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Formation of Nano-emulsions by Low-Energy Emulsification Methods at Constant Temperature

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Formation of nano-emulsions has been studied in the system water/Brij 30/decane at 25 °C by three low-energy emulsification methods: (A) stepwise addition of oil to a water–surfactant mixture, (B) stepwise addition of water to a solution of the surfactant in oil, and (C) mixing all the components in the final composition. Nano-emulsions with average droplet size of 50 nm and high kinetic stability have been obtained only at oil weight fractions, R , lower than 0.3 by emulsification method B. Independent of the oil weight fraction, R , emulsions obtained by method B have lower polydispersity than those obtained by methods A and C. Phase behavior studies have revealed that compositions giving rise to nano-emulsions consist of W_m , (O/W microemulsion), L_α (lamellar liquid crystalline), and O (oil) phases, at equilibrium. It has been shown that equilibrium properties cannot fully explain nano-emulsion formation. Low values of equilibrium interfacial tensions and phase equilibrium involving a lamellar liquid crystalline phase are probably required but not sufficient to obtain nano-emulsions in this system. The key factor for nano-emulsion formation has been attributed to the kinetics of the emulsification process. The change in the natural curvature of the surfactant during the emulsification process may play a major role in achieving emulsions with small droplet size.

Introduction

Emulsions, colloidal dispersions of at least two immiscible liquids, are nonequilibrium systems.^{1–3} Consequently, they are not formed spontaneously and their properties depend not only on thermodynamic conditions (i.e., composition, temperature, or pressure) but on preparation methods and the order of addition of the components.^{4–6} The structure of emulsions consists of droplets of the dispersed (or internal) phase in the continuous (or external) phase. Simple emulsions are classified as water-in-oil (W/O) or oil-in-water (O/W) depending on which phase constitutes the disperse phase. Generally, emulsion droplet size lies in the micrometer range, a size range in which droplets are attracted by gravity forces. An important aspect in the preparation of emulsions from both fundamental and technological viewpoints is to obtain a desired droplet size and a narrow size distribution.^{1–5,7,8}

Microemulsions, on the other hand, are equilibrium structures distinctly different from emulsions.^{9–11} They form spontaneously (their properties are independent of the order of addition of the components) and show a wider structural variety than emulsions.^{12–14} Although microemulsions are advantageous over emulsions from a formulation point of view, the relatively high surfactant concentration required for their formation limits their widespread use in practical applications.^{15,16}

In recent years, attention has been focused on emulsions with submicrometer droplet size, that is with sizes between those of conventional emulsions and microemulsions. These emulsions have been termed miniemulsions,^{7,17} nano-emulsions,^{18,19} fine-disperse emulsions,²⁰ submicron emulsions,²¹ unstable microemulsions,²² translucent emul-

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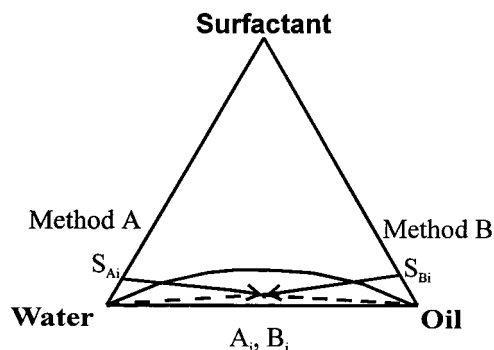


Figure 1. Schematic representation of the experimental path in two emulsification methods: method A, addition of decane to water/surfactant mixtures; method B, addition of water to decane/Brij 30 solutions.

sions,²³ and so forth. Because of their small droplet size (typically between 20 and 500 nm), nano-emulsions may appear transparent and are stable against sedimentation or creaming. They may have the appearance of micro-emulsions without requiring as much surfactant concentration for their preparation.

Reports on nano-emulsions have related their formation to aspects such as spontaneous emulsification,^{17,24,25} order of addition of the components,^{22,26} interfacial turbulence,²⁷ transitional inversion,²⁸ and so forth. Nano-emulsions are generally obtained by condensation or low-energy emulsification methods (the system goes through low interfacial tensions during the emulsification process)^{4,5,17,22,28–30} or by application of high energy input during emulsification, the so-called dispersion methods.^{18,19,21} We recently reported the preliminary results of a study on the relation between emulsification and phase behavior by three low-energy emulsification methods²⁹ (Figure 1): (A) stepwise addition of oil to a water–surfactant mixture, (B) stepwise addition of water to a solution of the surfactant in oil, and (C) mixing all the components in the final composition, pre-equilibrating the samples prior to emulsification.

In these studies, the system water/Brij 30/decane was chosen as a model system to obtain O/W emulsions. The results showed²⁹ that nano-emulsions with droplet sizes of the order of 50 nm and high kinetic stability were formed only when water was added to mixtures of surfactant and oil (emulsification method B). The low equilibrium interfacial tension values attained could not account for these results which were attributed to the phase transitions taking place during emulsification. In an attempt to interpret these results more deeply, a detailed study of the system phase behavior is reported in this paper. Conductivity changes during emulsification as well as emulsion properties, namely, droplet size and stability, are also reported.

