

Making Use of the Formulation–Composition Map To Prepare Highly Concentrated Emulsions with Particular Rheological Properties

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ABSTRACT: The effects of the formulation and dispersed-phase weight fraction on rheological properties of highly concentrated water-in-oil emulsions are reported. Because the surfactant concentration is kept constant, emulsion characteristics may be represented on a formulation–composition bidimensional map. The formulation variable is the hydrophilic–lipophilic balance (HLB) number of the nonionic surfactant or surfactant mixture which ranges from 4.3 to 10. Highly concentrated water-in-dodecane emulsions are prepared using a semibatch process, with a dispersed-phase weight fraction ranging from 0.90 to 0.98. Two major effects are observed in relation to the formulation influence: First, elastic modulus (G') remarkably decreases in the vicinity of optimum formulation whenever the affinity of the surfactant for the oil and water phases is exactly balanced (HLB = 10.5). Second, the elastic modulus value passes through a maximum, concomitant to a minimum drop size, at some distance of the so-called optimum formulation (HLB = 7.7). Hence, the use of a bidimensional formulation–composition map allows one to control and to modulate the final rheological properties of highly concentrated emulsions.

1. INTRODUCTION

Highly concentrated emulsions contain a volume fraction of dispersed phase larger than the volume fraction of 0.74, which corresponds to the most compact arrangement of uniform and undeformable spheres.^{1,2} They can contain a very large amount of dispersed phase, e.g., 99%, and have been also named high internal phase ratio emulsions (HIPRE),^{1,3,4} biliquid foams,⁵ aphrons,⁶ hydrocarbon gels,⁷ or gel emulsions.^{8,9} The continuous phase consists of thin liquid films which separate close-packed drops, mostly distorted as polyhedral cells.

In the past decade, the potential of highly concentrated emulsions in pharmaceuticals, cosmetics, food, explosives, and other applications has been uncovered. Several studies have been dedicated to understanding the relationships between the preparation processes and the formulation with the structure and properties of resulting emulsions. The relation between the dispersed-phase volume fraction (ϕ), the polydispersity, and droplet distortion has been reported; different modes of droplet packing were determined from theoretical models of mono-, bi-, and tridisperse sphere packings.^{10,11} The behavior of the elastic modulus (G') and critical stress (τ_c) based on the increase of volume fraction has been investigated; it was found that both the elastic modulus and the critical stress increase with an increase in the dispersed-phase proportion.^{3,12,13} The rheological behavior of highly concentrated water-in-fluorinated-oil emulsions as a function of temperature has been reported. The measurements of elastic properties were proposed as a simple tool to follow the emulsion aging. Additionally, the elastic modulus and the average drop size were found to exhibit respectively a maximum and minimum with the temperature variation.¹⁴

The effect of surfactant concentration was also examined; several studies showed that the continuous phase of the highly concentrated emulsions is formed of type S2 inverse (respectively

S1 direct) micelles for water-in-oil (W/O; respectively O/W) emulsions.⁹ The behavior and stability of emulsions prepared with aliphatic and aromatic hydrocarbons using different surfactants have been studied. For nonionic surfactants, the formation of highly concentrated emulsions was not feasible with some studied aromatic oils, whereas, with ionic surfactants, stable emulsions were achievable whatever the type of oil.^{15,16} The influence of electrolyte on the properties and stability of highly concentrated water-in-oil emulsions formulated with different hydrophilic–lipophilic balance (HLB) surfactants was studied. For the system water/surfactant/paraffin, the best emulsion stability was found for a HLB value around 5. At this formulation, the average droplet size remains almost constant. It was also observed that the rheological properties and stability of highly concentrated emulsions are significantly enhanced when an electrolyte (e.g., 2.5 wt % MgSO_4) is incorporated into the dispersed phase.¹⁷ Coupled effects of formulation and process conditions on the rheological characteristics of highly concentrated emulsions have been examined: the temporal evolution of the sample shear elastic modulus (G') and droplet average radius (R) was measured using a steady light transport technique. The relation between G' , R , and dispersed-phase volume fraction (ϕ) was found to differ from Princen's model and a model based on dominant van der Waals interactions was proposed.¹⁸

In spite of the many reported studies on highly concentrated emulsions, their rheological properties have not been related yet to the physicochemical formulation and the water/oil content at constant total surfactant concentration. Such an approach would

