

Emulsion inversion from abnormal to normal morphology by continuous stirring without internal phase addition

Effect of surfactant mixture fractionation at extreme water–oil ratio

Marianna Rondón-González^a, Véronique Sadtler^a, Lionel Choplin^a, Jean-Louis Salager^{b,*}

^a *Centre de Génie Chimique des Milieux Rhéologiquement Complexes (GEMICO), Ecole Nationale Supérieure des Industries Chimiques (ENSIC), Institut National Polytechnique de Lorraine (INPL), Nancy, France*

^b *Laboratorio FIRP, Ingeniería Química, Universidad de Los Andes, Mérida, Venezuela*

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Abstract

When the emulsion inversion from abnormal to normal morphology is induced by continuous stirring only, it takes place through the formation of a multiple emulsion in which the external phase is continuously included as droplets in the dispersed phase drops. In the studied case the system exhibits an initial O/W morphology, then a w/O/W multiple one before inverting into a W/O emulsion. The general trend reported in the literature is that the higher the initial water content, the longer the incorporating process to swell the drops in order to attain the critical dispersed phase volume that triggers inversion. The present study reports, for nonionic systems with a given hydrophilic–lipophilic balance (HLB = 6) and 7 wt.% of surfactant concentration, that this trend is found to be unexpectedly reversed when the initial water content increases beyond 80%. This anomalous result is attributed to an indirect increase in the lipophilicity of the formulation due to the variation of the interfacial surfactant mixture with the water/oil ratio, and to the formation of liquid crystals at high water contents.

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1. Introduction

An emulsion is a liquid–liquid dispersion stabilized by a surfactant. The classical emulsion preparation process consists in dissolving the surfactant in the suitable continuous phase (in which it has to be soluble), and to add the dispersed phase under appropriate agitation [1,2].

In the last decade, the interest in emulsion inversion, i.e. the change in the morphology from oil-in-water (O/W) to water-in-oil (W/O) or vice versa, has increased as it became a method to produce fine and concentrated emulsions at a low energy expense even with very viscous oils [3–5].

Depending on the changed variable, there are two types of emulsion inversion: the transitional inversion which is induced by the change of the surfactant affinity for the liquid phases, and the catastrophic inversion which is produced by a change in the

composition or physical factors of the system, e.g. the water-to-oil ratio, the viscosity of the phases, or the stirring protocol [6].

The catastrophic inversion is usually triggered by the continuous addition of the internal phase of the emulsion [7,8], but it could be also generated by the continuous stirring of an abnormal emulsion [9–11], i.e. an emulsion type that does not correspond to the normal curvature requirement of the interface, according to the Bancroft's rule [12,13], Langmuir's wedge theory [14] or Winsor's interaction energy analysis [15,16].

Abnormal emulsions frequently exhibit a multiple morphology in which the dispersed phase drops contain some tiny droplets of the continuous phase; the presence of these droplets satisfies Bancroft's rule and as a consequence, this inner emulsion is quite stable. Fig. 1 illustrates such a situation for a w/O/W multiple emulsion in which the low case “w” refers to the droplet phase which is inserted in the “O” drops [1].

When an abnormal emulsion is submitted to a continuous stirring, the external phase is continuously included as droplets in the dispersed phase drops and the process goes on indefinitely

* Corresponding author. Tel.: +58 274 2402954; fax: +58 274 2402957.
E-mail address: salager@ula.ve (J.-L. Salager).

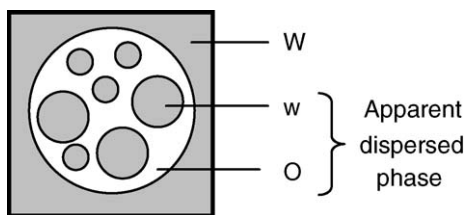


Fig. 1. Symbols for a w/O/W multiple emulsion.

since the inner droplets are stabilized against coalescence. As a consequence, the dispersed phase volume, i.e. $w + O$, increases until a critical dispersed phase content is reached at which the inversion is triggered [17,18], according to the so-called static inversion protocol. The validity of the critical dispersed phase concept was recently corroborated as the condition for an abnormal emulsion to invert into a normal one, no matter what protocol of inversion is used (dynamic, standstill dynamic, or static) [19].

The surfactant affinity and the water-to-oil ratio required to prepare an abnormal emulsion and to apply an inversion protocol are easily identified in a formulation–composition bidimensional map [6] (see Fig. 2).

The map is divided in three vertical 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. Multiple emulsions of the o/W/O and w/O/W type, are spontaneously formed upon stirring in the B^- and C^+ regions, respectively. Simple W/O (respectively O/W) emulsions are produced in A^+ and B^+ (respectively A^- and C^-) zones [20].

The sign after the letter indicating the regions corresponds to the affinity of the generalized formulation expressed through the hydrophilic–lipophilic deviation (HLD). It is positive if the surfactant affinity for the oil phase dominates and negative for the opposite case. $HLD = 0$ corresponds to the so-called optimal formulation at which the surfactant exhibits the same affinity for the oil and water phases. At this formulation many systems exhibit three-phase behavior with a microemulsion middle phase in equilibrium with excess oil and water. More information may be found in the recent literature [21–23].

This concept is based on the correlations for optimum formulation of enhanced oil recovery, which have been introduced 30 years ago [24]. The dimensionless generalized formulation expression for nonionic surfactant systems may be written as

follows:

$$HLD = \alpha - EON + b \times S - k \times ACN + t(T - 25) + a \times A \quad (1)$$

where α , k and t are surfactant parameters, EON the average degree of ethoxylation of the surfactant, ACN the alkane carbon number (or eventually EACN, the equivalent alkane carbon number if the oil is not an alkane), S and A the salt and alcohol concentrations, b and a the constants characteristic of each type of salt and alcohol and T the temperature.

