



Influence of organic acids on surfactant self-assemblies in surfactant/oil/water systems



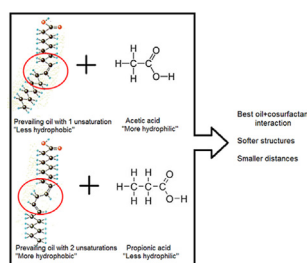
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HIGHLIGHTS

- The structure of surfactant self-assemblies was dependent on the affinity between the cosurfactant and oil.
- Oil more unsaturated allowed high solubilization of acid with bigger carbon chain.
- Oil less unsaturated allowed high solubilization of acid with smaller carbon chain.
- Acetic acid was more susceptible to partition in comparison to propionic acid.

GRAPHICAL ABSTRACT



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ABSTRACT

The cosurfactant effect of short-chain organic acids (acetic and propionic acids) and their behavior in relation to the oil prevailing unsaturation (HOSO or sunflower oil) was evaluated from SAXS and rheological measurements in systems formed by water, oil, Tween80 and the organic acid. Self-assembly of the surfactants was influenced by the structure and ratio of the components, which formed different structures (microemulsions and liquid crystal) with different rheological behaviors. The water content exerted influence on the organization of the surfactant moieties and on the dissociation of the cosurfactant, modifying its partition to the water phase. Systems with acetic acid formed more rigid structures with higher viscosity, shear-thinning behavior and bigger distances between the structures due to the tendency of this acid to migrate to water phase. On the other hand, propionic acid was less susceptible to dissociation, being in its neutral form, which makes it able to remain at the interface and solubilize higher oil content. As a result, structures were softer with lower viscosity and slightly smaller distances between them. The interaction between oil and cosurfactant exerted influence on the colloidal properties that reflected on bulky properties. In general, the more hydrophobic oil (sunflower oil) facilitated the partition of the acetic acid to the water, giving to this structure greater distance, as compared to HOSO + acetic acid. Thus, small differences in the structure of the components can influence the interaction between them, changing the partition of the components and the surfactant behavior.

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1. Introduction

Surfactant molecules can self-assemble into a large variety of morphologies, including microemulsions and liquid-crystalline (LC) phases, such as lamellar, hexagonal, or cubic phases [1]. These systems are formed spontaneously and they are composed by

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oil and water stabilized by an interfacial film of organized surfactant [2]. As these systems provide both organic and aqueous environment, they can simultaneously solubilize large amount of hydrophilic and hydrophobic compounds [3,4], including food additives, flavors, nutraceuticals, cosmetics, active ingredients, and drugs [5]. In addition, these systems are typically associated with a cosurfactant in order to make the interface more flexible, contributing to the formation of microemulsions or swollen micelles [6]. However, the properties of these spontaneous systems are dependent on various factors such as the rigidity of the amphiphilic surfactant, type of oil, cosurfactant, and temperature [7–9].

Many recent studies have been performed with the aim of preparing microemulsions using ingredients accepted by food industries, but most of the reported works have used at least one non-biocompatible ingredient or cyclic oils (which are highly susceptible to oxidation) [10–12]. Tryacylglycerols (vegetable oils) are an alternative to the use of cyclic oils, but the possibility of using vegetable oils as the oil phase has been scarcely investigated despite their economical and nutritional importance. Sunflower oil (*Helianthus annuus* L.) is one of the most commonly used vegetable oil consisting of about 90% of unsaturated fatty acids, which are mainly oleic (C18:1, 16–19%) and linoleic (C18:2, 68–72%) [13]. In order to enhance the use of sunflower oil, new varieties have been selected, where the main fatty acid is represented by oleic acid and this oil is denominated high oleic sunflower oil (HOSO) [14]. Polyoxyethylene sorbitan esters (Tweens) are probably the most widely used surfactants, showing the polyoxyethylene head groups attached to a sorbitan ring, which increases the hydrophilicity of the sorbitan fatty esters. Regarding the cosurfactants, alcohols are the most used in microemulsion formulations and ethanol is the less toxic between the alcohols [15,16], but the alcohol addition restricts their application. In this respect, the use of organic acids as cosurfactants have been recently reported as an alternative to the use of alcoholic compounds [8,17–20]. These acids increase the one transparent single region in the phase diagram, acting as cosurfactant and cosolvent. Behavior of different organic acids in microemulsions depends on their chain length at the same way of alcohols [17,19,20]. The *n*-alkyl acids with longer chain are capable of solubilizing higher water content in W/O region. Thus, the aim of this work was to construct phase diagrams using sunflower oil or HOSO, water, Tween 80 as surfactant and short-chain organic acids as cosurfactant in order to form W/O and O/W systems, evaluating the effect of the prevailing oil unsaturation in association with the cosurfactant characteristics on microemulsion and liquid crystalline production.