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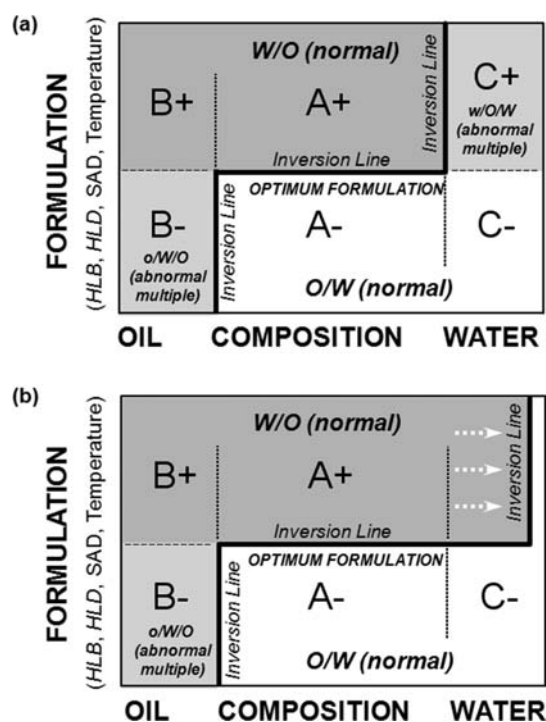


Figure 1. (a) Regions of the formulation–composition bidimensional map. (b) Shift of inversion line.

allow one to typify the system state on a formulation–composition bidimensional map, in which the emulsion properties have been reported to follow a general phenomenology pattern.^{19,20} This would characterize the highly concentrated emulsion phenomenology, just as for other regions which are segregated in the formulation–water/oil composition map according to the type and properties (interfacial tension, drop size, viscosity, and stability).²¹

The line that separates the regions in which water-external and oil-external emulsions are formed as the result of the stirring of an equilibrated surfactant–oil–water system is denominated the “standard inversion line” (stair-shaped bold line in Figure 1). The three branches of the inversion line allow one to divide the map in six regions: region A corresponds to a mid-range water-to-oil ratio, while the B and C regions are associated with low and high water content, respectively. The sign + or – that follows the letter indicating the regions corresponds to the expression of the generalized formulation expressed through the hydrophilic–lipophilic deviation (HLD)^{22,23} or another formulation variable such as the surfactant hydrophilic–lipophilic balance number. It is positive (+) if the surfactant affinity for the oil phase dominates and negative (–) for the opposite case.

Regions A+, B+, A–, and C– are called “normal” regions because the emulsion type corresponds to the normal curvature requirement of the interface, according to Bancroft’s rule,^{24,25} Langmuir’s wedge theory,²⁶ or Winsor’s interaction energy analysis^{27,28} among other equivalent formulation effect associated concepts. Simple W/O or O/W emulsion morphologies are usually produced in these normal regions. Regions C+ and B– are called “abnormal” regions because the external phase is not the one expected from the formulation influence. In these regions, there is actually a conflict between the formulation and composition effects, and, as a consequence, multiple o/W/O and w/O/W emulsion morphologies are spontaneously formed upon stirring.

In this symbolism, the lower case letter indicates the most inner phase, that is, the droplets inside the drops.

HLD = 0 corresponds to the so-called “optimum” formulation at which the surfactant exhibits exactly the same affinity for the water and oil phases. At this formulation, many systems exhibit very distinctive properties such as three-phase behavior with a microemulsion middle phase in equilibrium with excess water and oil, ultralow interfacial tension, and high solubilization of water and oil in the microemulsion.²⁹ The label of “optimum formulation” comes from the fact that an ultralow interfacial tension was the property sought by the researchers involved in enhanced oil recovery methods.³⁰ The trespassing of any horizontal (respectively vertical) branch of the inversion line produces a so-called transitional (respectively catastrophic) inversion,³¹ with characteristics discussed elsewhere.³²

The central (horizontal) branch of the inversion line is always at the same location (i.e., at optimum formulation), and it separates the regions where the hydrophilic and hydrophobic tendencies dominate. But, it was recently found that at extreme water–oil ratio there is an influence of surfactant mixture fractionation on the optimum formulation line, which might be slanted.³³ The lateral (vertical) inversion branches have been found to shift toward the center or the sides of the map, depending on the emulsification protocol and other variables such as the phase viscosity or the surfactant concentration.^{34,35}

The aim of the present work is to study the coupled effects of the physicochemical formulation and the dispersed-phase weight fraction on the rheological properties of highly concentrated W/O emulsions. In particular, we want to understand the evolution of the rheological properties in relation to the distance of the optimum formulation, which is represented by the HLB number of surfactant or surfactant mixture compared against the optimum HLB value determined experimentally. Highly concentrated emulsions are prepared according to a semibatch process (detailed later on) in which the lateral branch of the standard inversion line is shifted toward a higher water content as indicated by the arrows shown in Figure 1b and thus resulting in an extension of the region A+. The total surfactant concentration is kept constant as in the formulation–composition bidimensional map.

