



Birefringent Emulsions Stabilized with Steareth-2 and Steareth-21

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SUMMARY. In this research, birefringent emulsions stabilized with Steareth-2 and Steareth-21 were studied. Some authors attributed to them a liquid-crystalline structure, although the microphotographs presented by them as an evidence of such structure actually suggest the presence of solid crystals instead of liquid crystals. The purposes of this paper are to determine the true cause of the birefringence of this type of emulsions and to study how the composition of the oily phase influences the stability and the birefringence. Six emulsions stabilized with a mixture of Steareth-2 and Steareth-21 were prepared, each one with a different emollient. Four of them were birefringent while two were isotropic. The observed birefringence would be due to the presence of solid crystals and not of liquid-crystals. These solid crystals could be originated by the interaction between both emulsifiers, either between themselves, with stearic acid or cetyl alcohol presents in the formulations, or even because of the insolubility of stearic acid or cetyl alcohol in emollient oil. Moreover, the isotropic emulsions showed greater viscosity than the birefringent ones. This result is accorded to the fact that the birefringence is not related to the presence of a liquid-crystalline interphase, because this type of interphase leads to an increase of viscosity.

INTRODUCTION

Dahms¹ prepared birefringent emulsions stabilized with a mixture of emulsifiers formed by 60% of Steareth-2 and 40% of Steareth-21. This author attributed the birefringence to the formation of a lamellar liquid-crystalline interphase. However, the microphotographs "a" and "c" as in Figure 1 of his paper, suggest the presence of solid crystals, instead of liquid ones, in the aqueous phase. Loll² proposed some formulations of emollient creams, oil in water type that used the same mixture of Steareth-2 and Steareth-21 used by Dahms, as emulsifier. Loll also attributed the birefringence to the presence of a liquid-crystalline interphase; though the microphotograph in page 18 of Loll's paper suggests the existence of acicular-solid crystals around the globules. In an internet presentation of the Uniqema Company³ it is also proposed the use of this emulsifying mixture to obtain liquid-crystalline emulsions in similar proportion to

the one used by Dahms. Brinon *et al.*⁴ tested an emulsion containing 1.5% of Steareth-2 and 1.5% of Steareth-21 and reached the conclusion that this emulsion had a liquid-crystalline interphase, on the basis of freeze-fractures electron microphotographs. However, the magnification by which the microphotograph was obtained, according to the scale bar, was not large enough to distinguish the layers that form the lamellar phase.

The formation of an interphase with liquid-crystalline characteristics stabilizes the emulsions because it avoids coalescence⁵. In this type of emulsions, emulsifier molecules in the interphase (including those of fatty alcohols and fatty acids, among other amphiphilic substances) are adsorbed in the oil-water interphase forming a multilayer⁶⁻⁸. This multilayer that surrounds emulsion drops, reduces Van der Waals interactions among oil drops and acts like a barrier against the coalescence⁹. Suzuki *et al.*¹⁰ at-

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tributed the stability of the emulsions with liquid crystals to the increase of the mechanic resistance of the oil-water interphase and to the fixation of the emulsion drops to the liquid-crystalline structure.

When the emulsions with a liquid-crystalline interphase are observed with a polarizing microscope with crossed polarizers, they display characteristic textures¹¹⁻¹⁴ which are a consequence of the lamellar phase birefringence. However, the observation of an emulsion birefringence does not necessarily indicate the presence of a liquid-crystalline interphase, because it might be due to the presence of anisotropic solid crystals. Pasquali¹² and Pasquali & Bregni¹⁵ observed that in certain concentrated aerosols, with an assigned liquid-crystalline structure, the birefringence was actually due to the presence of solid crystals, which were a result of the interaction between surfactants with fatty alcohols and fatty acids.

During an investigation of the properties of emulsions, Barry¹⁶ observed the formation of deformed globules, with shapes that varied from flattened spheres to polyhedral and contained anisotropic crystals. The emulsions that Barry tested contained liquid paraffin, cetyl alcohol, sodium dodecyl sulfate and water. In a system formed by water, propylene glycol, aluminum chlorhydroxide, Brij 35 (Laureth-23), cetyl alcohol and white oil, Mapstone¹⁷ observed the separation of cetyl alcohol crystals from the emulsion's drops. These results, added to the probable presence of solid crystals in the emulsions studied by Dahms and Loll, suggest that the observed birefringence in the emulsions stabilized with a mixture of Steareth-2 and Steareth-21 might be due to the formation of solid crystals. The objectives of this paper are to determine the true cause of the birefringence in this type of emulsions and to study the influence of the composition of the oily phase in the stability and birefringence.

