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Stabilization of Foams by Amphiphilic Crystalline Solids and Liquid Crystals

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SUMMARY. In this work, it was experimentally studied the influence over the stability of foams on aerosol of concentrates with pearlescent aspect and, in some cases, with liquid crystalline characteristics, too. The pearlescent, such as the formation of liquid crystalline structures, is the result of the interaction of surfactants with fatty acids or long chain alcohols. Coincidentally with investigations of other authors, it was found that pearlescent concentrates produce very stable foams. It was also determinate that the pearlescent it is not a consequence of liquid crystalline phases, as other authors supposed, but because of solid crystals.

RESUMEN. "Estabilización de Espumas en Aerosol por Sólidos Cristalinos Anfifílicos y Cristales Líquidos". En este trabajo se estudió experimentalmente la influencia sobre la estabilidad de espumas en aerosol de concentrados con aspecto nacarado y, en algunos casos, además con características líquida cristalinas. Tanto el nacarado como la formación de estructuras líquidas cristalinas son resultantes de la interacción de tensioactivos con ácidos grasos o alcoholes de cadena larga. Coincidentemente con investigaciones de otros autores se encontró que los concentrados nacarados dan espumas muy estables. También se determinó que el nacarado no se debe a la presencia de fases líquida cristalinas, como suponían otros autores, sino de cristales sólidos.

INTRODUCTION

Miles *et al.* [1,2] observed that the speed of liquid drainage through foams of sodium lauryl sulfate diminished significantly with the aggregate of lauryl alcohol. This diminution of the drainage speed was attributed to the high viscosity resulting of the formation of a complex between sodium lauryl sulfate and lauryl alcohol. The hypothesis of complex formation was formulated initially by Schulman & Rideal [3], who announced, in 1937, that when a monomolecular film of cetyl alcohol or cholesterol was scattered over an aqueous solution of sodium cetyl sulfate, the cetylsulfate anions penetrated the alcohol film and formed a complex. Becher & Del Vecchio [4] obtained similar results to the ones obtained by Miles, Shedlovsky and Ross using ethoxylated lauryl alcohol joined with lauryl alcohol or cetyl alcohol. Investigating with the system formed by sodium lauryl sulfate, lauryl alcohol and water, Hume [5] observed the presence of abundant crystals that persisted over the melting point of the alcohol and the Krafft point of the soap. These crystals melted between 29 °C and 32 °C to give an isotropous solution which, at higher temperature, transformed into a turbid system with liquid crystalline characteristics.

Sanders [6] observed that, in aerosols formed by surfactants and water, the stability of the emulsions of the propellant on the concentrate and of the foams discharged increased with the presence of polar substances such as long chain alcohol or fatty acids. Sander attributed these results to the formation of complex between the molecules of the surfactants and the polar substances. On another paper, Sanders [7] got structures of pearlescent aspects in systems formed

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by ethoxylated long chain alcohols and water. In some cases, the pearlescent aspect keeps on the presence of the propellant. Sanders attributed this optic effect to the formation of complex that possibly had a liquid crystalline structure. In 1970, this author [8] assumed that as well as in the surface of the propellant emulsion droplet as in the foams on aerosol, the complex had a liquid crystalline structure. Later, in the same paper, Sanders contradicts himself, when proposing that the complexes are found in the solid state and that they stabilized emulsions and foams in the same way that some small inorganic solids particles do. In the same paper, the author suggests again that the pearlescent is the result of liquid crystalline structures. The hypothesis, which says that molecular complex stabilize foams on aerosols and emulsions, was objected by Friberg *et al.* [9] and by Jederström *et al.* [10], who proposed that the stabilization was because of the presence of a liquid crystalline structures. In 1996, Goutev & Nickolov [11] demonstrated, through the Raman dispersion, the presence of two phases on commercial shave foam: a laminar gel phase, formed by molecules of stearic acid (and stearic anions) with all the hydrocarbon chains in trans position and with a hexagonal order between them, and a liquid isotropous phase. According to these authors, the unilamellar structures, which are initially on the concentrate, gradually organize themselves in big multilamellar structures closed around the bubbles.

The influence of the aggregate of small solid particles over the formation and stability of aqueous foams stabilized by surfactants depend on the characteristics of the surfactant and on the size and concentration of the particles [12]. While for surfactants the HLB value is the principal characteristic, in the case of amphoteric particles that are adsorbed in the gas-water interfaces (foams) or water-in-oil (emulsions), the relevant parameter is the contact angle θ between the particle and the interface. For hydrophilic particles, θ is generally lower than 90° and an important part of the surface is in contact with water. For hydrophobic particles, θ is generally bigger than 90° and each particle is more in contact with air or oil than with water. In the first case, the solid particles stabilized aqueous foams and emulsions of the oil in water type, while in the second one stabilized aerosols and emulsions of water in oil type.

