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Studies of formation of W/O nano-emulsions

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Abstract

In this work, formation of water-in-oil nano-emulsions in water/mixed nonionic surfactant/oil system has been studied by a condensation method. Several mixtures of Span 20, Span 80, Tween 20 and Tween 80 were studied. It has been proved that mixtures of surfactants can provide better performance than pure surfactants. The appropriate ratio between two surfactants was studied. The existence of microemulsion, nano-emulsion and emulsion regions was investigated studying samples stability by evolution of backscattering with time multiple light scattering technique. These studies allowed to determine zones where nano-emulsions can be formed. Droplet sizes were measured by dynamic light scattering (DLS). Mean sizes between 30 and 120 nm were obtained; the higher the water concentration, the higher the size. On the other hand, nano-emulsions stability was studied by dynamic light scattering. The results showed the evolution with time of the average radius droplet. For low water concentration, nano-emulsions breakdown could be attributed to Ostwald ripening; and for high water concentration, nano-emulsions breakdown could be attributed to coalescence.

Keywords: Span/Tween; W/O nano-emulsion; Mixed nonionic surfactant

1. Introduction

It is well-known that certain mixtures of surfactants can provide better performance than pure surfactants for a wide variety of applications [1,2]. It is interesting to disperse the biggest quantity in water with the smallest quantity of surfactant [3]. In this work, we used different surfactant mixtures that show synergism in the dispersion of water in W/O nano-emulsions. The synergism can be defined like a situation where surfactant mixtures provide better states of minimum energy than a simple alone surfactant [4].

Nano-emulsions are a class of emulsions with a droplet size between 20 and 500 nm [5]. Their droplets are stabilized by surfactants. They are not formed spontaneously, their properties depend not only on thermodynamic conditions but on preparation methods and the order of addition of the components [6–8]. On the other hand, microemulsions are equilibrium structures distinctly different from emulsions [9–11].

Nano-emulsions may possess high kinetic stability and optical transparency resembling to microemulsions [5]. Nano-emulsions can be used as micro reactors of controlled size for the preparation of monodisperse particles [8].

2. Experimental

2.1. Materials

Span 20 (S20), Span 80 (S80), Tween 20 (T20) and Tween 80 (T80) technical grade were purchased from Sigma. *N*-Decane (purity > 99%) was obtained from Panreac. Deionized water by Mili-Q filtration was used. The systems studied were S80 T80/decane/water, S20 T80/decane/water and S20 T20/decane/water.

2.2. Methods

2.2.1. Phase diagram

Samples with constant surfactant/decane ratio in 5/95, varying the ratio between Span and Tween surfactants and

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the quantity of water, were prepared. All components were weighed, sealed in ampoules, and homogenized with a vibromixer. The samples were kept at a constant temperature of 25 °C.

2.2.2. Existent regions

The emulsions were formed by adding water to a mixture of the others components, using a magnetic stirrer at 700 rpm at 25 °C. The limit between the microemulsión region and nano-emulsion was determined observing the evolution of the back scattered light as a function of time. This study was carried out with multiple light scattering at a wavelength of 850 nm.

2.2.3. Nano-emulsion formation

Nano-emulsions were prepared by adding water to a mixture of Span–Tween and decane. The rate of addition was kept approximately constant, stirring at 700 rpm, all experiments were run at 25 °C.

2.2.4. Droplet size

Nano-emulsion droplet size was determined by dynamic light scattering (DLS) with a Malvern 4700 instrument at 25 °C.

2.2.5. Stability

The stability was measured at constant temperature (25 °C) by multiple light scattering and dynamic light scattering. A Turbiscan MA 2000 and a Malvern 4700 were used, respectively.

3. Results and discussion

3.1. Phase diagram

This work has been carried out with several surfactant mixtures of Span and Tween. Three different surfactant mixtures were investigated. Fig. 1 shows water solubilization in water-in-oil microemulsions for binary mixtures of Span and Tween. The mixtures studied were S20 T80, S20 T80 and S80 T80.