2. MATERIALS AND METHODS

2.1. Materials. Water is deionized and Milli-Q filtered with a Millipore apparatus. Dodecane is obtained from Aldrich (Reagent Plus, 99% Purum) and used as received. NaCl is supplied by Aldrich (98% Purum). Three nonionic surfactants are used as received: sorbitan monooleate (SPAN 80, HLB = 4.3), sorbitan monolaurate (SPAN 20, HLB = 8.6), and polyethoxylated (20EO) sorbitan trioleate (TWEEN 85, HLB = 11) supplied by Sigma and Fluka.

2.2. Determination of the Optimum Formulation. To determine the optimum formulation of the studied system, two procedures are employed. First, the so-called unidimensional formulation scan technique is used.^{20,36} Formulation scans are carried out at three (water) dispersed-phase volume fractions ($\varphi = 0.50, 0.75,$ and 0.90). The HLB number of surfactant or surfactant mixture is used as the formulation variable, and it is calculated according to a linear mixing rule on a weight basis. The total surfactant concentration is 4 g/(40 mL of total system volume). To increase the conductivity of the aqueous phase and allow the detection of the inversion point, 2 wt % NaCl is incorporated in the water. All systems are left to equilibrate 24 h in a closed jar and are then stirred with an Ultra-Turrax turbine blender (IKA

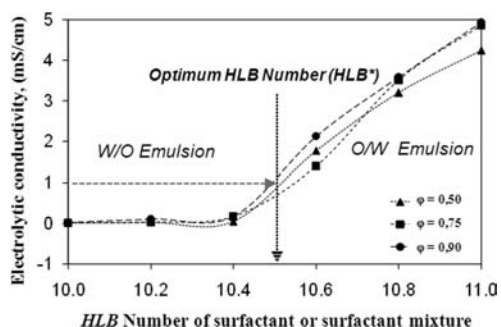


Figure 2. Electrolytic conductivity measurements as a function of the HLB number.

T25 basic/dispersion tool S25-NK-19G, Staufen, Germany) rotating at 8000 rpm during 30 s. The electrolytic conductivity (κ) of emulsions is measured with a CDM210 conductimeter and a CDC749 platinized platinum cell, both provided by Radiometer Analytical. Since the 2 wt % NaCl brine conductivity is 26.3 mS/cm, while the dodecane conductivity is 0.01 S/cm, the emulsion type is readily determined as O/W (respectively W/O), whenever the conductivity is higher (respectively lower) than 1 mS/cm, which is taken as the cutoff value. It is worth remarking that the NaCl is only used to determine the optimum formulation using the so-called unidimensional formulation scan technique.

Highly concentrated emulsions are prepared using a semi-batch process detailed next. Three dispersed-phase weight fractions ($f_w = 0.92, 0.95,$ and 0.98) are studied, which cover the right part of the map where the highly concentrated W/O emulsions are prepared (Figure 1b). The HLB range to be tested to determine the so-called optimum formulation is selected from 10 to 11. Emulsions are stocked at 27 °C for visual observation during 24 h after their preparation.

2.3. Preparation of the Highly Concentrated Emulsions. A 100 g amount of highly concentrated water-in-dodecane emulsions is prepared using a semibatch process.¹⁸ First, the surfactant (mixture) is incorporated into the oil phase, and the agitation turbine is positioned at the free surface. Then, the aqueous phase (pure water) is added at a flow rate (Q_w) of 15 g/min under an agitation speed of 500 rpm. Finally, the emulsion is homogenized during 10 min at the same agitation speed. The emulsification vessel is a jacketed cylindrical glass tank (70 mm diameter) with 600 mL of capacity. The temperature of the system is controlled at 27 ± 1 °C by circulating a liquid from a Polystat 12HT thermostatic bath (Bioblock Scientific) through the jacket of the vessel. The agitation system used to prepare the highly concentrated emulsions is a Turbo Test 33/750 P (Rayneri Groupe VMI) equipped with a 45° pitched-blade turbine of 50 mm diameter. A speed controller ensures a constant stirring rate, independent of the evolution of the emulsion viscosity. Five (water) dispersed-phase weight fractions are studied: $f_w = 0.90, 0.92, 0.94, 0.95,$ and 0.98 . The studied formulations in terms of HLB number are 4.3, 5.6, 7.7, 8.6, and 10. The surfactant concentration is maintained constant and equal to 1 wt %, relative to the emulsion.