MATERIALS AND METHODS

Isopropyl myristate, decyl oleate (Cetiol V), octyldodecanol (Eutanol G) and cetyl isononanoate (Cetiol SN) were provided by Cognis. The castor oil is from Castoroil (Argentina). Mineral oil had a viscosity of 168 mPa.s at 20 °C. Stearic acid had a commercial quality and was provided by Materia Oleochemicals (Argentina); its mean relative molecular mass, calculated according to the acidity index, was 270. Methylparaben and propylparaben were provided

by Ueno Fine Chemicals Industry Ltd and cetyl alcohol by Godrej Industries Ltd (India).

Preparation of the emulsions

Emulsion composition, similar to ones tested by Dahms, is described in Table 1. They were prepared at 70-75 °C, adding slowly the aqueous phase over the oily phase and stirring until the mix reached the lab temperature. Emollients tested were isopropyl myristate, octyldodecanol, decyl oleate, mineral oil, castor oil and cetyl isononanoate.

Oil phase	
Steareth-2	3.00%
Stearic acid	1.50%
Emollient	9.00%
Cetyl alcohol	1.00%
Propylparaben	0.05%
Aqueous phase	
Steareth-21	2.00%
Propylene glycol	4.00%
Water	79.35%
Methylparaben	0.10%

Table 1. Composition of the emulsions.

pH

pH was measured by diluting 10 g of each of the emulsions with 90 g of distilled water and 0.3 mL of a potassium chloride saturated solution. The instrument used was Altronix TPA III and the final value for each emulsion was the average of three measurements and it was expressed with a decimal unit.

Physical stability

Samples were stored during six months at laboratory temperature and three months at 40 ± 2 °C. At the end of these tests, it was visually observed phase separation and creaming.

Centrifugation

It was used a Rolco centrifuge 2036 model. Ten grams of each emulsion were centrifuged during 15 minutes at 2500 rpm. The distance from the centre of each tube to the axis of the centrifuge is of 8.5 cm, which originates an acceleration 590 times higher than gravity one.

Microscopic observation

A Carl Zeiss microscope, Axiostar plus model, with phase contrast objective, polarizers and photographic camera was used.

Viscosity

The measurements of viscosities of the emulsions were made 15 days after being prepared at $25 \pm 0,5$ °C using a viscometer Brookfield RVT with spindle N° 5 and an angular velocity of 0.5 rpm. Readings were made every 5 min during 30 min.

Appearance of the oily phases

Samples of the oily phases were prepared at 70-75 °C, with and without emulsifiers. Their appearances were observed at 25 °C and they were examined with a polarizing microscope x 400.

Appearance of aqueous phase with emulsifier mixture

A sample with water (79.35 g), Steareth-2 (3.00 g), Steareth-21 (2.00 g) and propylene glycol (4.00 g), was prepared.

Type of emulsion

A paper-indicator with cobalt chloride (II) was employed in order to confirm that the prepared emulsions were of the oil in water type: the turning from blue to pink in the paper-indicator in a few seconds showed that the external phase is the aqueous one. Also, the specific electrical conductivity was measured with a Parsec conductimeter, Antares VI model, at 25 ± 0.5 °C.

RESULTS AND DISCUSSION

The differences among pH of the emulsions (Table 2) were small, reason why this parameter can be disabled as a factor to explain the differences among them.

Emulsions with isopropyl myristate and octyldodecanol showed cremate after being stored at 40 °C during 3 months, while the others remained stable (Table 3). Under centrifugation, the only unstable emulsion (with oil separation) was the one that contained castor oil (Table 3).

The emulsions with isopropyl myristate and mineral oil were isotropic (Table 4) and were formed by very small globules of a rather uniform size (Figs. 1 and 2). The remaining ones, however, were birefringents and size of globules presented great variation: between approximately 5 μ m to 50 μ m. When observed under the optical microscope with phase contrast objective, the emulsion with castor oil showed abundant acicular crystals in the aqueous phase. Emulsions with octyldodecanol, decyl oleate and cetyl isononanoate (Fig. 3) were the following ones. The emulsions with greater viscosity were the ones that did not display birefringence, in which the emollients were mineral oil and isopropyl myristate (Fig. 4). These emulsions were formed by much smaller globules than those presenting birefringence.