Experimental Section

Materials. Technical grade polyoxyethylene lauryl ether with an average of 4 mol of ethylene oxide (EO) per surfactant molecule (Brij 30) was purchased from Sigma. *n*-Decane (purity > 99%) and NaCl (purity > 99.5%) were obtained from Merck. All products were used without further purification. Water was deionized by Milli-Q filtration.

Methods. *Phase Diagram.* All components were weighed, sealed in ampules, and homogenized with a vibromixer. The samples were kept at 25 °C to equilibrate. Liquid crystalline phases were identified by polarizing microscopy. The boundary lines drawn on the phase diagram lie equidistant between consecutive experimental measurements on either side of the phase boundary. Dashed lines mean that the boundary could not be determined accurately.

Conductivity. Conductivity was determined with a Conductimeter Crison model 525, with a Pt/platinized electrode. The samples were prepared with an electrolyte solution (NaCl 10^{−2} M) instead of pure water.

Interfacial Tensions. Static interfacial tensions were determined with a spinning drop tensiometer Krüss Site 04, at 25 °C. Samples were prepared with a surfactant concentration of 5.0 wt %, which corresponds to the final composition of the studied emulsions.

Emulsion Formation. Emulsions were prepared by adding one of the components, oil or water, to a mixture of the other two components (methods A and B, respectively, Figure 1) or by mixing all of the components in the final composition (method C), using a magnetic stirrer at approximately 700 rpm at 25 °C. The rate of addition of the components in methods A and B was kept constant at approximately 0.5 mL/min. The concentration of surfactant in all emulsions was kept constant at 5.0 wt %.

Droplet Size. Emulsion droplet size was determined by optical microscopy (Reichter Polyvar 2 Leica), laser light refraction (Mastersizer-S Malvern), or laser light scattering (Malvern 4700), depending on the size range of the emulsion droplets.

Stability. Emulsion stability was assessed by measuring the volume of the emulsion as a function of time. Emulsions were kept in sealed vials at 25 °C.

Results and Discussion

Phase Behavior. The phase diagram of the water/Brij 30/decane system at 25 °C is shown in Figure 2. Although the surfactant used is of technical grade and the Gibbs phase rule does not apply to this pseudoternary system, the general features of its phase behavior agree with those of typical ternary water/polyoxyethylene alkyl ether nonionic surfactant/oil systems.^{31–33}

Three distinct one-phase regions are observed in Figure 2: an isotropic region, *O_m*, along the oil–surfactant axis; a shear birefringent region, *D'*, in the center of the diagram; a lamellar liquid crystal region, *L_α*, extending from the water–surfactant axis toward the oil vertex. According to the literature,^{32–35} the structure of compositions in the *O_m* region would correspond to inverse micelles or W/O microemulsions whereas that of region *D'* would correspond to a bicontinuous or sponge-type structure.^{34,35} The boundaries of region *D'* are difficult to determine because the process leading to phase equilibrium for samples in the neighboring regions is extremely slow. Because of this fact, in the earlier report²⁹ the area of region *D'* was overestimated. The rest of the diagram consists of several two- and three-phase regions. At low surfactant concentration, a miscibility gap consisting of

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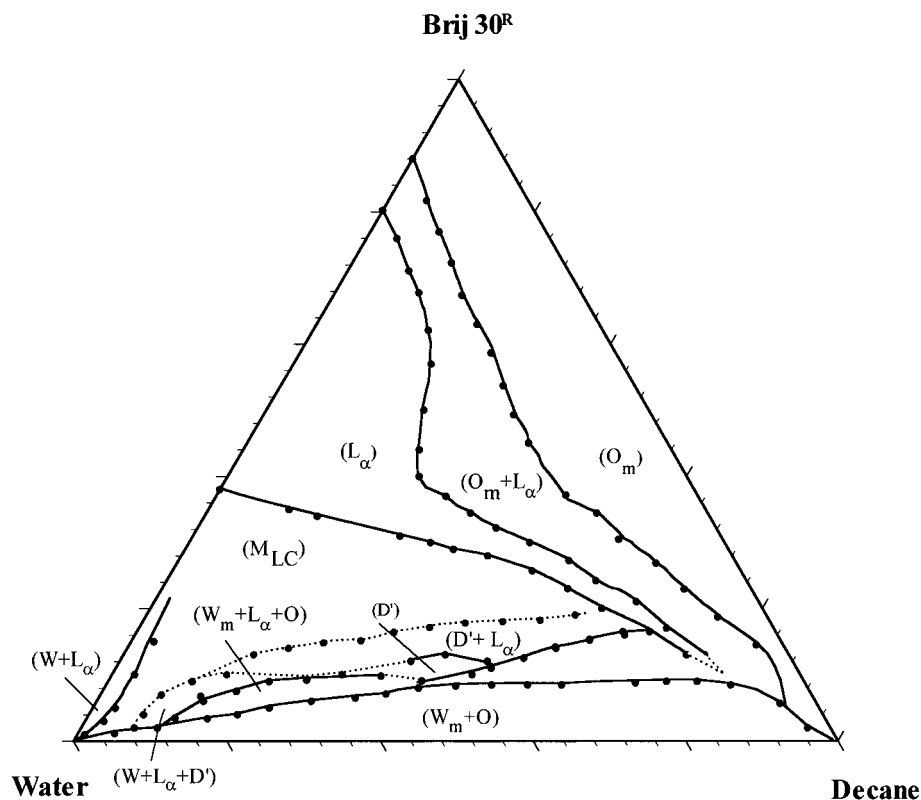


