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Studies of the relation between phase behavior and emulsification methods with nanoemulsion formation

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Abstract The main aim of this work was to study the relationship between the type of phases present during the emulsification process, the order of addition of components and the droplet size of the resulting emulsions. In this study, a pseudo-ternary water/poly(oxyethylene) nonionic surfactant/decane system was chosen as a model system to form oil-in-water emulsions at 25 °C. The phase behavior of the model system was determined at constant temperature in order to know the equilibrium phases and also those involved in the emulsification process. The low-energy emulsification methods studied were

- A. Addition of oil to an aqueous surfactant dispersion.
- B. Addition of water to a surfactant solution in oil.

C. Mixing preequilibrated samples of the components.

Emulsion droplet size distributions were obtained by means of laser diffraction and scattering methods as well as by optical microscopy. The emulsions obtained with methods A and C were more polydisperse than those obtained by method B. Furthermore, with method B very small droplet size emulsions, nanoemulsions, could be obtained. The results have been interpreted according to the changes in the natural curvature of the surfactants during the emulsification process.

Key words Emulsification · Nanoemulsion · Ethoxylated nonionic surfactant · Phase behavior

Introduction

Emulsions are thermodynamically unstable liquid/liquid dispersions stabilised, generally, by surfactants, polymers or solids particles [1]. The sizes of the droplets, which constitute the dispersed phase, are in the range from 0.5 to 100 μm , approximately. In this range, gravity forces attract emulsion droplets. As nonequilibrium systems, emulsion properties depend not only on physicochemical variables (nature of components, composition, temperature and pressure) but also on preparation methods and the order of addition of the components [1–4].

On the other hand, microemulsions are thermodynamically stable, isotropic liquid/liquid dispersions with

characteristic sizes of the order of 0.01 μm [5–12]. They form spontaneously when the aqueous, oily and amphiphilic components are brought into contact. A major disadvantage of microemulsions for practical applications lies in the fact that microemulsion formation requires higher amounts of surfactant than emulsions, typically over 10 wt%.

In this context, a new class of emulsions with droplet sizes in the range of nanometers, similar to those of microemulsions, has been reported in recent years [13–15]. These emulsions, termed nanoemulsions, miniemulsions or ultrafine emulsions, are transparent or translucent and show high kinetic stability. Due to their characteristic properties, namely extremely small droplet size (between 20 and 500 nm), kinetic stability and

transparency, nanoemulsions are attracting increasing theoretical and practical interest.

The main objective of this work was to study the relationship between the type of phases present during the emulsification process, the order of addition of components and nanoemulsion formation.

Experimental

Products

The surfactant was a technical grade polytetraoxyethylene dodecyl ether with four oxyethylene groups purchased from Sigma, abbreviated as $C_{12}(EO)_4$. The oil component was *n*-decane and water was deionized by Milli-Q filtration.

Methods

Phase diagram

The phase behavior of the water/ $C_{12}(EO)_4$ /decane system was determined at constant temperature (25 °C). All components were weighed, sealed in ampoules and homogenized with a vibromixer. These samples were equilibrated at 25 °C. The phase boundaries were determined by visual inspection. The type of liquid crystal was identified using a polarising microscope.

Hydrophile–lipophile balance temperature determination

The hydrophile–lipophile balance (HLB) temperature, T_{HLB} , was determined by conductivity with a Crison model 525 conductimeter with a Pt/platinized electrode with a cell constant of 0.960 cm^{-1} . The samples were prepared with an electrolyte solution ($\text{NaCl } 10^{-2}\text{ M}$) instead of water.

Emulsion formation

Emulsions were prepared at 700 rpm with a magnetic stirrer and the speed of addition of the components was kept constant. The final surfactant concentration in all the emulsions was 5 wt% and the temperature was 25 °C.

Droplet size

The droplet size of the emulsions was determined by optical microscopy (Reichter Polyvar 2, Leica), laser light refraction (Mastersizer-S, Malvern) or laser light scattering Photon Correlator Spectrometer 4700 PS/MV Malvern depending on the size range.