Ingredient	S1	S2
Cetyl alcohol		4.8 %
Propylparaben		0.03 %
Polyethylene glycol 400 dilaurate	7.64 %	7.64 %
Methylparaben	0.10 %	0.07 %
Water	92.26 %	87.42 %

Table 1. Composition of the concentrates S1 y S2.

In this investigation, it was experimentally studied the influence over the stability of aerosol foams of concentrates with pearlescent aspect and, in some cases, with liquid crystalline characteristics, too.

MATERIALS AND METHODS

Cetyl alcohol is from Godrej Industries Ltd (India). Stearic acid was provided by Materia Oleochemicals (Argentina); its average relative molecular mass, calculated through the acid value, is equal to 270. Polyethylene glycol 400 dilaurate is from Vasana (Argentina), polyoxyl 10 oleyl ether (Brij 97) is from Uniquema, polyoxyl 20 cetyl ether (Dehydol TA 20) is from Cognis and sodium lauryl sulfate (minimum purity 95%) was obtained from Mallinckrodt Chemical Works. Triethanolamine, of commercial grade, fulfils the established requirements on the Farmacopea Argentina VI. Methylparaben and propylparaben were provided by Ueno Fine Chemicals Industry Ltd (Japan).

Composition of the concentrates

The concentrates are dispersions of surfactants in water with or without the aggregate of stearic acid or cetyl alcohol. These last substances are united to the surfactants and form insoluble crystalline compounds. Concentrates S1 and S5 was prepared in cold and with stirring until dissolution of surfactant and methylparaben. Concentrates S2, S3, S4, S6, S8, S10 and S11 were prepared adding, with stirring, the oleous phase on aqueous phase and concentrates S7 and S9 were prepared mixing the components at 70-75 °C until dissolution.

The concentrate S1 is an aqueous dispersion that contains 0.01 mol of polyethylene glycol 400 dilaurate in 100 grams. The S2 has also 0.02 mol de cetyl alcohol (Table 1).

The concentrate S3 has equimolecular quantities of stearic acid and triethanolamine (0.0185 mol of each one in 100 grams) and the S4 contains, in moles, the double of stearic acid according to triethanolamine (Table 2).

The concentrate S5 posses 0.02 mol of sodium lauryl sulfate per 100 grams, while the S6 has, also, 0.02 mol of cetyl alcohol (Table 3).

Ingredient	S3	S4
Stearic acid	5.00 %	10.00 %
Propylparaben	0.03 %	0.03 %
Triethanolamine	2.75 %	2.75 %
Methylparaben	0.07 %	0.07 %
Water	92.15 %	87.15 %

Table 2. Composition of the concentrates S3 y S4.

Ingredient	S5	S6
Cetyl alcohol		4.84 %
Propylparaben		0.03 %
Sodium lauryl sulfate	5.76 %	5.76 %
Methylparaben	0.1 %	0.07 %
Water	94.14 %	89.30 %

Table 3. Composition of the concentrates S5 y S6.

Ingredient	S7	S8
Cetyl alcohol		2.42 %
Propylparaben		0.03 %
Polyoxyl 10 oleyl ether	7.09 %	7.09 %
Methylparaben	0.1 %	0.07 %
Water	92.81 %	90.39 %

Table 4. Composition of the concentrates S7 y S8.

Ingredient	S9	S10
Cetyl alcohol		2.42 %
Propylparaben		0.03 %
Polyoxyl 20 cetyl ether	11.22 %	11.22 %
Methylparaben	0.1 %	0.07 %
Water	88.68 %	86.26 %

Table 5. Composition of the concentrates S9 y S10.

Ingredient	S11
Stearic acid	10.00 %
Propylparaben	0.03 %
Polyethylene glycol 400 dilaurate	5.00 %
Triethanolamine	2.75 %
Methylparaben	0.07 %
Water	82.15 %

Table 6. Composition of the concentrate S11.

The concentrate S7 posses 0.01 mol of polyoxyl 10 oleyl ether per 100 grams. On the concentrate S8 was incorporated 0.01 mol of cetyl alcohol, too (Table 4).

The concentrate S9 contains 0.01 mol of polyoxyl 20 cetyl ether per 100 grams. On the concentrate S10 it was added 0.01 mol of cetyl alcohol (Table 5).

