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Geranyl acetate emulsions: Surfactant association structures and emulsion inversion

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ABSTRACT

Three emulsions of geranyl acetate (GA)-in-water (W) with identical GA/W ratios and varying surfactant (S), Laureth 4, a commercial $C_{12}EO_4$ compound, fractions were investigated for nature and stability. The emulsions with up to 6% surfactant were W/O, as expected with respect to the solubility of the surfactant in the oil. At 10% surfactant, the aqueous phase became the continuous one and the apparent stability of the emulsion was significantly enhanced.

Analysis of the phase diagram and experimental evidence showed the high water content emulsion to be a liquid crystal-in-water emulsion; a kind that did not change even at extreme O/W and LC/W ratios.

1. Introduction

The properties of emulsions have recently received renewed attention, particularly in the area of fragrance formulations. These have traditionally been based on ethanol solutions and the research into these entities has become highly sophisticated [1–4], however the preference for such formulations has been shifted to aqueous solubilized systems for environmental reasons. As a result, the properties of emulsions [5] have become the focus of attention.

The key factor for fragrance emulsion applications is undoubtedly their evaporation profile and significant progress in the fundamentals of this process has recently been made with the Hull group as the leading institution. Their research has successfully clarified the mechanism of evaporation from pure liquids [6], demonstrating that the rate-limiting step for pentane and hexane evaporation is connected with the vapor diffusion across the stationary gas layer above the liquid [7]. In the investigations into water-in-oil emulsions and microemulsions [8–10] it was found inter alia that, the rate-limiting step for water evaporation from a mixture with the nonionic surfactant *n*-dodecyl hexaoxyethylene glycol ether ($C_{12}EO_6$) was the mass transfer barrier of the highly structured lamellar liquid crystal [7].

These latter results combined with the early reports of Saettone et al. [11], of Friberg et al. [12] and of Vathey et al. [13] indicated that association structures play a substantial role in the evaporation and prompted investigations into these phenomena utilizing phase diagrams and an algebraic system to extract additional information [14,15]. This research provided information about potential phases that would be encountered during evaporation of emulsions and among other results, the potential to formulate emulsions in which the fragrance evaporates under constant vapor pressure [16] should be mentioned. The results by the theoretical approach have recently been confirmed by experimental results from selected emulsions [17].

These reports demonstrated that association structures play a vital role in the evaporation from fragrance emulsions and the authors felt that a more detailed investigation into the different structures in a fragrance emulsion *per se* would be of value. In a preliminary report on the association structures in a fragrance emulsion [18], surprising indications were found that surfactant association structures may affect what kind of emulsions are obtained. To our knowledge, such a phenomenon has not earlier been made public and we found a first report on the fact to have more than average interest.

2. Materials and methods

2.1. Materials

Nienty-eight percent Laureth-4 (Brij® 30) and 3,7-dimethyl-trans-2,6-octadien-1-yl-acetate 98%, mixture of isomers (geranyl acetate) were obtained from Acros (Geel, Belgium) and used without further purification. Water was deionized and distilled.

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2.2. Instrumentation

Weights were determined using a Mettler AJ150 Analytic Balance and a Vibrofix VFI Electronic (shaker) was used to prepare the emulsions. A Labofuge 200 centrifuge with maximum speed of 5500/min was used to separate the phases. A standard light microscope equipped with crossed polarizers and a camera was used to view the detailed structure of the emulsions.

2.3. Sample preparation methods

Three different samples were prepared, each in triplicate so that different methodologies of preparation could be investigated. The samples each had a total weight of 10 g and were comprised of constant ratio equal to 3.0 between geranyl acetate and water and different ratios of Laureth-4. The composition details of the samples, shown in Table 1 and Fig. 1, were selected to evaluate the effect of the liquid crystalline phase on the nature of the emulsion, and in particular, determine the reason why the emulsions "inverted" from the expected W/O emulsion for low surfactant sample (A) to the opposite O/W system for sufficiently large fraction of surfactant (sample C).

2.3.1. The first set

Three samples A, B and C were prepared by layering the geranyl acetate/ Laureth-4 solution on top of water layer. A solution of geranyl acetate and Laureth-4 was prepared according to the composition in Table 1 for each sample, water was weighed in a 2 cm diameter flat test tube, then the test tube tilted to gently introduce the geranyl acetate/Laureth-4 solution so it slowly spreads onto the top of the water. The sample was watched with time to follow the changes and the LC formation.