2.4. Rheological Characterization. The rheological properties of highly concentrated emulsions are determined with a stress-controlled AR 2000 rheometer (TA Instruments). A plate/plate geometry device with a 40 mm diameter (aluminum coated) and a 1.5 mm gap is used. Low-shear oscillatory measurements are carried out 1 h after the end of the emulsion preparation at 27 °C. Frequency sweeps are carried out at a strain within the linear

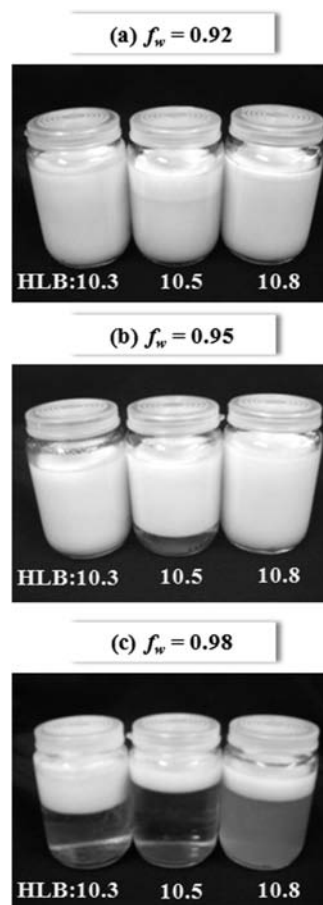


Figure 3. Photographs of highly concentrated emulsions prepared using the semibatch process.

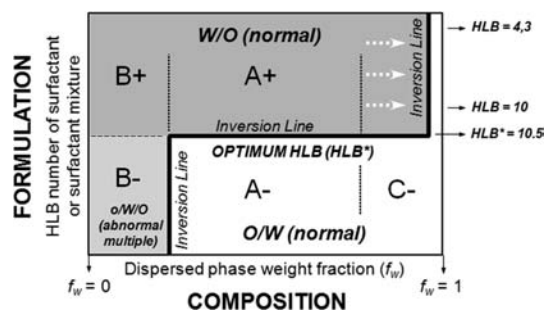


Figure 4. Optimum formulation and region studied of the formulation–composition bidimensional map.

viscoelastic region in the range of 0.01–100 rad/s. Time sweeps are realized at a strain within the linear viscoelastic region over a time range of 0–3600 s, where $t = 0$ corresponds to the termination of the emulsification protocol. Stress sweeps are made at a frequency of 10 rad/s over a stress range of 0.008–600 Pa, for different aging times of the emulsion over the range of 1–384 h.

2.5. Interfacial Tension. The interfacial tension is determined at 27 °C with a spinning drop tensiometer Model 300, from the University of Texas, modified to control the sample temperature.

2.6. Average Drop Size. The average drop size values are determined using the analysis of incoherent polarized steady light transport (AIPSLT) and the geometrical model proposed in a previous work.³⁷

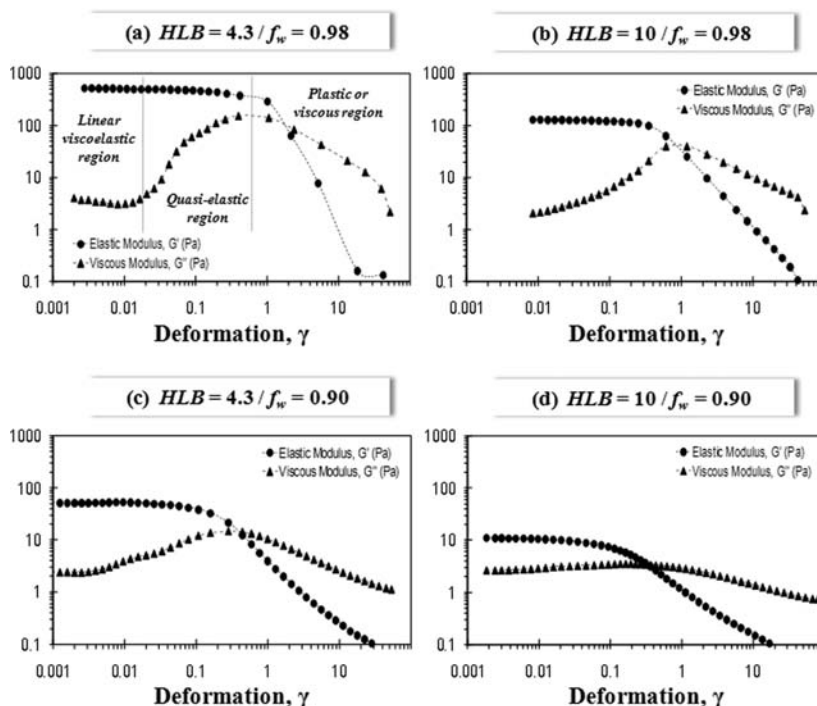


Figure 5. Elastic and loss moduli as a function of the deformation ($27\text{ }^{\circ}\text{C}$, frequency = 10 rad/s).

3. RESULTS AND DISCUSSION

3.1. Optimum Formulation. Figure 2 shows the variation of the electrolytic conductivity of the emulsions prepared from pre-equilibrated water/surfactant/dodecane systems along the so-called unidimensional formulation scan previously described. For the three dispersed-phase volume fractions ($\varphi = 0.50, 0.75,$ and 0.90), the formulation was scanned stepwise, changing the HLB number from 10 to 11 with 0.2 unit increments.