Results and discussion

To determine the relationship between nanoemulsion formation, the type of phases present during the emulsification process and the order of addition of the components, a model system, water/ $C_{12}(EO)_4$ /decane, was chosen. The phase behavior of the system was first determined in order to know the equilibrium phases and also those involved in the emulsification process. Then, oil-in-water (O/W) emulsions were prepared according

to different methods. Finally, emulsion droplet sizes were determined in emulsions with constant surfactant concentration as a function of the oil weight fraction, $R = \text{oil}/(\text{oil} + \text{water})$.

Phase behavior of the water/ $C_{12}(EO)_4$ /decane system

The phase diagram of the water/ $C_{12}(EO)_4$ /decane system at 25 °C is shown in Fig. 1. The behavior of this system conforms to that of similar nonionic surfactant systems [16–18]. The main characteristics are as follows. A one-phase region of lamellar liquid crystal (I_{CL}). A zone of one liquid phase (I), considered to be formed by inverse micelles or water-in-oil (W/O) microemulsions, with a subregion (I') characterized by its birefringence under shear. There is a multiphase region of lamellar liquid crystal (II_{LC}), a two-phase region (II_V) composed of a dispersion of vesicles in water and a region of two liquid phases (II). The water–surfactant binary system is a dispersion of lamellar liquid crystal in water (vesicles) at surfactant concentrations below 17 wt%.

The nonionic surfactant used in this work was of technical grade; therefore, the HLB temperature is not a system property, but depends on the water/oil ratio and surfactant concentration [16]. The HLB temperature at a constant surfactant concentration (5 wt%) and different oil-weight fraction, R , was determined by conductivity, using aqueous NaCl solution instead of water, as indicated in the Experimental section. The conductivity is shown as a function of R in Fig. 2. Independent of the R ratio, initially, the conductivity is high and increases slightly with temperature. At a certain temperature (T_{HLB}), the conductivity decreases suddenly, reaching

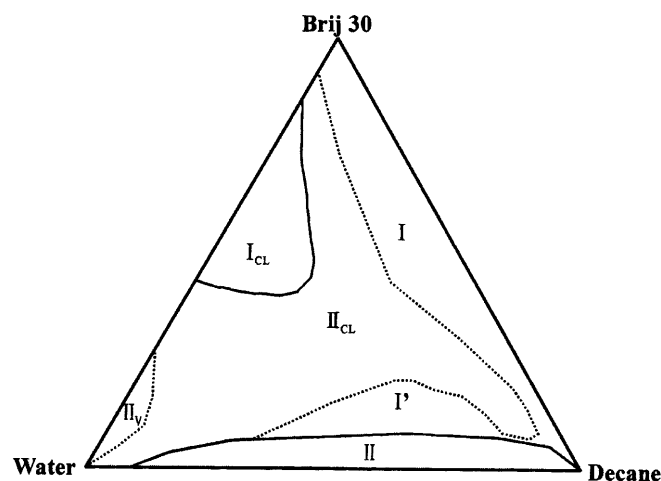


Fig. 1 Phase behavior of the water/poly(oxyethylene lauryl ether) $C_{12}(EO)_4$ /decane system at 25 °C. *I*: isotropic liquid phase; *I'*: shear birefringence liquid phase; I_{CL} : lamellar liquid-crystalline phase; II_{CL} : multiphase region including lamellar liquid crystal; II_V : lamellar liquid-crystal dispersion (vesicles); *II*: two liquid phases