The concentrate S11 contains 0.0370 mol of stearic acid, 0.0185 mol of triethanolamine and 0.0065 mol of polyethylene glycol 400 dilaurate per 100 grams (Table 6).

Aerosols filling

The aerosol valves, provided by Summit de Sudamérica SRL (Argentina), possessed a body (code 97300) with an orifice of an internal diameter of 2.03 mm on the extreme of insertion of the deep tube and a stem (code 77250) with two lateral orifice of 0.46 mm and an exit orifice of 0.66 mm. The actuator (code 77814) is the one used for shaving foam. The propellant used, denominated A-46, is a mixture of propane and isobutane. The aerosols contain 100 g of concentrate and 5.6 g of propellant. The filling of aerosols was doing in Summit de Sudamérica SRL (Argentina).

Essays done over the foams

Stability

It was discharged approximately 1 gram of foam of each aerosol over two filter papers Whatman 91 of 18.5 cm of diameter, collocated one over the other. It was observed the persistence of the foam alter 1 min, 5 min, 15 min, 30 min, 1 h, 2 h and 3 h. This methodology was proposed by Sanders [6].

Drainage

In order to evaluate drainage, a technique proposed by Sanders [6] was used. It was discharged 5.0 grams of foam on a funnel of glass of 5.1 cm of internal diameter, with an angle of 60 grades and a stem of 5 cm large and 4 mm of internal diameter. It was determined the mass of drained liquid after 1 min and then, alter intervals of 1 min until 10 min passed; and, finally, at 15 and 30 min. On foams with high stability, it was measured the drainage during a maximum lapses of 5 h with intervals of half an hour. Graphically it was determined the time at which the 50% of the mass of each foam drained.

Microscopic observation

It was used an optic microscope Arcano model XSZ-107 E provided of a graduated ocular and a photographic camera; and a polarizing microscope Nikon model HFX-DX, with photographic camera, too. The concentrates were observed with ordinary light and with crossed polarizers.

RESULTS

Concentrates characteristics

S1 is a fluid liquid, white and translucent. At the polarizing microscope, it appears like an isotropic emulsion. There are observed gouts of 1 to 10 µm of diameter. S2 is a liquid of greater viscosity than S1, white, opaque and a bit pearlescent. At the microscope, there are observed crystals surrounded by a similar structure than the one observed in crystals with a spiral growing With the crossed polarizers it is distinguished an abundant amount of extinction crosses, typical of the crystal liquid laminar phase. S3 is a fluid liquid, white and pearlescent. At the microscope, aciculate crystals can be observed, not very contrasted with the back. S4 is a fluid liquid, white and pearlescent. At the microscope crystals with spiral growing with 50 µm of diameter can be observed, not very contrasted with the back. S5 is a transparent fluid liquid. At the polarizing microscope it looks like isotropic. S6 is a fluid liquid, white and pearlescent. At the polarizing microscope there are observed polygonal crystals producing double refraction with a spiral growing (Figs. 1 and 2). S7 is a fluid liquid, transparent and isotropic. In the case of S8, at the first sight, two fluid liquid phases are distinguished: the inferior one is colourless and the superior one is white and pearled. At the microscope; long aciculate crystals producing double refraction are observed, that are disposed parallel between themselves. There are also observed crystals with an approximately circular shape. S9 is a transparent isotropic liquid. In S10. at the first sight, two fluid liquid phases are distinguished: the inferior one is colourless and the superior one is white and pearled. At the microscope aciculate crystals producing double refraction are observed; they present a polygonal shape with spiral growing. In S11, at the first sight, two fluid liquid are distinguished: the inferior one is colourless and the superior one is white and pearled. At the microscope long aciculate crystals are observed, which disposed parallel between themselves, similar to the ones of the concentrate S8. There con also be seen polygonal crystals, not very contrasted with the back, with and without spiral growing; with crossed polarizers, it presents a non geometrical texture (Fig. 3).

Characteristics of the foams

Stability

The most stable foams are those which present a pearlescent aspect.

