different samples at different total concentration (C_T) and mixed ratios, α_F (where α_F is the mole fraction of the anionic surfactants in the mixture, without considering the solvent) were prepared and analyzed by visual inspection. Only samples which exhibit viscoelastic properties were studied in detail. For the system CTAB-C12CHONa this was just possible for a total concentration (C_T) of 90 mM and mixed ratio of $\alpha_F = 0.6$. Polarized microscopy has been used to characterize the phase behavior of this system at higher concentrations. It has been observed that the system present a strong tendency to form a hexagonal liquid crystalline phase formed by non isotropic elements. The striated and fanlike texture from Fig. 1a and b, respectively, of hexagonal phase are based on arrangements of the cylindrical molecular aggregates. The fanlike texture is the type of focal conic variation designated “fan structure”. The fan is a composite of focal domains whose hyperbolas are so elongated that they appear as a group of straight lines converging from their respective focal regions to a common point; the focal conic geometry, if visible at all, would thus be sought at the outer edge of each sector of the fan [19a,b]. The rheological study performed for this system is illustrated in Fig. 2. At intermediate shear rates, the sample show non-newtonian shear thinning, whereas at higher shear rates a shear thickening behavior can be observed with a critical shear rate of about $3 \times 10^3 \text{ s}^{-1}$. Shear thickening has been reported for other surfactant systems usually containing diluted rod-like micelles a few tens nanometers long [20]. These micelles undergo free Brownian motions at equilibrium state or under slow shear rates. However, they tend to align in the shear flow when the applied shear rate is above a critical value. In the end, larger aggregates are formed and flow birefringence is increased [18].

3.2. CTAB-C8FONa system

Following the same protocol, we have centered our measurements in the total concentration range from 200 to 300 mM and mixed ratio of $\alpha_F = 0.1$. Polarized microscopy of this sample show a typical Maltese cross texture which is typical of lamellar structures. Other surfactant solutions in the lamellar region had smooth sand-like or marble-like textures that are also consistent with lamellar phases [21] (Fig. 3). The rheological behavior is presented in Fig. 4. For both concentrations and at low shear rates, the samples show Newtonian behavior; however, above a certain critical shear rate the viscosity decreases as in a shear thinning fluid, also known as pseudoplastic system. The onset of thinning behavior takes place at a lower critical shear rate as the surfactant concentration increases. This non-Newtonian flow response and the corresponding increase in viscosity with concentration are attributable to structure-forming interactions and the anisometric nature of vesicles that orient themselves at high shear rates [22]. In fact, based in the phase diagram reported for this system by Hentze et al. [23] our samples are placed in the vesicle + lamellar liquid crystal region. The results of oscillatory shear measurements are shown in Fig. 4b. In these systems, liquid-like behavior ($G' < G''$) is observed in the low-frequency region, but both G' and G'' increase with frequency and viscoelastic behavior ($G' > G''$) is observed in the high frequency region for the most concentrated sample. The system is thus viscoelastic in a wide range of frequencies.

3.3. C8TAB-C10FONa system

For this system we have focused on a concentration range from 10 to 20 mM (with $\alpha_F = 0.6$ and 0.8). Polarized microscopy (not

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