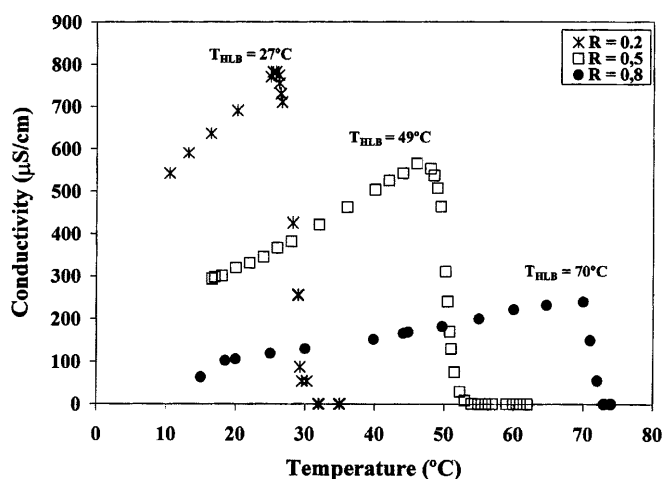


Fig. 2 Conductivity as a function of temperature for the system of an aqueous solution of 10^{-2} M NaCl/ $C_{12}(EO)_4$ /decane. $R = \text{oil}/(\text{oil} + \text{water})$, $S = 5 \text{ wt}\%$

very low values, an indication that surfactant molecules change their affinity. O/W (high conductivity) emulsions are formed when $T < T_{HLB}$ and W/O (low conductivity) emulsions are formed when $T > T_{HLB}$. As expected, at constant surfactant concentration, T_{HLB} diminishes when the oil weight fraction increases due to the different partition of the surfactant homologues between the water and the oil phases.

The requirement of low values of interfacial tension for nanoemulsion formation has been a subject of debate [13, 15, 19]. The formation of nanoemulsions has been related to the order of addition of the components. In order to find out whether a relationship between interfacial tension and nanoemulsion formation could be established, the interfacial tensions for equilibrated samples were measured as a function of R at a surfactant

Fig. 3 Droplet size as a function of R for emulsions obtained by emulsification methods A and C

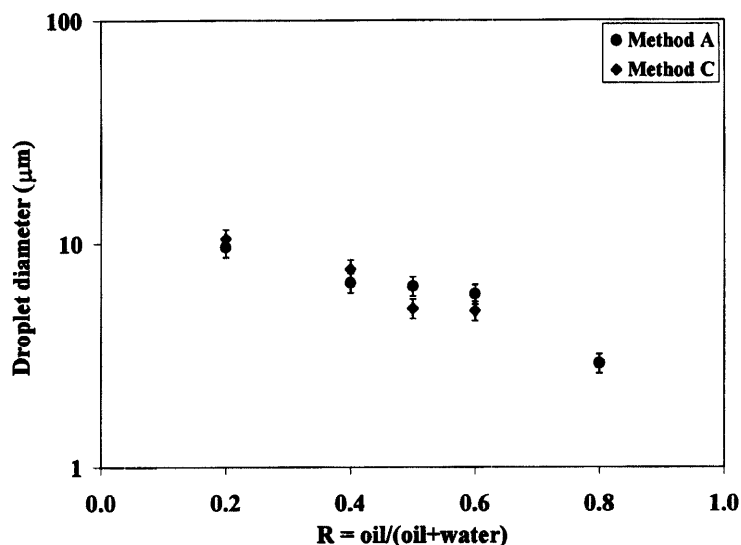


Table 1 Interfacial tensions for equilibrated samples of water/ $C_{12}(EO)_4$ /decane as a function of the oil-to-water weight ratio, R . The surfactant concentration was 5 wt% and the temperature was 25 °C

$R = \text{oil}/(\text{oil} + \text{water})$	Interfacial tension (mN m^{-1})
0.25	6.0×10^{-3}
0.50	7.1×10^{-2}
0.80	2.7×10^{-1}

concentration of 5 wt% at 25 °C. Table 1 shows that the interfacial tensions increase with R . The lower measurable interfacial tensions were obtained at R values close to 0.25, in the region where nanoemulsions can only be formed by method B (see later).