The surfactant mixture that provided higher water solubilization was S20 T80. At the maximum level of solubilization, the ratio Span–Tween was 62:38 for S20 T80, 49:51 for S80 T80 and 60:40 for S20 T20.

3.2. Existent regions

The studies permitted to determine zones where nano-emulsions can be formed (Fig. 2). The samples were prepared with the more suitable ratio of Span–Tween found as stated above. The microemulsion, nano-emulsion and emulsion regions appear as water concentration increases for a constant surfactant:decane ratio. For surfactant concentrations lower than 5 wt.%, water is not solubilized or dispersed in appreciable quantity, so it was considered that no microemulsion or nano-emulsion regions were formed. The system formed with Span20–Tween80/decane/water has the biggest microemulsión, nano-emulsion area. The system formed with Span20/Tween20/decane/water presents lower area than the others systems studied.

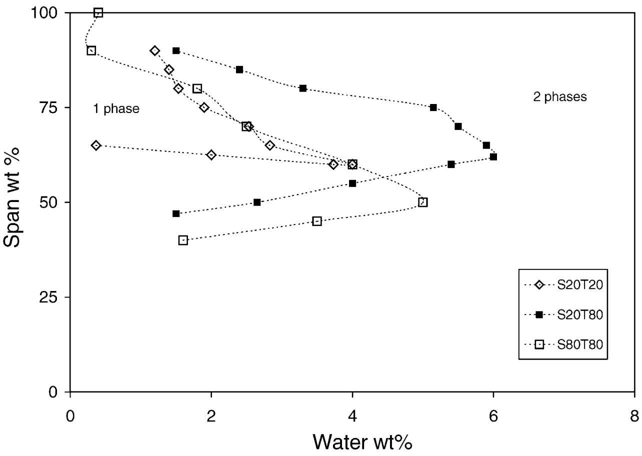

Fig. 1. Maximum water solubilization (as a W/O microemulsión) vs. Span ratio for Span–Tween mixtures.

3.3. Nano-emulsion formation

3.3.1. Droplet size

The droplet size increases as the amount of water increases, for all the systems studied. For 15:85 surfactant:decane ratio (Fig. 3), the system with smaller droplet size is for S80 T80/decane/water. For 10:90 surfactant:decane ratio, the system with larger droplet size is for S20 T20/decane/water, but it is quite unstable due to the polydispersity of the system (data not showed).

In this study, at a same concentration of dispersed phase, the droplet size decreases with the amount of surfactant due

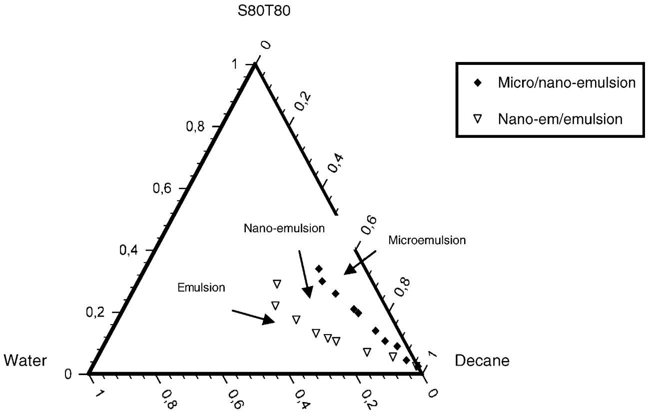

Fig. 2. Existence regions of microemulsion, nano-emulsion and emulsion. Span 80–Tween 80 (49:51)/decane/water.

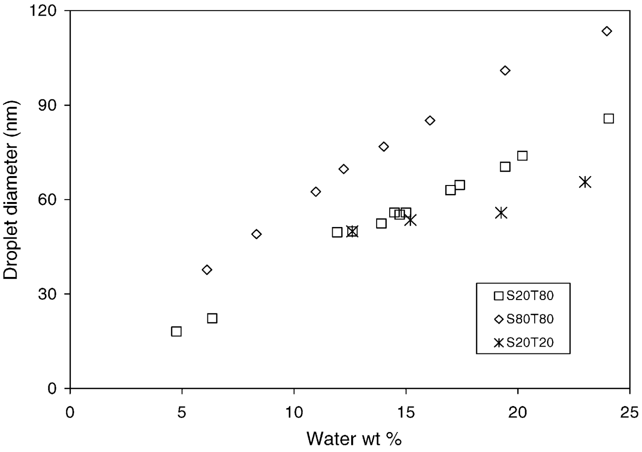

Fig. 3. Droplet size vs. water concentration. Surfactant/decane (15:85)/water. Surfactants: S80 T80 (49:51), S20 T80 (62:38), S20 T20 (60:40).

to the increase in interfacial area and the decrease in the interfacial tension [12].

