NANO-ÉMULSIFICATION DES HUILES TRIGLYCÉRIDES AU MOYEN D'UNE MÉTHODE D'INVERSION

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NANO-EMULSIFICATION OF TRIGLYCERIDE OILS BY MEAN OF A INVERSION METHOD

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RÉSUMÉ

Une émulsion est un mélange de deux liquides non miscibles, l'une des substances étant dispersée dans l'autre sous forme de gouttelettes. Lorsque la taille des gouttelettes est comprise entre 20 et 500 nm, on parle communément de nano-émulsion, de mini-émulsion ou d'émulsion submicronique. Différentes méthodes ont été proposées en vue de préparer des nano-émulsions, parmi lesquelles la transition de phase (à composition fixée) appelée méthode de température d'inversion de phase (TIP), qui est fréquemment utilisée dans les systèmes formulés à base de tensio-actif non ionique éthoxylé. En règle générale et de façon plus particulière avec d'autres types de tensio-actifs, l'inversion transitionnelle peut être effectuée en modifiant n'importe quelle autre variable de la formulation susceptible d'altérer la différence hydrophyle-lipophile (HLD) du système respectivement à la formulation optimum pour le comportement triphasique, comme la salinité de la phase aqueuse, l'hydrophilie du tensio-actif ou du mélange de tensio-actifs ou l'effet co-tensioactif. Le présent compte-rendu aborde la réalisation de nano-émulsions Huile/Eau avec un système tensio-actif non ionique/ huile triglycéride/eau. Les systèmes initiaux étaient formulés à des valeurs HLD différentes et avec des mélanges de tensio-actifs non ioniques Span/Tween différents. L'émulsification a été réalisée par dilution, à savoir par un changement du rapport eau-huile. La taille des gouttes et la stabilité de la nano-émulsion sont liées à la HLD du mélange de tensio-actifs non-ioniques et à l'existence d'une phase cristalline liquide lamellaire pendant le processus d'émulsification. Les données recueillies mettent l'accent sur l'importance particulière qu'il convient d'accorder aux phases lamellaires dans la formation et la stabilisation de la nano-émulsion.

ABSTRACT

Emulsions are mixtures of two immiscible liquids, one of them being dispersed as droplets in the other. When droplet size is in the range of 20 to 500 nm it is often called nano-, mini- or submicron emulsion. Different methods have been proposed to prepare nanoemulsions, among which the transitional inversion (at fixed composition) so-called phase inversion temperature (PIT) method, commonly used in systems formulated with nonionic ethoxylated surfactant. In general and in particular with other types of surfactant, the transitional inversion can be carried out by changing any other formulation variables likely to alter the hydrophilic-lipophilic deviation (HLD) of the system with respect to optimum formulation for three-phase behavior, like the salinity of the aqueous phase, the surfactant or surfactant mixture hydrophilicity or the cosurfactant effect. The present report deals with the attainment of O/W nanoemulsions with a nonionic surfactant/triglyceride oil/water system. The initial systems were formulated at different HLD values and different Span/Tween nonionic surfactant mixtures. Emulsification was carried out by dilution, i.e., by a water-to-oil ratio change. The nanoemulsion drop size and stability are related to the nonionic surfactant mixture HLD and to the existence of a lamellar liquid crystalline phase during the emulsification process. The data highlight the particular importance of lamellar phases in nanoemulsion formation and stabilization.

Mots clés : Nano-émulsion, Différence hydrophile-lipohile, Cristaux liquides, Inversion

Key words: *Nanoemulsion, HLD, Liquid Crystal, Inversion*

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Nano-Emulsification of triglyceride oils by mean of a inversion method

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-1 End use properties
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1. Introduction

Emulsions and microemulsions are important systems containing principally surfactant,oil and water (SOW system). They are utilized in many industrial field and daily life products including dermocosmetic creams and pharmaceuticals (1). Emulsions are dispersed system of at least two immiscible liquids one of the being dispersed as droplets in the other (2). Contrarily, microemulsions are thermodinamicaly stable system that can solubilize water and oil but the surfactant required is high (3).