The conductivity variation indicates that the change from a low-conductivity (W/O) emulsion to a (O/W) high-conductivity one approximately takes place at a surfactant mixture HLB number equal to 10.5. This value thus corresponds to the horizontal branch of the inversion line on a formulation–composition bidimensional map, i.e., the optimum formulation of studied system where the affinity of the surfactant is exactly balanced for the two phases.^{29–31} For φ beyond 0.90, it was not possible to use this technique because the electrolytic conductivity is always high in the millisiemens per centimeter range. This indicates that the emulsion morphology corresponds to the C+ region of the formulation–composition bidimensional map, with an aqueous external phase (see Figure 1a).

To determine the optimum formulation in the case of a dispersed-phase weight fractions ranging from 0.90 to 0.98, a second procedure is used. Highly concentrated emulsions are prepared using the semibatch process that shifts the vertical branch of this inversion line toward the high water content side (Figure 1b). Figure 3 shows pictures of the emulsions 24 h after their preparation, for the three dispersed-phase weight fractions ($f_w = 0.92, 0.95,$ and 0.98) and three formulation cases (HLB = 10.3, 10.5, and 10.8). For emulsions prepared at $f_w = 0.92$ and 0.95 , it is seen that the optimum formulation may be located at around HLB = 10.5 by the electrolytic conductivity change. Visual observation indicates that the emulsions formulated at HLB = 10.5 present a quick phase separation (Figure 3a,b), a hint that confirms it matches the optimum formulation.^{29–31}

Table 1. Interfacial Tensions as a Function of the HLB Number of Surfactant or Surfactant Mixture

HLB	(mN/m)	HLB	(mN/m)
5.6	5.7	8.6	3.6
7.7	4.8	10	1.6

At $f_w = 0.98$, for the three formulations (HLB = 10.3, 10.5, and 10.8), the emulsions exhibit a phase separation immediately after the preparation. From these observations, it may be said that the optimum formulation is around HLB = 10.3 and that the horizontal branch of the inversion line is slightly slanted. As mentioned before in the Introduction, this behavior has been already observed at extreme water–oil ratio, where an interfacial composition change of the surfactant mixture induces this slanting, particularly with ethoxylated nonionic surfactants.^{33,38} However, it may be said that, in the present case, the optimum formulation is well-defined at HLB = 10.5 (Figures 2 and 3). Accordingly, this value may be taken as the optimum HLB* (Figure 4). It is worth remarking that, for emulsions formulated at HLB = 10, no phase separation was observed during several days. Consequently, a HLB = 10 limit was chosen as the highest value of the HLB range for the study of highly concentrated water-in-oil emulsions (Figure 4).

3.2. Elastic and Loss Moduli as a Function of the Deformation. To determine the linear viscoelastic region of the prepared emulsions, the oscillating stress sweeps (τ) were carried out for the most extreme values of the studied formulation (HLB number) and dispersed-phase weight fraction ranges; i.e., HLB = 4.3 and 10, and $f_w = 0.90$ and 0.98 . These measurements are used to determine where the rheological properties are independent of the applied stress and to identify the critical rheological properties. Figure 5 shows the general variations of the elastic modulus (G') and loss modulus (G'') as a function of the deformation. It is worth remarking that the elastic and loss moduli have been represented as a function of the deformation in order to show that

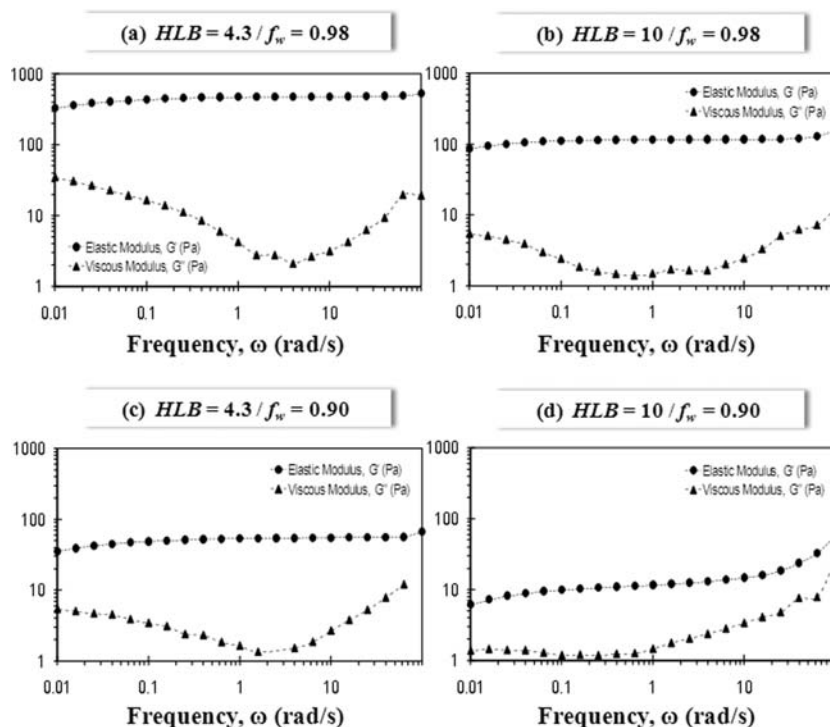


Figure 6. Elastic and loss moduli as a function of the frequency (27 °C, stress within the linear viscoelastic region).

there is essentially not a change in the critical deformation (cross-over point).