3.3.2. Stability

The nano-emulsions prepared presented a good stability without phase separation during weeks but with a slight increase of droplet size with time. The experiments by multiple light scattering show that the two most probable breakdown processes in these systems must be coalescence and Ostwald ripening. If coalescence was the driving force for instability, the change of droplet size with time may follow Eq. (1),

$$\frac{1}{r^2} = \frac{1}{r_o^2} - \left(\frac{8\pi}{3}\right)\omega t \qquad (1)$$

where r is the average droplet radius after t, r_o is the value at $t = 0$, and ω is the frequency of rupture per unit of surface of the film [13].

The Lifshitz–Slezov and Wagner (LSW) theory [14–17] gives and expression for the Ostwald ripening rate, in this case, droplet size increases with time following Eq. (2).

$$\omega = \frac{dr_c^3}{dt} = \frac{8c(\infty)\gamma V_m D}{\rho RT} \qquad (2)$$

where r_c is critical radius of the system at any given time; $c(\infty)$, the bulk phase solubility; γ, the interfacial tension; V_m, the molar volume; D, the diffusion coefficient in the continuous phase; ρ, the density of the water; R, the gas constant and T, the absolute temperature.

The results by DLS show the evolution with time of the average radius droplet. Fig. 4 shows the adjusts made for the experimental data by LSW theory. So the nano-emulsion breakdown could be attributed to Ostwald ripening. However, when water concentrations is increased (16.6 wt.%) also nano-emulsion breakdown could be adjusted to the Deminière equation for the coalescence mechanism with a rupture frequency equal to 3×10^{-8} m^{-2}/s. When the concentration of dispersed phase increases, the droplet sizes increases and possibly the interfacial film thickness decreases. In this situation, the coalescence mechanism can take place easily than other mechanism.

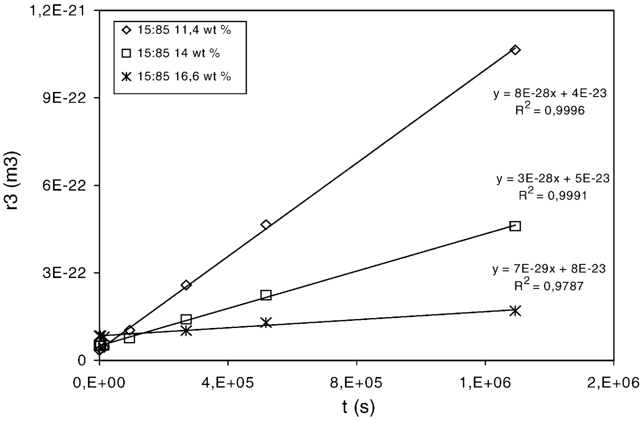

Fig. 4. Nano-emulsion r^3 as a function of time at 25 °C in the system, S80:T80 (49:51)/decane/water. Surfactant:decane, 15:85. Water concentration: 11.4, 14, 16 wt.%.

4. Conclusions

The ratio Span–Tween that provides higher water solubilization and higher system stability was found varying the ratio Span–Tween and the water quantity. The existent regions study allowed to identify regions where nano-emulsions can be formed.

W/O nano-emulsions with mean droplets sizes between 30 and 120 nm were obtained with higher size the higher water quantity. The nano-emulsions prepared presented good stability without phase separation, sedimentation or creaming, during weeks. But, they presented a slight increase of droplet size with time.

Stability studies show that nano-emulsion breakdown could be attributed to Ostwald ripening and coalescence mechanism, depending on water concentration.

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