Taking into account the importance to produce stable (or kinetically stable) systems with low surfactant concentration, some investigators were interested in produce emulsions with a droplet size lower than 0.5 mm, this system have been denominated nanoemulsions, miniemulsions or submicron emulsion (4). Nanoemulsions can be attained by mechanical devices or by physicochemical methods, particularly by transitional inversion which can be carried out by changing not only temperature, PIT method (5), but any other formulation variables likely to alter the hydrophilic-lipophilic deviation (HLD) of the system with respect to optimum formulation, e. g., the salinity of the aqueous phase, the surfactant or surfactant mixture hydrophilicity or the cosurfactant type or concentration (1). When emulsification is carried out, at constant temperature, by dilution of the oil phase containing surfactants it is possible to attain fine droplet by phase inversion method if the liquid crystalline phase (LC) is present during the emulsification (6). Given that the HLB of the system is well balanced in the range of the lamellar phase (corresponding to optimum formulation), the surfactant might dissolve large amount of oil to come across the transitional inversion required to generate fine droplets when water is added to the system. However, to obtain O/W nanoemulsions with triglyceride oils are more difficult than to get them with hydrocarbons oils (analogous to microemulsions) (6-8) because hydrophilic surfactant cannot solubilize enough oil in the surfactant phase. It is well known that certain mixtures of surfactants can provide better performance than pure surfactant to solubilize oil (7, 8).

The aim of this work is to study the relation between the nonionic surfactant mixture of the sorbitan esters type for different HLB value and explore how the molecular kind of surfactant can affect the nano-emulsification process of paraffin and a triglyceride oil (soybean oil).

2. Experimental

2.1. Materials

Technical grade nonionic surfactants: sorbitan monolaurate, monoestearate and monooleate, (referred in this work as S20, S60, and S80 respectively) and polyoxyethylene (20) sorbitan monooleate (T80), were supplied by FLUKA. Commercial soybean oil (ρ:.919 Kg/m^3, viscosity: 57.4 mPa s at 25ºC) was acquired from Branca, Venezuela and liquid paraffin mineral oil (with an equivalent alkane carbon number, EACN = 13). Water was deionized, all products were used as received.

2.2. Methods

2.2.1. Preparation of nanoemulsions. Emulsions were prepared by addition of water to a surfactant-oil blend and stirred in a thermostat bath at 60 ^{o}C with gentle stirring. The final emulsions are composed by 16 wt% of oil and 8 wt% of surfactant mixture. Mixtures of the two nonionic surfactants T80/S (20, 60 or 80), were used to get an specific HLB calculated by

$$HLB_{mixture} = HLB_A.X_A + HLB_B.X_B \qquad (1)$$

where X_A, and X_B are the weight fraction of the surfactant present in the mixture.

2.2.2. Droplet size determination. The mean droplet size and size distribution of emulsions were measured by the laser light scattering technique using a Coulter® LS-230 Particle Size Analyzer (measurement range 0.04-2000 m). Each sample was diluted with distilled water until the appropriate concentration for measurement was achieved.

2.2.3. Rheology. A Rheological study of lamellar liquid crystal phases, detected by optical microscopy, was made through steady state and dynamic (stress and frequency sweeps) tests at constant temperature. The rheometer used was a stress controlled device, model SR-5000 manufactured by Rheometric Scientifics.

3. Results and Discussion

Figures 1 shows the emulsion droplet size of the water/T80/S/paraffin oil system, at ^{o}60. It can be seen that the minimum droplet size is in the order of 0.3 μm independently of the surfactant mixture used. Nevertheless, this minimum is obtained at different HLB depending on the type of T80/S mixtures. That is, HLB for the smalest droplet size are 10.6, 11.2 and 12.0 for T8/S80, T80/S60, T80/S20 mixtures respectively. Similar results have been reported in system with sorbitan nonionic surfactant with similar paraffin oil (6). It has been identified a lamellar liquid crystalline phase during the emulsification process and its rheological study (not shown) could explain a relationship between the characteristics of this mesophase as a function of HLB and the nanoemulsion formation. The G''/G' ratio (that is, the ratio of loss and storage modules) goes through a minima when water is added to the system in which the nanoemulsion were formed.

