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Temperature and composition effects on the morphology of o/w dispersions based on poly(oxyethylene 20) sorbitan monolaurate and sorbitan monolaurate

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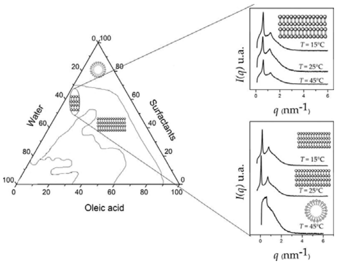
GRAPHICAL ABSTRACT



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ABSTRACT

Phase behavior of colloidal systems containing oleic acid, poly(oxyethylene 20) sorbitan monolaurate, sorbitan monolaurate, and water were studied as a function of composition and temperature. The pseudo-ternary diagram of the resultant dispersions showed the presence of regions related to the occurrence of microemulsions, gel microemulsions, high viscosity emulsions, and low viscosity emulsions. SAXS indicated that compositions with surfactant contents above 50% presented lamellar structures. The same technique was used to detect that this structure was destroyed at 45 °C for systems with oleic acid contents of 10%, while dispersions with 1.5, 2, and 5% of oleic acid did not have their lamellar structure disrupted at this temperature. It indicated that, at the highest oleic acid content used in this work, non-ionic surfactants tended to interact with each other, destroying lamellar structure and promoting cloud point-related phenomena, as indicated by turbidimetry and DLS.

1. Introduction

Surfactants commonly are components of formulations used in plastics, fibers, detergents, paints, agriculture, pharmaceuticals, cosmetics, food, and oilfield formulations [1–3]. Among them, non-ionic ones have extensively been studied, due to their low toxicity and because their physicochemical properties remain unaltered over a broad pH range, which is a key factor for their use in many manufacturing activities, as markedly is the case of food, pharmaceutical, and cosmetic industries [4–7].

It is well-known that the formation of self-assembled structures, such as micelles, vesicles, microemulsions, and liquid crystals, needs (besides amphiphilic molecules as surfactants) adequate composition and emulsification process [8]. In order to obtain these systems, emulsification sometimes requires high-energy input from stirring, resulting in phase transition taking place through the emulsification process [9,10]. One must point out, however, that there may be interconversion between different forms of colloidal association as a function of temperature [11]: *e.g.*, at a specific temperature, called phase inversion temperature (PIT), the molecular effect of temperature on the

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hydration of hydrophilic heads of non-ionic surfactants translates into a decrease in this layer, resulting in micelle curvature decrease and increase in micellar swelling [12]. Alkyl ethoxylate nonionic surfactants are soluble in aqueous media due to hydrogen bonding between water and surfactant molecules, which breaks down as temperature is increased, resulting in cloudy or turbid solutions. This particular temperature is called the cloud point [13].

One may find in the literature some examples of transparent microemulsions formed with high surfactant/organic (or oil phase) ratio: *e.g.*, Koneva et al. have prepared microemulsions made with two nonionic surfactants and an alcane as organic phase, with 13% of surfactant content and a surfactant:decane mass ratio of 35:65 [14]. Lecithin may self-assemble as wormlike micelles, resulting in transparent and viscous gel-like systems [15]. Stable colloidal systems may be formed with lower surfactant:oil ratios: in this case, these translucent systems required high surfactant contents [16]. The resultant emulsion droplets were trapped in a viscous liquid crystal matrix, preventing coalescence and emulsion-breaking.

The dependence of solubility on temperature and concentration of polyoxyethylene and polyoxyethylene based surfactants have widely been characterized [17–20]. Streck et al. have shown that systems with medium chain triglycerides can be used in pharmaceutical applications [21]. In order to achieve a better understanding of these systems using nonionic surfactants, we chose to work with oleic acid as the oil phase, since this molecule is less complex than ordinary triglycerides: the resultant analysis, as a consequence, is expected to be more representative of the influence of the surfactants on the system as a whole. In order to do it, in this work we aim to study the influence of composition and temperature on the form of colloidal association of systems based on non-ionic surfactants [poly(oxyethylene 20) sorbitan monolaurate and sorbitan monolaurate], oleic acid, and water, obtained by high-energy emulsification method. Colloidal structure interconversion, as a function of temperature, will be followed using small-angle X-ray scattering (SAXS), turbidimetry, and dynamic light scattering (DLS) and the resultant morphological transitions will be correlated to dispersion composition.