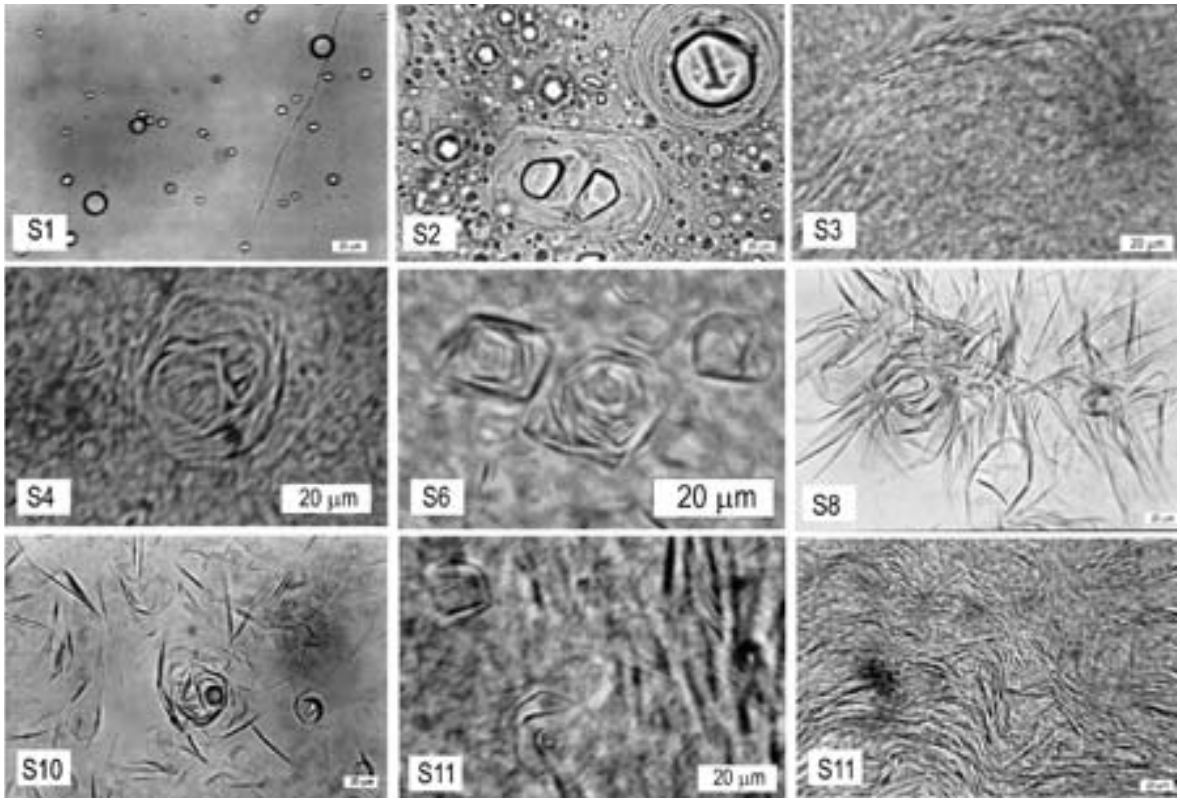

Figure 1. Microphotographies of the concentrates.

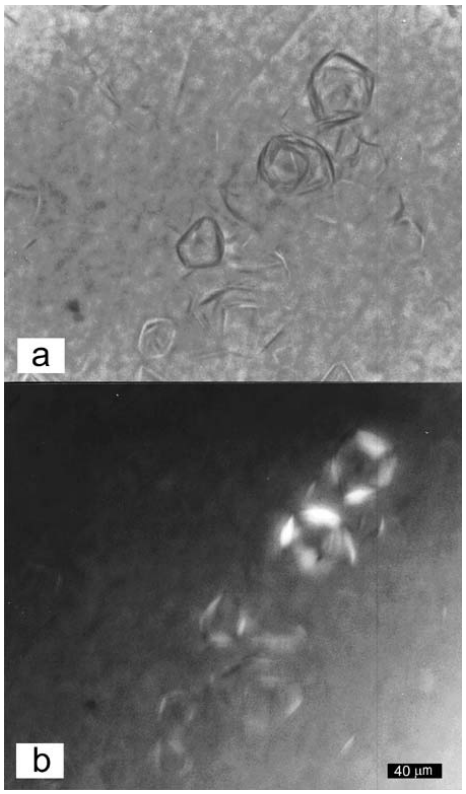

Figure 2. Microphotographies of the concentrate S6: (**a**) with parallels polarizers; (**b**) with crossed polarizers.