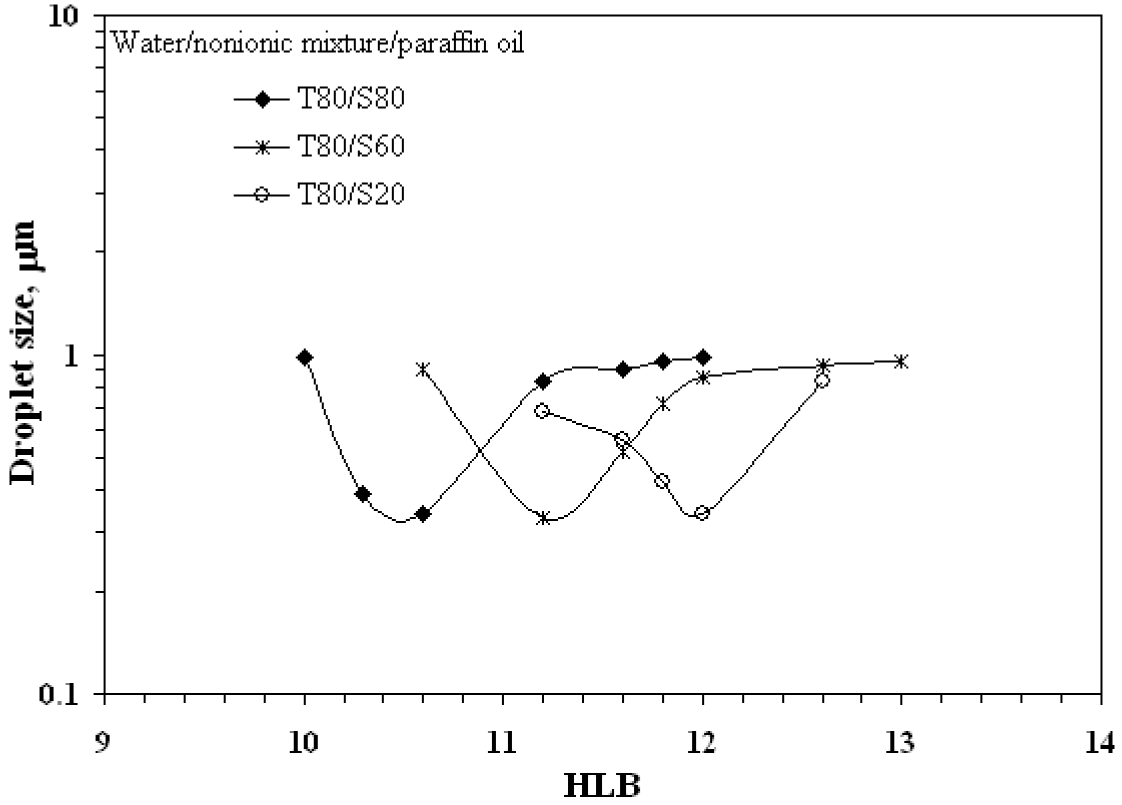

Figure 1. Droplet size as a function of HLB of surfactant mixture for emulsions containing paraffin oil.

Emulsifications of soybean oil with similar mixtures of nonionic surfactants (T80/S molecules) are shown in Figure 2. It can be seen that nanoemulsions were obtained in the HLB range between 11.5 to 13 for T80/S80 mixtures and at HLB values of 12.5 and 13 in T80/S0 systems. Nevertheless, emulsion formed with T80/S20 surfactants mixture have fine droplet size at HLB values of 12.5 and 13, but they are not consider nanoemulsion due to their white appearance and low stability (droplet size > 0.5 μm).