Figure 2. Phase behavior of water/Brij 30/decane system at 25 °C: O_m , isotropic liquid phase; L_α , lamellar liquid crystalline phase; D' , shear birefringent liquid phase; W_m , bluish liquid phase (O/W microemulsion); W , aqueous liquid phase; O , oil liquid phase; M_{LC} , multiphase region including lamellar liquid crystal.

two liquid phases, an aqueous and an oil phase ($W_m + O$), exists along the water–decane axis. At higher surfactant concentration, the two-phase region denoted as ($D' + L_\alpha$) consists of a lower liquid birefringent phase in equilibrium with an upper lamellar liquid crystalline phase. A two-phase region forms between O_m and L_α regions in which both phases are in equilibrium, with the L_α phase being the lower phase. Along the water–surfactant axis, near the water corner an aqueous phase is in equilibrium with a lamellar liquid crystalline phase ($W + L_\alpha$) giving rise by simple mixing to a vesicle dispersion, as detected by optical microscopy. Above the boundary of the ($W_m + O$) region and at oil weight fractions between $R = 0.10$ and $R = 0.45$, the three-phase region ($W_m + L_\alpha + O$) consists of a bluish liquid phase (an O/W microemulsion), a lamellar liquid crystalline phase, and a transparent liquid oil phase. Next to this region but at lower R -values, another three-phase region, ($W + L_\alpha + D'$), is formed, consisting of aqueous, lamellar liquid crystalline, and liquid birefringent phases in equilibrium. The region M_{LC} denotes compositions in which the lamellar liquid crystalline phase is present, but the equilibrium has not been determined yet.

To gain insight on the types of dispersions, the conductivity of samples with compositions belonging to different regions of the diagram was determined at 25 °C. The results are shown in Figure 3.

As expected for inverse-type structures, the conductivity of samples in region O_m is low ($0.3 \mu S cm^{-1}$). Within the lamellar liquid crystalline region (L_α), the conductivity is about $30 \mu S cm^{-1}$ at a low decane concentration but it decreases smoothly with the increase in the oil content, down to values of approximately $0.7 \mu S cm^{-1}$ along the line corresponding to a Brij 30/water ratio of 53/47. In the D' region, the conductivity values, around $250 \mu S cm^{-1}$, are of the same order as those reported for bicontinuous structures.³⁵ In region ($W_m + O$), as expected, the

conductivity increases as the oil weight fraction decreases, as shown by the isoconductivity lines indicating that the flow of ions is less obstructed. In this region, experimental conductivity values can be predicted by the Maxwell equation,³⁶ considering oil-in-water type emulsions (Figure 4):

$$K_{O/W} = K_w(1 + 2B\Phi)/(1 - B\Phi)$$

where $K_{O/W}$ is the conductivity of the oil-in-water emulsion, K_w is the conductivity of the continuous phase, Φ is the volume fraction of the dispersed phase, and $B = (K_o - K_w)/(K_o + 2K_w)$, with K_o being the conductivity of the dispersed phase.

The conductivity values in the ($W + L_\alpha$) region are relatively high, decreasing with the decrease in water concentration, an indication that water is the external phase (vesicle dispersion). The low conductivity values of compositions in region ($W + L_\alpha + D'$) are in contrast to the higher values of those in region ($W_m + L_\alpha + O$). From the values of conductivity in the latter region, it could be inferred that it may be continuous in W_m , the conductivity values being lower than in the ($W_m + O$) region, at similar oil weight fractions, probably because of the presence of the lamellar liquid crystalline phase, L_α . Compositions of region ($D' + L_\alpha$) show low conductivity at high water concentrations; however, the conductivity values are higher at a high decane content. The low conductivity values of compositions belonging to region M_{LC} close to the water-rich corner indicate that water is not the continuous phase, as could be inferred from their location in the diagram.