2. Experimental

Poly(oxyethylene 20) sorbitan monolaurate (Tween 20) and sorbitan monolaurate (Span 20) were purchased from Sigma Aldrich Co. (St. Louis, MO, USA). Oleic acid was purchased from Vetec (Brazil) and bi-distillated water was used in all experiments.

2.1. Pseudo-ternary phase diagram

A pseudo-ternary phase diagram was built to identify the occurrence of different organized regions of dispersed systems with different mass contents of four components: oleic acid (w_O), surfactants (w_S) Span 20 and Tween 20 (at constant mass ratio of 1:1.5), and bi-distilled water (w_W). These surfactants usually are combined in formulations, as they have a considerable difference in HLB: a mix of them, consequently, decreases surface tension more efficiently than many single surfactants [22]. The ratio used in this work was based on preliminary experiments we carried out, as at this very ratio we could obtain o/w dispersions both in the form of viscous liquids and gels. The diagram was obtained by titrating with water a mixture of oleic acid with surfactants with compositions ranging from 10:90 to 90:10 (*w/w*) [23]. The areas in the diagram were identified by flow and appearance. If transparent and flow resistant with no separation on further dilution and stirring was observed, it was considered to be a gel microemulsion. If not transparent and flow resistant with no separation on further dilution and stirring was observed, it was considered to be high viscosity emulsion. Finally, if it was fluid, without phase separation, it was considered to be a low viscosity emulsion.

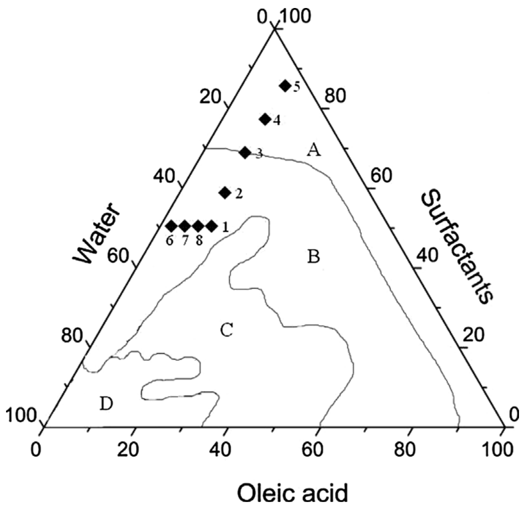

Fig. 1. Pseudo-ternary phase diagram of system based on surfactants Span 20 and Tween 20 at mass ratio of 1:1.5, oleic acid and water. (A) microemulsion region, (B) gel emulsion region, (C) high viscosity emulsion region, and (D) low viscosity emulsion region. The chosen compositions listed on Table 1 are indicated by numbers 1–8.

Table 1
Systems composition according to pseudo-ternary diagram points selected in Fig. 1.

	Systems							
Composition	1	2	3	4	5	6	7	8
Water (%)	50.0	40.0	30.0	20.0	10.0	49.0	47.5	45.0
Oleic acid (%)	10.0	10.0	10.0	10.0	10.0	1.0	2.5	5.0
Surfactants (%)	40.0	50.0	60.0	70.0	80.0	50.0	50.0	50.0

2.2. Sample preparation

The systems were prepared by stirring the components with an ultraturrax DI basic stirrer equipped with dispersing element S 25 N-18 G (YellowLine, Ika GMBH & CO, Germany). Initially the sample was submitted to 20,500 rpm, for 2 min, followed by stirring at 9500 rpm, for 18 min. The resultant sample was taken to the desired analysis after resting 24 h at room temperature. All components were accurately weighted at 0.0001 g.

2.3. Turbidimetry

Turbidity was determined using a Hatch turbidimeter model 2100N (Loveland CO, USA). The instrument was equipped with a tungsten filament lamp, a 90° detector to monitor scattered light, and another one for transmitted light. According to manufacturer, the lamp yielded white light with a continuous spectrum. The instrument's microprocessor calculated the ratio of the signals from the 90° and transmitted light detectors, correcting interferences from color and/or light absorbing materials. All the measurements were taken at 25 °C.

2.4. Dynamic light scattering (DLS)

Dynamic light scattering experiments were carried out using a 90 Plus Particle Analyzer (Brookhaven Instruments Corporation, USA). Data related to the intensity correlation function (ICF), $g^{(2)}(t_D)$, where t_D is the delay time, were collected at 25, 35, 45, 55, 65, and 74 °C (within a precision of 0.1 °C) with a scattering angle $\theta = 90°$.

2.5. Small angle X-ray scattering (SAXS)

SAXS experiments were carried out using a SAXSess camera (Anton