The oily phases of all the emulsions, with

Emollient	Electrical conductivity at 25 °C (μ S/cm)	Type of emulsion (with CoCl_2)	pH	Viscosity* (Pa.s)	Birefringence
Isopropyl myristate	7.8	o/w	4.1	94	No
Octyldodecanol	7.8	o/w	4.3	26	High
Decyl oleate	8.4	o/w	3.8	60	High
Mineral oil	7.0	o/w	4.1	128	No
Castor oil	5.0	o/w	4.3	60	High
Cetyl isononanoate	6.7	o/w	4.2	69	Low

Table 2. Characteristics of the emulsions.

Emollient of the emulsions	Stability at laboratory temperature (6 months)	Thermal stability (3 months at 40 °C)	Stability under centrifugation (15 min at 2500 rpm)
Isopropyl myristate	Stable	Unstable	Stable
Octyldodecanol	Stable	Unstable	Stable
Decyl oleate	Stable	Unstable	Stable
Mineral oil	Stable	Stable	Stable
Castor oil	Stable	Stable	Unstable
Cetyl isononanoate	Stable	Stable	Stable

Table 3. Results of the tests of stability of the emulsions.

Emollient of the emulsions	Aspect of the oily phase without emulsifier	Aspect of the oily phase with emulsifier
Isopropyl myristate	L + S	G
Octyldodecanol	L + S	L + G
Decyl oleate	G	G
Mineral oil	G	G
Castor oil	G	G
Cetyl isononanoate	G	G

Table 4. Appearance of the oily phase at lab temperature, with and without emulsifiers. **G** = gel; **L** = liquid; **S** = solid.

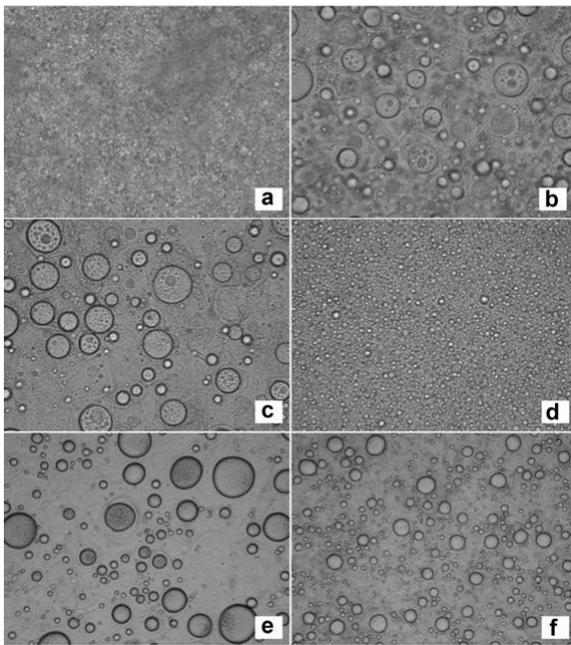


Figure 1. Microphotographs of the emulsions with different emollients: (a) Isopropyl myristate, (b) octyldodecanol, (c) decyl oleate, (d) mineral oil, (e) castor oil and (f) cetyl isononanoate.

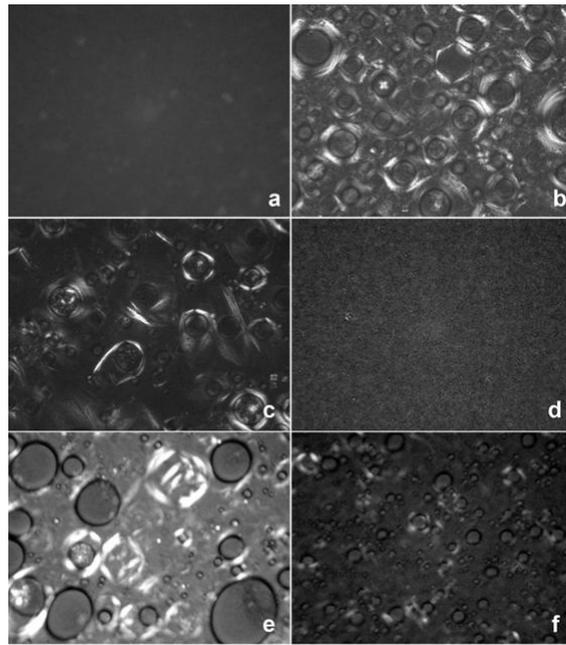


Figure 2. Crossed polarizers microphotographs of the emulsions with different emollients: (a) Isopropyl myristate, (b) octyldodecanol, (c) decyl oleate, (d) mineral oil, (e) castor oil and (f) cetyl isononanoate.