The observed tendency for the elastic modulus G' is first a plateau (constant value) over some deformation range, followed by a steady decrease after a break point. As far as the loss modulus (G'') is concerned, it is observed that it first exhibits a plateau in the so-called linear viscoelastic region (Figure 5a). Then, G'' increases in the so-called quasi-elastic region before passing through a maximum (Payne effect)³⁹ to finally decrease in the plastic or viscous region (Figure 5a). The maximum in G'' approximately corresponds to the break point in the elastic modulus, at the critical deformation (ϵ_c).

From graphs shown in Figure 5 it may be noticed that the elastic modulus values in the nondependent deformation region (plateau) are influenced by the formulation and the dispersed-phase weight fraction. First of all, if we compared the graphs horizontally, i.e., at dispersed-phase weight fraction constant, we can observe the influence of the formulation (HLB number). Elastic modulus values decrease in the proximity of optimum formulation. In effect, it is well-known that at optimum formulation, the properties of surfactant–oil–water systems are quite particular: additionally to the ultralow interfacial tension, the viscosity and stability of the emulsion both exhibit a minimum.^{30,40} This may clearly explain the particular behavior of emulsions in terms of viscoelasticity; i.e., its resistance to deformation and to flow in such circumstances is much lower than expected for emulsions prepared far of this region.⁴¹

This particular behavior may be also explained using the proposed models in the literature for the behavior of G' as a function of the interfacial tension (σ), the droplet average radius (R), and the dispersed-phase volume fraction (φ).^{18,42} In all models, the elastic modulus is directly proportional to the interfacial tension and dispersed-phase volume fraction. Table 1 shows the interfacial tension values as a function of the HLB number of surfactant or

surfactant mixture. It can be observed that the interfacial tension of the studied system decreases when the optimum formulation is approached, as expected. Therefore, for the emulsions prepared at HLB = 10, G' values decrease with the interfacial tension.

Second, the composition effect is observed if the graphs are vertically compared, i.e., at HLB number constant. From graphs shown in Figure 5, it may be observed the increase of G' with the internal phase content f_w for all formulations, as reported in the literature.^{3,12–14} The key feature is that this behavior is observed even in the vicinity of optimum formulation, where the systems exhibit some distinct properties (see Figure 5b,d). So, we can modulate the two effects (formulation and composition) to obtain highly concentrated emulsions with the desired final properties. For example, for the emulsion of HLB = 10 and $f_w = 0.90$ (see Figure 5d), the observed behavior is slightly different from the other systems. The elastic and loss moduli have very similar values. The break point in the elastic modulus values is not well-defined, and the maximum in the loss modulus has essentially vanished. The appearance of this emulsion is liquid-like. However, for the emulsion of HLB = 10 at $f_w = 0.98$ the appearance is gel-like.

3.3. Elastic and Loss Moduli as a Function of the Frequency. Frequency sweeps were carried out in the linear viscoelastic region and for the most extreme values of studied HLB and dispersed-phase weight fraction, as realized for the strain sweeps. It may be remarked that the elastic modulus of the prepared emulsions is essentially independent of the frequency (ω), which is a characteristic behavior of concentrated dispersions and gels.⁴³ The experimental data in Figure 6 show that, whatever the formulation and the dispersed-phase weight fraction, the elastic modulus is higher than the loss modulus, which indicates that the elastic response of the system is stronger. This means that the loss modulus values might be negligible, and the rheological behavior can be characterized and interpreted