Hydrophilic–Lipophilic Balance (HLB) Temperature. As already stated, the nonionic surfactant used in

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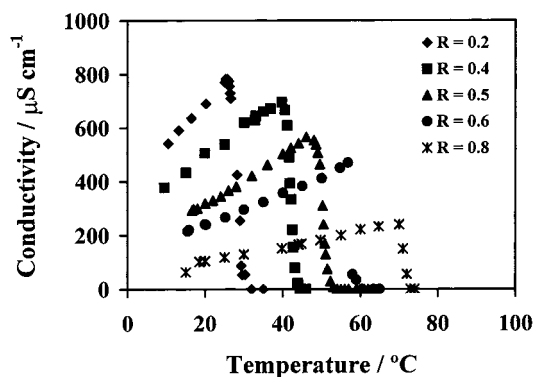
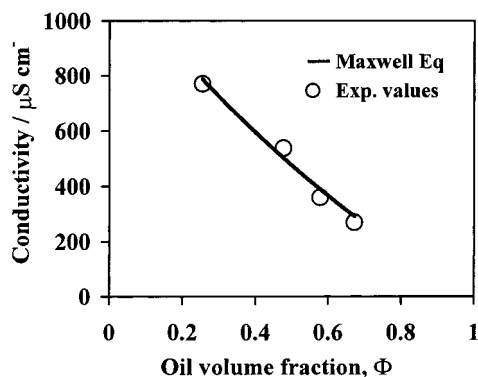
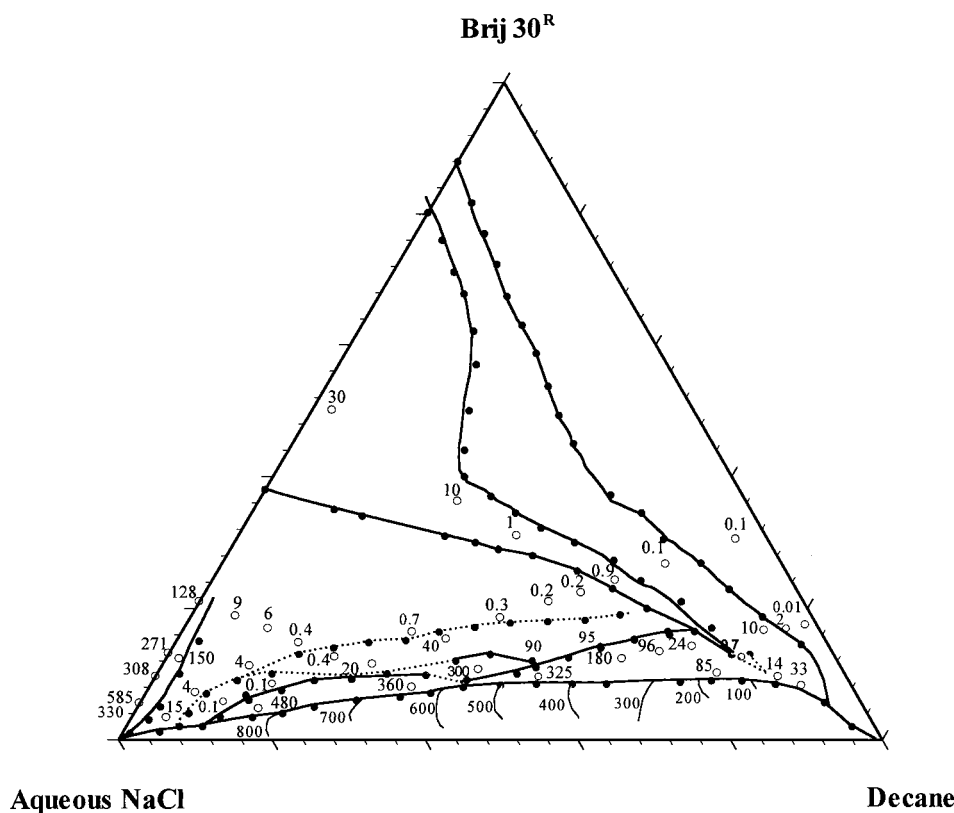


Figure 4. Experimental conductivity values of samples belonging to the ($W_m + O$) region as a function of oil volume fraction, Φ . The solid line corresponds to the calculated values according to the Maxwell equation.

Figure 5. Conductivity as a function of temperature in the system aqueous 10^{-2} M NaCl/Brij 30/decane at different values of the oil weight fraction in water, $R = O/(O + W)$, and constant surfactant concentration (5 wt %).

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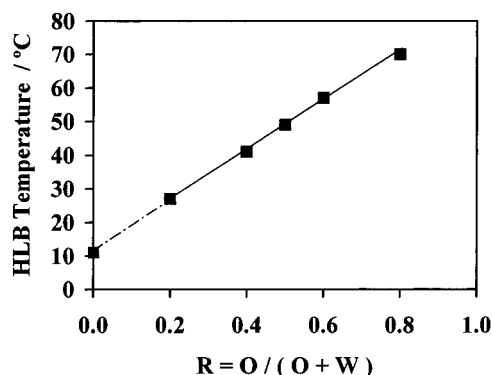


Figure 6. HLB temperature (T_{HLB}) as a function of the oil weight fraction in water, R , at a constant surfactant concentration (5.0 wt %) for the system aqueous 10^{-2} M NaCl/Brij 30/decane.