2.3.2. The second set

Three samples A1, B1and C1 were prepared with the same composition as the first set but with moderate mixing of the sample after layering of the geranyl acetate/Laureth-4 solution onto the water layer by inverting the tube there upside down three times and then monitoring the changes with time. A small aliquot of the white layer for each sample was taken for microscopic examination immediately after the mixing step and at intervals over time.

2.3.3. The third set

Three samples A2, B2 and C2 were prepared as in the first and second sets but with the mixing step of inversion of the test tube three times and microscopy studies being performed after having been stored overnight.

2.3.4. Additional studies for sample C

Sample C was consisted of (W: 6.75 g, GA: 2.25 g, S: 1.0 g). The surfactant was added to the water in the test tube and mixed on the vibrator at its highest speed setting for 2 min, then centrifuged to remove air bubbles. The geranyl acetate was carefully layered on top of the aqueous dispersion, then the sample monitored over time.

Table 1
The composition of the samples.

Sample[a]	Water (g)	Geranyl acetate (g)	Laureth-4 (g)
A, A1, A2	7.3425	2.4475	0.2100
B, B1, B2	7.0425	2.3475	0.6100
C, C1, C2	6.7500	2.2500	1.000

[a] The first set consisted of sample A, B, C. The second set consisted of sample A1, B1, C1. The third set consisted of sample A2, B2, C2.

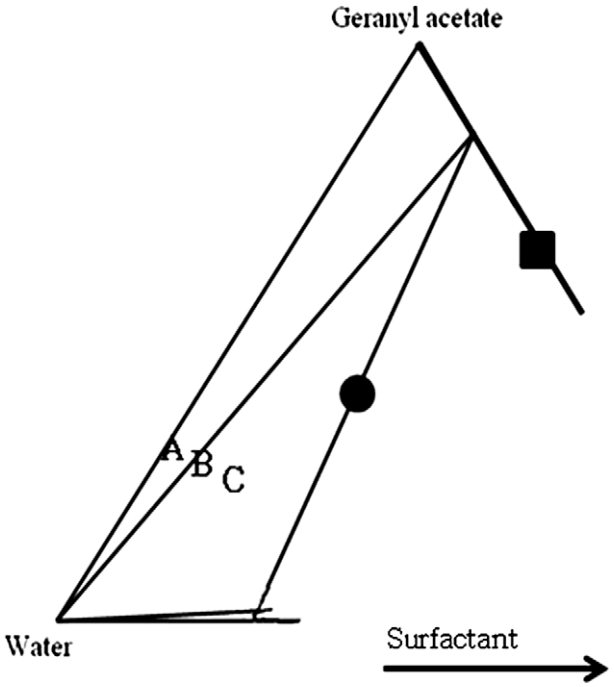

Fig. 1. The location of the emulsion compositions, A, B and C in partial phase diagram. The filled square and the filled circle refer to a specific experiment described in Section 2.

2.4. Relationship between emulsion composition and the phase diagram

Since it appears reasonable to assume that the phase conditions in the emulsions may be responsible for the inversion between emulsions B and C, the relationship between composition and the relevant parts of the phase diagram are given in Fig. 1.

The three emulsions were selected specifically to evaluate the effect of the liquid crystal on the nature of the emulsion; and especially to determine why the emulsions "inverted" from the expected W/O variety for low surfactant fractions to the opposite O/W emulsion for sufficiently large fractions of surfactant. The different phases were calculated from the phase diagram [18] and the emulsions in the present contribution have the following fractions of liquid crystal. Sample A, zero; sample B, 0.073 and sample C 0.26.

2.5. Stressed emulsions, sample C

In the first experiment, the emulsification energy input was reduced to turning the test tube once upside down and back.

In the second experiment, the interaction between the liquid crystal and the oil was maximized in the following manner. Of the total emulsion, 0.1 fraction of surfactant was dissolved in 0.225 fraction of oil (the square in Fig. 1) and this solution was then poured on top of 0.15 fraction of water. The composition is now at the point marked by a circle in Fig. 1. This composition was then emulsified by turning the test tube upside down and back three times. Photographs were taken immediately, after 1, 2, 5, 15 min, and after 1 day. A parallel experiment added a fraction of 0.525 of water to the freshly formed emulsion and re-emulsified it with the same mixing procedure.

In the third experiment the fraction of oil and of liquid crystal was increased, the emulsion formed in the same manner as the original sample C, and the appearance observed after 2 days.