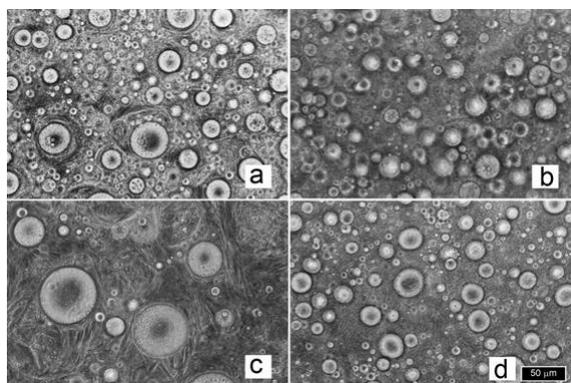


Figure 3. Phase contrast microphotographs of the emulsions that present birefringence with different emollients: (a) octyldodecanol, (b) decyl oleate, (c) castor oil and (d) cetyl isononanoate.

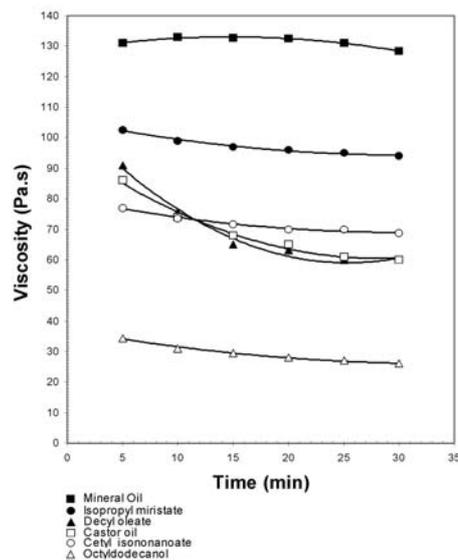


Figure 4. Viscosity of the emulsions.

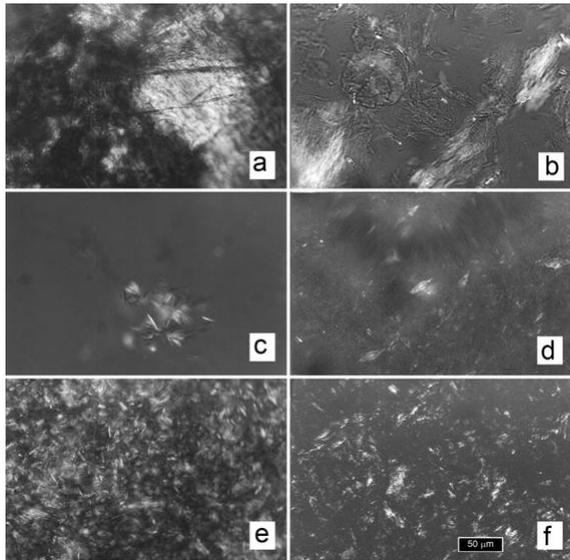


Figure 5. Oily phases of the emulsions without emulsifiers with different emollients observed with crossed polarizers: (a) Isopropyl myristate, (b) octyldodecanol, (c) decyl oleate, (d) mineral oil, (e) castor oil and (f) cetyl isononanoate.