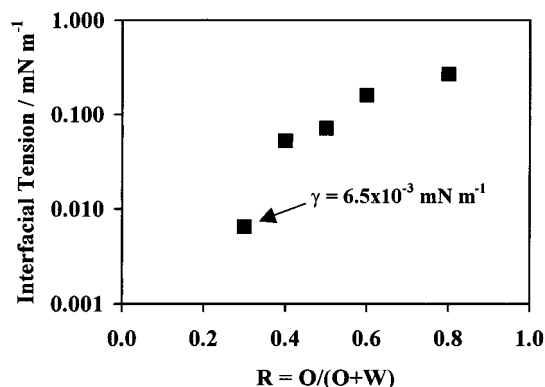


Figure 7. Interfacial tension as a function of the oil weight fraction in water, R , at a constant surfactant concentration (5.0 wt %) and temperature (25 °C).

Interfacial Tension. The interfacial tensions between the water and oil phases for equilibrated samples were measured as a function of R at a constant temperature (25 °C) and surfactant concentration (5 wt %). Interfacial tensions could be measured only for samples belonging to region ($W_m + O$) because of the difficulties in achieving phase equilibrium in region ($W_m + L_\alpha + O$). The results (Figure 7) show that with the decrease in the R value interfacial tension decreases about 2 orders of magnitude from $2.67 \times 10^{-1} \text{ mN m}^{-1}$ at $R = 0.8$ to $6.5 \times 10^{-3} \text{ mN m}^{-1}$ at $R = 0.3$.

Emulsification and Emulsion Droplet Size. Emulsions were prepared according to the low-energy emulsification methods A, B, and C, described earlier²⁹ and in the Introduction. A schematic representation of the experimental paths, followed in methods A and B, is shown in Figure 1. The emulsions studied were composed of 5.0 wt % surfactant and had an oil weight fraction, R , ranging between 0.2 and 0.8. The notation, A_i and B_i (emulsions prepared according to methods A and B, respectively), and the corresponding R values are listed in Table 1.

The log of the droplet diameter of emulsions prepared by the three methods is plotted as a function of the oil weight fraction, R , in Figure 8. The results shown in Figure 8 were obtained by laser light diffraction except those corresponding to emulsions with R values lower than 0.3 prepared by method B. Because of their small size, lower than the limit of detection of the instrument, droplet size was estimated by laser light scattering.

Droplet size increases from 6 to $10 \mu\text{m}$ with the decrease in R in emulsions obtained by method A. The size remains practically constant, approximately $6 \mu\text{m}$, in emulsions

Table 1. Notation and Composition of Samples Used to Determine the Changes in Conductivity during Emulsification and of the Final Emulsions

final emulsion		initial samples	
notation	$R = O/(W + O)$ at Brij 30 = 5.0 wt %	notation	water/ Brij 30 decane/ Brij 30
B_0	0.10	S_{B0}	65.6/34.4
A_1	0.20	S_{A1}	93.8/6.2
B_1		S_{B1}	79.2/20.8
A_2	0.30	S_{A2}	93.0/7.0
B_2		S_{B2}	85.0/15.0
A_3	0.40	S_{A3}	91.9/8.1
B_3		S_{B3}	88.4/9.6
A_4	0.50	S_{A4}	90.5/9.5
B_4		S_{B4}	90.5/9.5
A_5	0.60	S_{A5}	88.4/11.6
B_5		S_{B5}	91.9/8.1
A_6	0.65	S_{A6}	87.0/13.0
B_6		S_{B6}	92.5/7.5
A_7	0.80	S_{A7}	79.2/20.8

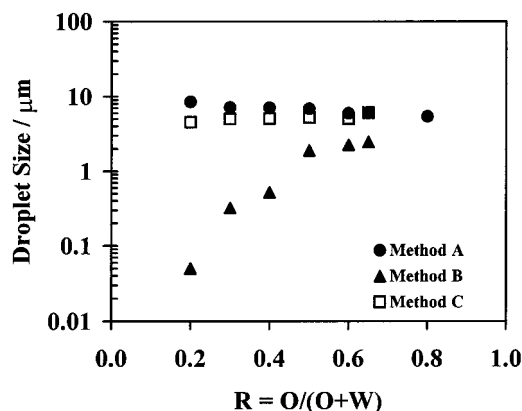


Figure 8. Droplet size as a function of R for emulsions obtained by emulsification methods A, B, and C.

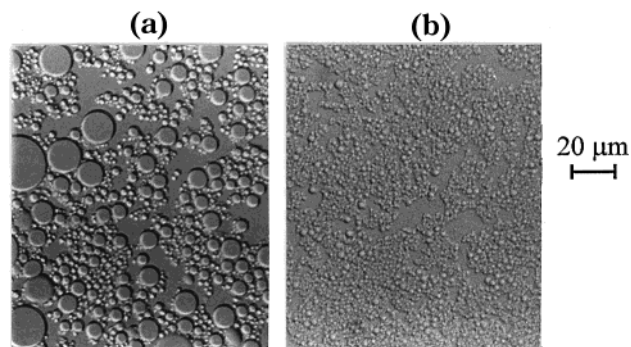


Figure 9. Photomicrographs of (a) emulsion A_4 and (b) emulsion B_4 with identical composition: surfactant concentration of 5 wt % and $R = 0.5$.

obtained by method C. It should be noted that all emulsions obtained by methods A and C are highly polydisperse. On the other hand, droplet diameter decreases from $6 \mu\text{m}$ to 50 nm with the decrease in R in emulsions obtained by method B. Moreover, all emulsions obtained by method B show narrow size distributions. Figure 9a,b shows photomicrographs of emulsions obtained by methods A and B at $R = 0.5$. The polydispersities of emulsions obtained by method B are considerably lower than those obtained by method A.