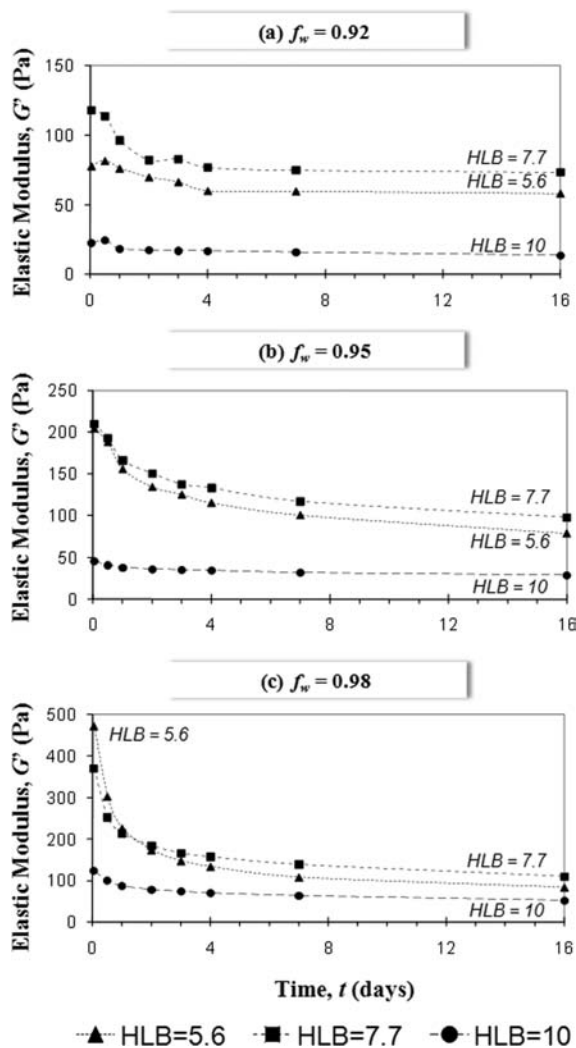


Figure 7. Evolution of the elastic modulus with time as a function of the formulation and the dispersed-phase weight fraction.

essentially from the elastic modulus values. For the emulsions near an optimum formulation, i.e., HLB = 10 and $f_w = 0.90$ and 0.98, the same behavior is observed as for the strain sweeps (Figure 5). The effects of the formulation and composition can be clearly identified in Figure 6, as observed for the strain sweeps. For the emulsion of HLB = 10 and $f_w = 0.90$ (see Figure 6d), the observed behavior is slightly different from the other systems. Due to the decreasing of G' while G'' remains almost unchanged, elastic and loss moduli have very similar values.

3.4. Elastic Modulus as a Function of the Aging Time.

Figure 7 shows the evolution of the elastic modulus (G') as a function of the formulation (HLB) and dispersed-phase weight fraction (f_w), at different aging times from 1 h up to 16 days. We can remark on the dramatic effect of the aging time on G' , i.e., the considerable loss of the elastic effect exhibited for all cases as aging takes place. The general trend is a rapid decline of the elastic modulus with aging, with an asymptotical value attained after about 4 days. For the emulsions with HLB far from the optimum formulation, i.e., HLB = 5.6 and 7.7, the elastic modulus decreases 2–5 times with respect to its initial value in the studied aging time (16 days). On the other hand, close to optimum formulation (HLB = 10), the elastic modulus is found to stay

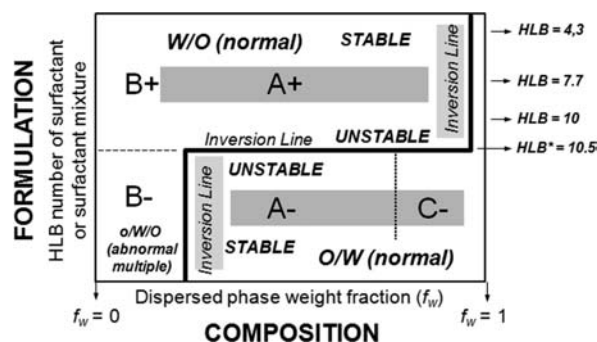


Figure 8. Formulation–composition bidimensional map showing the (shaded) zones where smallest drop size is attained, adapted from Pérez et al.⁴⁵

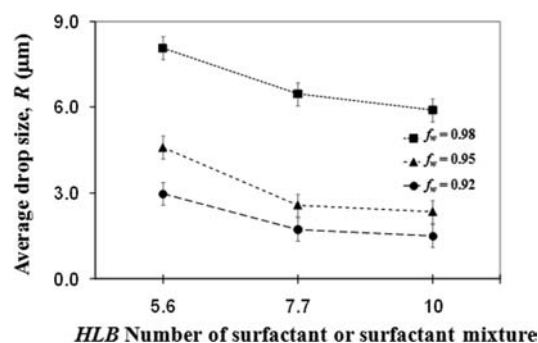


Figure 9. Average drop size as a function of the formulation and the dispersed-phase weight fraction 1 h after the end of the emulsion preparation process.

essentially constant and their values are much lower, due to interfacial tension decrease as discussed before.