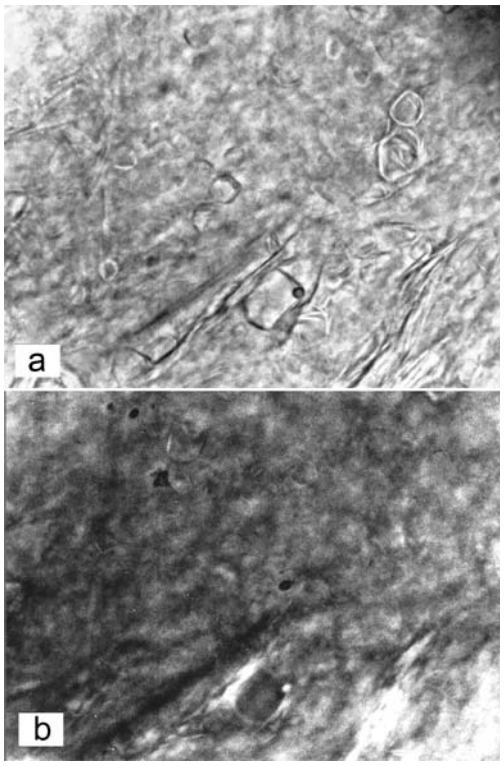

Figure 3. Microphotographies of the concentrate S11: (**a**) with parallels polarizers; (**b**) with crossed polarizers.

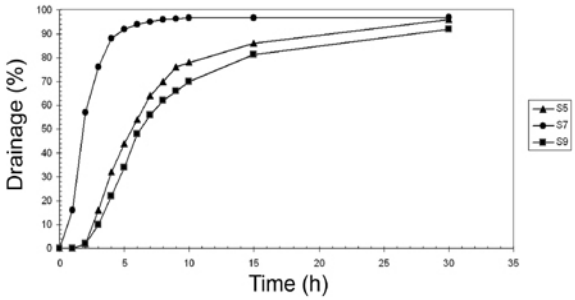

Figure 4. Drainage of the foams S5, S7 y S9.

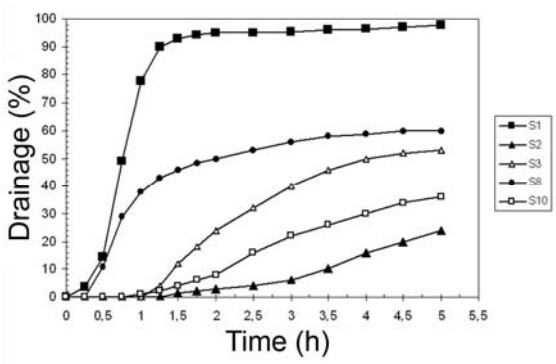

Figure 5. Drainage of the foams S1, S2, S3, S8 y S10.

Drainage

On the foams produced by concentrates S4, S6 and S11, it was not observed drainage during the 5 h that lasted the essay. The drainage curves of the remaining foams are shown in Figs. 4 and 5. On Table 7, there are shown the time in which drained 50% of the mass of each foam.

DISCUSSION

From the experimented concentrates, four of them were isotropic (S1, S5, S7 and S9), five presented solid crystals in suspension (S3, S4, S6, S8 and S10) and in two of them were distinguished simultaneously solid particles and liquid crystals (S2 and S11).

In all the concentrates with pearlescent aspect (S2, S3, S4, S6, S8, S10 and S11) were observed solid crystals. Consequently, it can be concluded that the pearlescent aspect is given because of the presence of solid crystalline particles.

All the isotropic concentrates (S1, S5, S7 and S9), which are dispersions of surfactants of high HLB values in water, produced foams with low stability and high speed of drainage. These results are concordant with the ones obtained by Sanders. The other concentrates possess solid

Concentrate	Stability of the foam (h)	Time in which drained 50% of the mass of foam (h)
S1	0.25-0.5	0.75
S2	> 3	> 5.0
S3	> 3	4.0
S4	> 3	> 5.0
S5	0.25-0.5	0.094
S6	> 3 h	> 5.0
S7	0.083-0.25	0.031
S8	> 3 h	2.0
S9	0.25-0.5	0.10
S10	> 3 h	> 5.0
S11	> 3 h	> 5.0

Table 7. Stability and drainage of the foams.

crystalline particles in suspension and produce foams of high stability and low speed of drainage. These concentrates, with exception of S3, are formed by dispersions of surfactants and cetyl alcohol or stearic acid. The concentrate S3 is constituted by an aqueous dispersion of a surfactant (triethanolamine stearate) resulting of the reaction of equimolecular quantities of stearic acid and triethanolamine However, and in spite of not having an excess of stearic acid according to triethanolamine, it presents a pearlescent aspect. The origin of this optic phenomenon could be given to the formation of a solid complex produced between triethanolamine stearate and stearic acid by hydrolysis of part of the anion stearate.

$$C_{17}H_{35}COO^- + H_2O \rightarrow C_{17}H_{35}COOH + OH^-$$

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