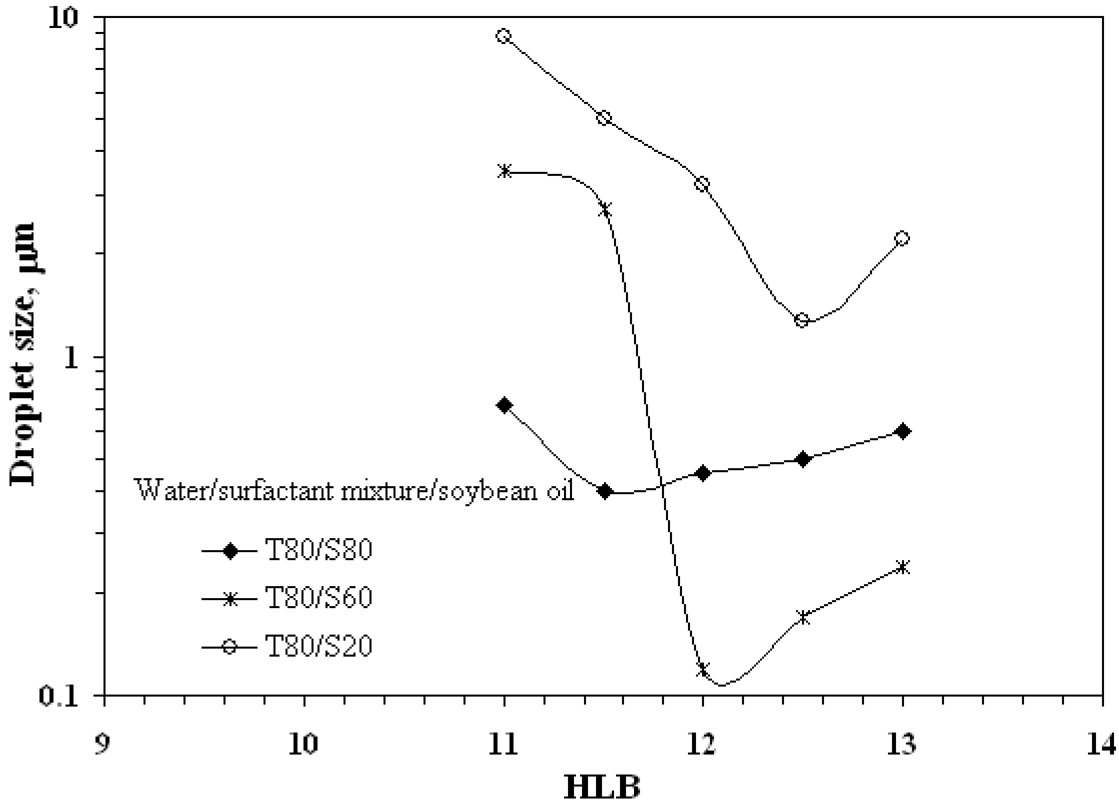

Figure 2. Droplet size as a function of HLB of surfactant mixture for emulsions containing in soybean oil.

The formation of O/W fine emulsion with triglyceride oil using transitional inversion method (or Phase-Inversion emulsification) has not been reported yet. It has been argued that the difficulty comes from the higher solubility of surfactant in vegetable oils compared with paraffin oil (6). To avoid this difficulty, in this study the scan in HLB number was realized and it was found that the HLB required to prepare nanoemulsion with soybean oil is greater that to obtain nanoemulsion with paraffin as expected. In a mixed nonionic surfactant system, the hydrophilic-lipophilic properties are dependent on the surfactant mixing ratio at constant temperature and the self-organizing, like microemulsion or lamellar liquid crystal, are determined by the interaction between surfactant, water and oil (9). Consequently, to form the lamellar liquid crystalline phases necessary for the Phase-Inversion emulsification method involves adjust the HLB of the nonionic surfactant.

4. Conclusions

The present study illustrates that the preparation of nanoemulsion containing triglyceride oil (soybean oil) by a transitional method, at constant temperature required a fine-tuning of HLB values of the nonionic surfactant mixtures.

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