The most striking result in the emulsification studies (shown in Figure 8) is the formation of extremely fine emulsions in compositions with R values lower than 0.3 by method B. These emulsions, with droplet sizes of the order of 50 nm and a transparent and bluish appearance,

fall in the category of nano-emulsions. Considering the results of phase behavior (Figure 2), T_{HLB} (Figure 6), interfacial tensions (Figure 7), and emulsification (Figure 8), it was noted that these nano-emulsions form in the $(W_m + L_\alpha + O)$ region. Their T_{HLB} temperatures are close to 25 °C, and the equilibrium interfacial tensions reach very low values, of the order of 10^{-3} mN m $^{-1}$. The requirement for low values of interfacial tensions for nano-emulsion formation has been subject of debate.^{17,19,24,26,27,42} Our results clearly show that nano-emulsion formation cannot be fully explained by the equilibrium properties; low interfacial tensions are probably necessary but not sufficient to explain nano-emulsion formation. According to our results, nano-emulsions can be produced in the studied system, depending on the order of addition of the components, in compositions showing a phase equilibrium consisting of aqueous, lamellar liquid crystalline, and oil phases and similar low interfacial tension values. Consequently, the key factor should be attributed to the kinetics of the emulsification processes.

To explore the above assumption, emulsification methods A and B were followed by conductivity. The notation of the initial samples (S_{A1} and S_{B1}) and their initial compositions (W/Brij 30 and O/Brij 30 weight ratios) are given in Table 1. Figure 10a–c shows conductivity as a function of decane weight fraction. Decane was added to mixtures of water and surfactant in approximately the same way as in emulsification method A.

The conductivity profiles were obtained for different W/Brij 30 ratios. The initial samples, without decane, presented high conductivity values ranging approximately from 125 to 600 $\mu\text{S cm}^{-1}$. These samples belong to the $(W + L_\alpha)$ region, and its conductivity increased with the increase in water concentration.

Addition of decane reduced conductivity until a plateau close to zero was reached. According to the phase diagram, the system crosses first the M_{LC} region and then the $(W + L_\alpha + D')$ region. The low conductivity indicates that L_α is the continuous phase in the dispersion. The plateau occurs at decane weight fractions approximately between 0.05 and 0.12 for a W/Brij 30 ratio equal to 93.8/6.2 (Figure 10a). The range of this plateau increases with the increase in Brij 30 content. It is approximately between 0.05 and 0.17 for a W/Brij 30 ratio equal to 90.5/9.5 (Figure 10b) and between 0.1 and 0.3 for the ratio equal to 79.2/20.8 (Figure 10c). These ranges are consistent with the phase boundaries displayed in Figure 2.

At higher decane concentrations, conductivity increases again, reaching a maximum in the $(W_m + L_\alpha + O)$ region, indicating that water is the continuous phase in dispersions belonging to such a region. The maximum position also depends on the W/Brij 30 ratio. The larger the aqueous NaCl content, the higher the conductivity. Finally, as expected, a decrease in conductivity is observed in the $(W_m + O)$ region, because of the increase in the disperse phase volume fraction in the O/W emulsion.

Figure 11a–c shows conductivity plots when water is added to solutions of decane plus Brij 30 (additions according to method B).

Conductivity values are also consistent with the phase changes predicted by phase behavior studies (Figure 2). When water is added to the samples, there is an inverse micelle solution, O_m , which presents very low conductivity. As the water content increases, conductivity values increase monotonically, except for a large Brij 30 content