Emulsification and emulsion droplet size

In this study, emulsions were prepared using low-energy emulsification methods. The surfactant concentration was kept constant at 5 wt%. The emulsification methods used were the following:

- Adding, slowly, hydrocarbon to mixtures of water and surfactant.
- Adding, slowly, water to surfactant and hydrocarbon solutions.
- Weighing all components and letting the samples equilibrate prior to emulsification.

Figure 3 shows that droplet sizes decrease with an increase in R when emulsions are obtained by methods A and C. Nanoemulsion formation was not observed using these methods. The lowest sizes are of the order of 3 μm . It is worth noting that using a high-energy input (ultraturrax at 10000 rpm) nanoemulsions could not be

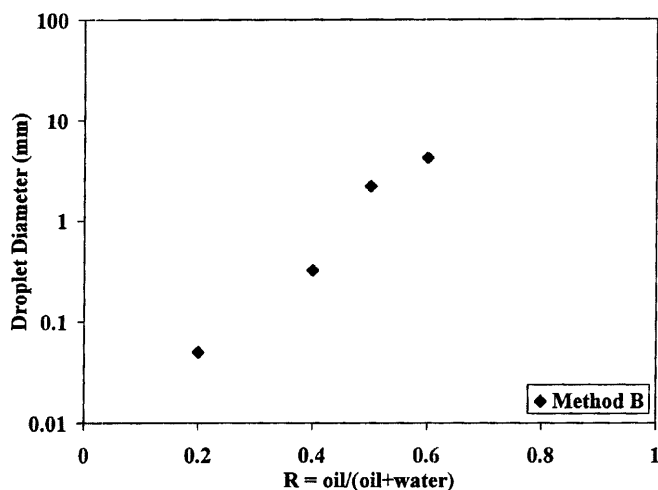


Fig. 4 Droplet size as a function of R in emulsions obtained by emulsification method B

formed by these methods. Moreover, all emulsions obtained were highly polydisperse.

On the other hand, droplet size increases with an increase in R in emulsions obtained with method B (Fig. 4). All the emulsions show narrow size distributions. It should be noted that small droplet sizes (of the order of 50 nm) were obtained in emulsions with R lower than 0.35. These emulsions, which have a transparent appearance and are bluish, can be considered as nanoemulsions.

These results clearly show that nanoemulsions could be formed when the interfacial tension was very low; however, low equilibrium interfacial tension is not the only requirement. For instance, at $R = 0.25$, the equilibrium interfacial tension is $6 \times 10^{-2} \text{ mN m}^{-1}$, and depending on the order of addition of the components, emulsions of $10 \mu\text{m}$ (method A, C) or 50 nm (method B) are obtained; therefore, the key to nanoemulsion forma-

tion could be attributed to the phase transitions that occur during the emulsification process. With emulsification method A, initially the system is formed by a dispersion of liquid crystal and water (vesicles). Addition of decane to the system leads to O/W emulsions via a multiphase region with lamellar liquid crystal (Fig. 1). In emulsification method B, the transitions during emulsification are the following (Fig. 1): an isotropic phase, I, (a W/O microemulsion); a multiphase region including lamellar liquid crystal (II_{LC}); a shear birefringent (bicontinuous) phase (I'); an O/W emulsion. Similar transitions can be produced at constant compositions by changes in temperature [15–17]. In emulsification method B there is a more pronounced change of curvature of the surfactant during the emulsification process from W/O to O/W than in method A. Consequently, the interfacial tensions achieved during the emulsification process are probably not as low as in method B.

Conclusions

Nanoemulsions have been obtained with emulsification method B (addition of water to surfactant in oil solution) at certain oil weight fractions where very low values of interfacial tensions are achieved; however, low values of equilibrium interfacial tensions are not the only requirement to obtain nanoemulsions. The change in the natural curvature of the surfactant during the emulsification process could play a major role. Independent of the oil weight fraction, emulsions obtained by method B have lower polydispersity than those obtained by method A (addition of oil to surfactant in water mixture).

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