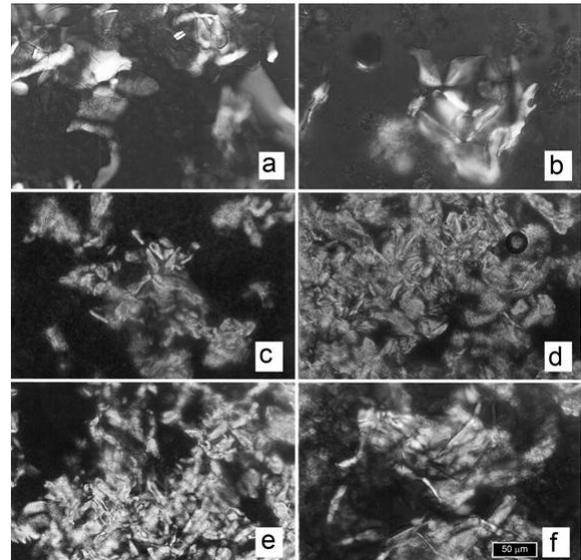


Figure 6. Oily phases of the emulsions with emulsifiers with different emollients observed with crossed polarizers: (a) Isopropyl myristate, (b) octyldodecanol, (c) decyl oleate, (d) mineral oil, (e) castor oil and (f) cetyl isononanoate.

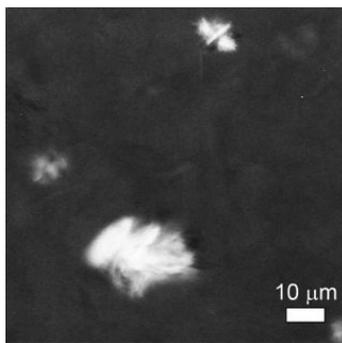


Figure 7. Birefringent crystals in the system formed by stearic acid, Steareth-21, water and propylene glycol in the same proportions as in the emulsions.

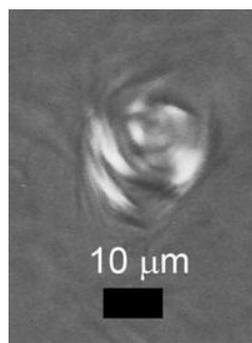


Figure 8. Birefringent crystal in the system formed by cetyl alcohol, Steareth-21, water and propylene glycol in the same proportions as in the emulsions.

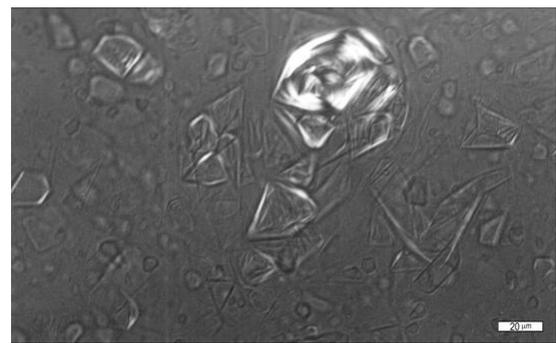


Figure 9. Birefringent crystals formed by the interaction of the emulsifiers (Steareth-2 and Steareth-21) dispersed in the aqueous phase.

and without the addition of emulsifiers, were birefringent (Fig. 5 and 6). Also, the systems formed by stearic acid, Steareth-21, water and propylene glycol (Fig. 7); cetyl alcohol, Steareth-21, water and propylene glycol (Fig. 8); and Steareth-2 and Steareth-21 dispersed in the aqueous phase (Fig. 9) presented birefringence. All these systems were in the same proportion as in the emulsions.

CONCLUSIONS

The birefringence observed in the emulsions stabilized with a mixture of Steareth-2 and

Steareth-21 should be due to the presence of solid crystals and not liquid crystals. These solid crystals could be originated either by interaction of both emulsifiers between them, or with the stearic acid, or the cetyl alcohol, or because of insolubility of stearic acid or cetyl alcohol in the emollient oil.

In most of the studied systems the dispersed phase is formed by a lipogel, which birefringence is a consequence of the networks of gellators¹⁸. This fact indicates that they are not emulsions strictly speaking, since the dispersed phase is a gel and not a liquid.

The isotropic emulsions have greater viscosity than the birefringent ones. This result is accorded to the fact that the birefringence is not due to the presence of a liquid-crystalline interphase, because this type of interphase leads to an increase of viscosity.

The stability of the liquid-crystalline emulsions is higher than the ordinary ones. However, the most stable ones among the studied emulsions were those that contained mineral oil (isotropic) and cetyl isononanoate (low birefrin-

gence) as emollients, respectively. If birefringence had been due to a liquid-crystalline structure, a low birefringence or the absence of it would have been correlated with a low stability of the emulsions, in opposition to the observed results in this research.

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