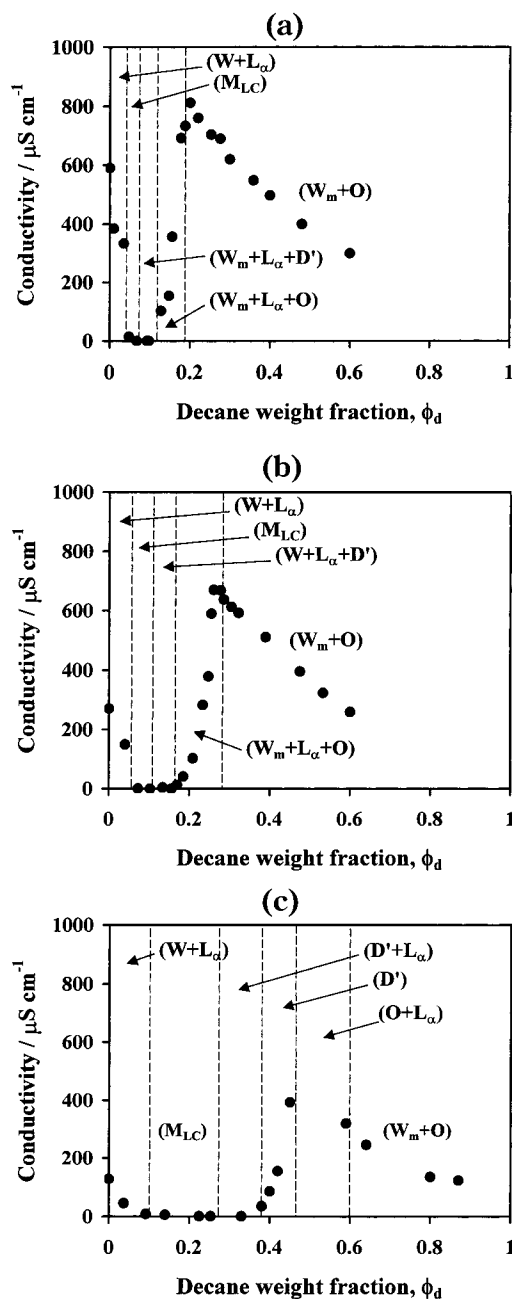


Figure 10. Conductivity as a function of decane weight fraction, ϕ_d , at $T = 25$ °C: (a) emulsion A₁, obtained by emulsification method A. The final value of R is 0.2. (b) emulsion A₄, obtained by emulsification method A. The final value of R is 0.5. (c) emulsion A₇, obtained by emulsification method A. The final value of R is 0.8.

(Figure 11d), in which conductivity remains low. Within the regions $(O_m + L_\alpha)$ and the L_α birefringent phase, conductivity values are small but they become gradually higher through $(D' + L_\alpha)$ and the spongelike D' regions. Eventually the largest conductivity is measured in the $(W_m + L_\alpha + O)$ region. At this region where nano-emulsions can form, the conductivity increases until the last composition is reached. The last two regions are not crossed if the decane/Brij 30 ratio is larger than 2.1, and because of that, conductivities remain low as displayed in Figure 11d.

The values from Figure 10 are consistent with the values in Figure 11. Approximately the same values are obtained by method A and by method B when reaching the same final points, without any significant hysteresis, which was

(42) Lyons, C. J.; Moore, B. P.; Elbing, L. E.; Collier, B. A. W.; Wilson, I. R. *J. Dispersion Sci. Technol.* **1990**, *11* (2), 125–141.

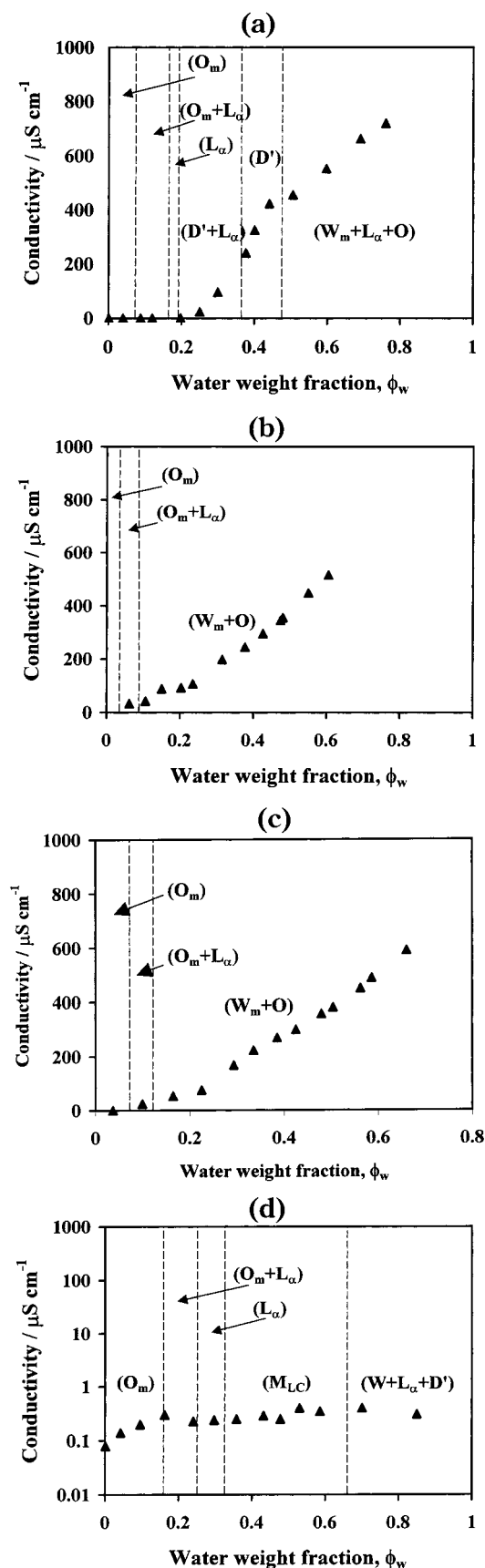


Figure 11. Conductivity as a function of water weight fraction, ϕ_w , at $T = 25\text{ }^\circ\text{C}$: (a) emulsion B₁, obtained by emulsification method B. The final value of R is 0.20. (b) emulsion B₄, obtained by emulsification method B. The final value of R is 0.5. (c) emulsion B₅, obtained by emulsification method B. The final value of R is 0.6. (d) emulsion B₀, obtained by emulsification method B. The final value of R is 0.1.