In the range of f_w studied, emulsions prepared at HLB = 7.7 present G' values higher than those at other formulations. It is well-known that G' increases when emulsion drop size decreases. Hence, for all our emulsions at HLB = 7.7, the maximum elastic modulus could be matched to the occurrence of a minimum drop size at some distance from optimum formulation (Figure 8). This last effect has been shown to be the result of two opposite influences when the optimum formulation is approached, e.g., both an easier coalescence and an easier breakup. The breakup of droplets is favored by a decrease in the interfacial tension, whereas the stability is still high enough for the drops not to coalesce instantly.^{44,45}

To relate this concept to our experimental data, the average drop size (R) was determined for three dispersed-phase weight fraction ($f_w = 0.92, 0.95,$ and 0.98) and three formulations (HLB = 5.6, 7.7, and 10) 1 h after the end of the emulsion preparation (see Figure 9). For all fractions, it is seen that the R values decrease from HLB = 5.6 to HLB = 7.7 and then remains constant. In Figure 9, the occurrence of a minimum drop size at some distance from optimum formulation is not observed, as expected. One key factor could contribute to this situation: the stability. We can notice from visual observations that there is a faster decrease of the stability from HLB = 10 to HLB = 10.3. In fact, highly concentrated emulsions are not stable at HLB = 10.3. In some cases, the separation of phases is immediately observed at this last formulation (see Figure 3). Consequently, this could be considered as an evidence that the average drop size increases when the

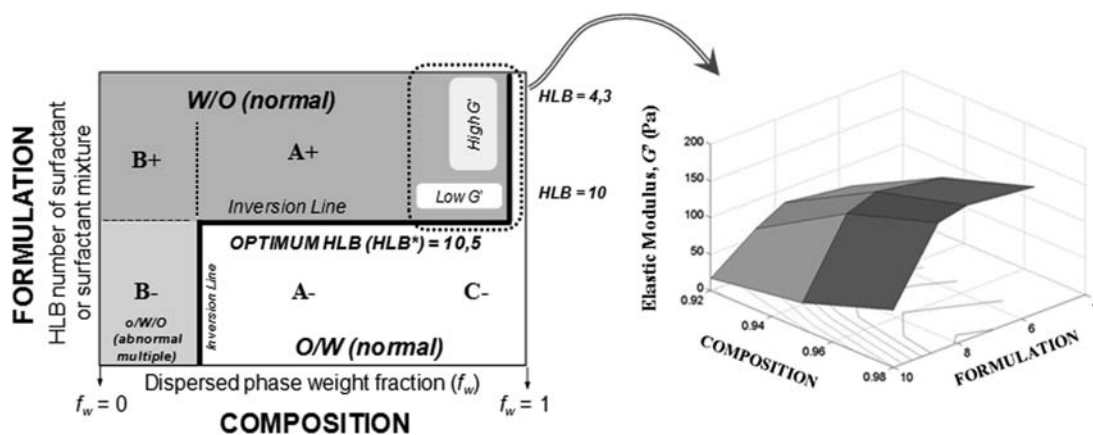


Figure 10. Representation of the elastic modulus on a formulation–composition map and a tridimensional graph (G' values 1 h after the end of the emulsion preparation process).

optimum formulation is approached. On the other hand, it has been reported in a previous study⁴⁴ that when the average drop size is lower, the minimum drop size is less pronounced and it is more difficult to observe it clearly. So, this notion of minimum average drop size at some distance from optimum formulation may explain the particular behavior observed of elastic modulus values for the emulsions prepared at $HLB = 7.7$.

For highly concentrated water-in-fluorinated oil emulsions prepared at $\varphi = 0.94$, Langenfeld et al.¹⁴ have observed that the elastic modulus and emulsion drop radius undergo a maximum and minimum, respectively, at the same temperature ($35\text{ }^{\circ}\text{C}$). The authors have explained this behavior by the variation of emulsification ratio (τ) with the temperature. This parameter is directly linked to the average radius of water droplets and is defined as the ratio of the experimental elastic modulus and the theoretical elastic modulus (G'_{max}) determined using the model proposed by Princen and Kiss. Nevertheless, we pointed out that this maximum elastic modulus can be better related to the attainment of a minimum emulsion drop radius due to the best compromise between low interfacial tension and coalescence rate when the optimum formulation is approached. Moreover, in their study, Langenfeld et al.¹⁴ have shown a decrease of the interfacial tension with temperature, i.e., when the system becomes more hydrophilic or the optimum formulation is approached.

4. CONCLUSIONS

Both the formulation and dispersed-phase fraction influence the rheological properties of highly concentrated emulsions. As expected from its impact on the emulsion structure, the dispersed-phase fraction induces the major effect on the rheological properties. However, two significant effects are produced by a change in formulation. First, the elastic modulus (G') remarkably decreases in the vicinity of the so-called optimum formulation ($HLB = 10.5$). So, it is possible to formulate highly concentrated emulsions with a particular low viscosity, property with potential applications in cosmetics and food. Second, the elastic modulus value passes through a maximum, matching a minimum average drop size (between $HLB = 7.7$ and $HLB = 10$) and presenting an improved stability, at some distance of the so-called optimum formulation. Finally, the formulation–composition map promises to be a useful tool for the preparation of highly concentrated emulsions with controlled rheological properties (see Figure 10).

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