2. Material and methods

2.1. Material

Sunflower oil and HOSO were kindly donated by Cargill (Mairinque, Brazil) and surfactant polyoxyethylene sorbitan monooleate (Tween 80) was purchased from Sigma-Aldrich Co. (EUA). The cosurfactants propionic acid 99.5% (Vetec, Brazil) and acetic acid 99% (Synth, Brazil) were of analytical grade.

2.2. Phase behavior and diagram construction

The four-component systems (Table 1) were described using pseudo-ternary diagrams produced by spontaneous emulsification method at room temperature (25 °C). The influence of the prevailing oil unsaturation was performed using sunflower oil or HOSO with different cosurfactants. An initial mixture of surfactant, cosurfactant, and oil was prepared under magnetically stirring at different ratios of surfactant:oil + cosurfactant (10:90, 20:80,

30:70, 40:60, 50:50, 60:40, 70:30, 80:20, and 90:10) [21]. The oil:cosurfactant ratio (1:2) was used in order to obtain a higher one single phase area and make easier the microemulsion formation [22]. Then, deionized water was titrated to the initial mixture under constant stirring with volume increments of 10% (w/w) forming water dilution lines 1 up to 9. Line 1 corresponds to the initial mixture of surfactant 10% (w/w) and oil + cosurfactant 90% (w/w), and so on up to line 9, with surfactant 90% (w/w) and oil + cosurfactant 10% (w/w). Each system was named according to its formulation: first, in accordance to the initial surfactant concentration and then with the water content. For example, a system on line 8 (initial surfactant concentration 80%, w/w), diluted with water 40% (w/w) was denominated as 8040. Each formulation was kept for 15 min under stirring and then they were stored at 25 °C for at least 1 week before to construct phase diagrams.

2.3. Phase diagram characterization

After the construction of phase diagrams, they were delimited in different regions. The transparent one phase region was characterized as microemulsion O/W (L_1), W/O (L_2), or liquid crystalline (LC) from polarized light microscopy, electrical conductivity, small-angle X-ray scattering (SAXS), and rheological measurements. Firstly, the polarized light microscopy was performed to identify the liquid crystalline zone, and conductivity measurements were carried out in order to identify the continuous phase of the microemulsions (L_1 or L_2). The conductivity of the samples was determined at 25 °C using a bench top conductivimeter Orion 3 Star (Thermo Electron Co., USA) coupled to a conductivity cell (Orion 013016MD). For light-polarized microscopy, a drop of the sample was placed between a cover slip and a glass slide to be examined under polarized light. An optical microscope Olympus BX51TF (Olympus, Japan) equipped with a digital camera was used to analyze the samples at room temperature. The isotropic or anisotropic behavior of the samples could be observed and pictures were taken at a magnification of 20×. In addition, characteristic parameters of the systems were obtained, including the total LC region (A_{LC}), the microemulsion area ($A_{O/W}$ and $A_{W/O}$), the maximal amount of aqueous phase dispersed in the W/O ME (W_m), and the minimum surfactant concentration at this corresponding condition (Sm) [12,23]. At last, systems corresponding to the dilution lines 8 and 9 (single phase) were subjected to SAXS and rheological measurements in order to better define and characterize the microemulsions and liquid crystalline structures.

2.4. Microemulsions and liquid crystalline characterization

2.4.1. Small-angle X-ray scattering (SAXS)

Quantitative information of the LC and microemulsion structures was obtained by means of small-angle X-ray scattering (SAXS) measurements performed at room temperature using the beamline of the National Synchrotron Light Laboratory (LNLS, Campinas, Brazil). The beamline is equipped with an asymmetrically cut and bent silicon (111) monochromator that yields a monochromatic ($\lambda = 1.54 \text{ \AA}$) and horizontally focused beam. A position-sensitive X-ray detector and a multichannel analyzer were used to record the SAXS intensity, $I(q)$, as a function of modulus of scattering vector q , where $q = (4\pi/\lambda) \sin(\theta/2)$, with θ being the scattering angle. Each SAXS pattern corresponds to a data collection time of 100 s. Microemulsion patterns are formed by one peak, which can be related to the distance between the micellar structures according to Eq. (1):

$$d = \frac{2\pi}{q} \quad (1)$$

where d is the structure distance and q the scattering vector.

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