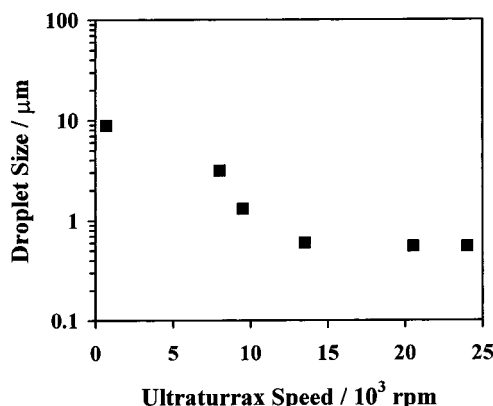


Figure 12. Droplet size as a function of homogenizer speed for emulsion obtained by emulsification method C.

observed only in the compositions inside the (W_m + L_α + O) region which are close to the (W_m + L_α + D') boundary.

In this study, nano-emulsions were obtained depending on the order of addition of components and R -values studied. This relationship is explained as a function of the phase transitions during the emulsification process (Figure 1) and conductivity (Figures 10 and 11). In emulsions obtained by method A, initially the system is formed by a dispersion of liquid crystals in water (vesicles). When decane is added to the system, O/W emulsions are obtained. However, in emulsification method B the transition goes from an isotropic liquid phase through a multiphase region including lamellar liquid crystals, a shear birefringent isotropic phase, and finally an O/W emulsion. In emulsification method B, the natural curvature of the system during the emulsification process changes structure from W/O to O/W.^{31,34}

The low interfacial tension in the system, $6 \times 10^{-3}\text{ mN m}^{-1}$ at $R < 0.35$, is necessary but not sufficient to obtain nano-emulsions. To prove that, the emulsification process was performed with high energy input by emulsification method C using a high-energy device (ultraturrax) at high rpm, and a nano-emulsion was obtained only above 15 000 rpm. Figure 12 shows droplet size evolution when the emulsification speed is increased. Emulsion droplet size decreases as a function of speed, and at approximately 15 000 rpm the emulsion droplet size is very small, in the nanometer range. Nevertheless, the high-shear method leads only to the formation of coarse emulsions whereas emulsions obtained by method B are translucent. Similar results have been reported in the literature.²⁶

Emulsion Stability. The stability of emulsions obtained by methods A and B at $R = 0.2$ is shown in Figure 13 where V_f/V_i is represented as a function of time (V_f and V_i are the final and the initial emulsion volumes, respectively).

The emulsion obtained by emulsification method A experienced phase separation in less than 1 h, whereas the nano-emulsion obtained by method B (with the same final composition) is a kinetically stable emulsion that did not show phase separation within the measuring time (1 year). The difference in polydispersity and droplet size of the emulsions is the factor that could explain the difference in stability.

Conclusions

Nano-emulsions have been obtained in the system water/Brij 30/decane by stepwise addition of water to surfactant–oil solutions (emulsification method B) at oil weight fractions, R , lower than 0.3. In contrast, nano-emulsions are not formed by adding oil to water–

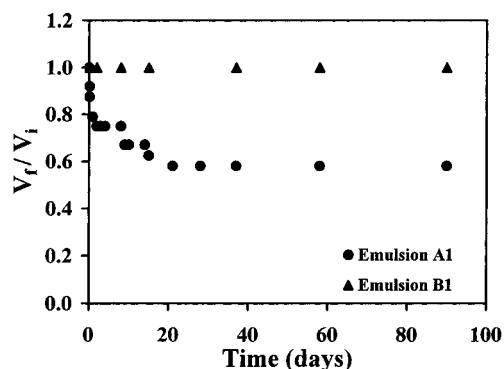


Figure 13. Stability of emulsions A₁ and B₁, $R = 0.2$. V_i and V_f are initial and final emulsion volumes, respectively.

surfactant mixtures (emulsification method A) or by mixing all the components at the final composition (emulsification method C). Independent of the oil weight fraction, R , emulsions obtained by method B have lower polydispersity than those obtained by method A. Study of the system phase behavior has revealed that nano-emulsions are produced in compositions showing phase

equilibrium consisting of three phases: W_m (O/W micro-emulsion), L_α (lamellar liquid crystalline), and O (oil). However, it has been shown that equilibrium properties cannot fully explain nano-emulsion formation. Low values of equilibrium interfacial tensions and phase equilibrium involving a lamellar liquid crystalline phase are probably required but not sufficient to obtain nano-emulsions in this system. The key factor for nano-emulsion formation should be attributed to the kinetics of the emulsification process. The change in the natural curvature of the surfactant during the emulsification process may play a major role in achieving emulsions with small droplet sizes.

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