Eq. (1) could be written as follows by defining the surfactant parameter $\beta = (\alpha - EON)/k$, which is available for many different surfactants in the literature [23].

$$HLD = k \times \beta + b \times S - k \times ACN + t(T - 25) + a \times A \quad (2)$$

Optimal formulation ($HLD = 0$) coincides with the horizontal branch of the standard inversion line (stair like bold line in Fig. 2), which is determined by stirring an equilibrated surfactant–oil–water system and measuring its electrolytic conductivity. The trespassing of the horizontal branch produces a transitional inversion, while the crossing over the lateral branches corresponds to a catastrophic inversion [25].

The central (horizontal) branch of the inversion line is always at the same location (i.e. at optimal formulation), whereas the lateral (vertical) inversion branches can move toward the center or the sides of the map, depending on the protocol and other variables such as phase viscosity or surfactant concentration [26,27]. As a consequence essentially all effects can be rendered in a three-dimensional diagram as introduced by Salager et al. [28].

In this paper, the influence of the water-to-oil ratio and the phase behavior in the emulsion inversion produced by continuous stirring only is interpreted on the two-dimensional generalized formulation–composition map. Since the formulation and composition remain constant, the point that represents the system in Fig. 2 map does not change position.

Hence the emulsion inversion is due to a change in condition, which shifts the A^+/C^+ branch of the inversion line from left to right as stirring goes on.

2. Experimental section

2.1. Surfactants and other reagents

In all experiments, the oil phase used is a kerosene cut equivalent to a mixture of nonane and decane ($EACN = 9.6$) supplied by Fluka. The aqueous phase consists of purified water (Milli-Q Millipore, France) in which 1 wt.% of NaCl (purity >98%, Aldrich) is incorporated to increase the conductivity of the water phase and allow the detection of the inversion point. Two nonionic surfactants supplied by Aldrich are used: Span80, a sorbitan monooleate ($HLB = 4.3$), is dissolved in the kerosene phase; Igepal CO-630, a polyethoxylated (9 EO) nonylphenol ($HLB = 13$) noted NP9EO is added to the water phase. The total surfactant concentration is 7 wt.%, and the Span/Igepal wt.% proportion is 80/20, and results in $HLB = 6$ when a linear mixing rule is used. A concentration of 7 wt.% of 2-butanol, supplied

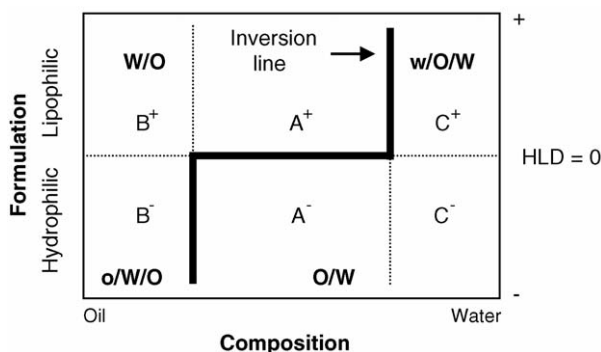


Fig. 2. Bidimensional formulation–composition map illustrating emulsion types and standard inversion frontier.

by Prolabo, is used to study the phase behavior of the surfactant-oil-water system and in some of the inversion experiences.

The surfactant parameter β for the NP9EO is calculated according to the literature [22] by using $\alpha = 6.5$ and $k = 0.15$, as $\beta_{\text{NP9EO}} = -16.7$.

The Span80 surfactant parameter is not known, but it is deduced from an experiment which is reported later, i.e. the NP9EO/Span80 mixture with an averaged HLB = 7 exhibits three-phase behavior at 7 wt.% surfactant and unit water/oil ratio, with kerosene (EACN = 9.6) and water with 7 wt.% sec-butanol at 25 °C.

Since the base HLB values for the Span80 and NP9EO surfactants are 4.3 and 13, respectively, a linear mixing rule on the HLB values for reaching the optimum mixture (HLB = 7), i.e. $7 = 4.3x + 13(1 - x)$ leads to a composition $x = 69\%$ Span80.

Eq. (2) allows to calculate the β parameter of this optimum mixture by using $\alpha x_A = -0.16$ for the asymptotic contribution of sec-butanol. It is found to correspond to $\beta_{\text{optmix}} = 10.7$. Since this mixture contains 69% Span80, this surfactant parameter may be calculated from

$$\beta_{\text{optmix}} = 10.7 = 0.69 \beta_{\text{Span80}} + 0.31 \beta_{\text{NP9EO}} \quad (3)$$

It is worth remarking that the resulting value $\beta_{\text{Span80}(f_w=0.5)} = +23$ corresponds to the conditions of experiment, i.e. 7 wt.% surfactant and unit water/oil ratio.

2.2. Continuous stirring or static inversion protocol

The abnormal systems, located inside the C^+ region of the formulation–WOR map, with initial water phase fractions of 0.6, 0.7, 0.8, 0.85 and 0.9 are prepared and initially emulsified with an Ultraturrax turbine blender (IKA T25 Basic/Dispersion Tool S25-NK – 19G, Germany) rotating at 8000 rpm during 40 s. Then, the initial emulsion is poured into a rheomixer device and is submitted to a continuous stirring protocol shortly described next and fully detailed elsewhere [11], until the phase inversion is detected by the abrupt change in conductivity and viscosity.

The conductivity value allows the estimation through Bruggeman's equation of the proportion of external water W (see Fig. 1), so-called effective water fraction f_{Wef} , because it is the one that conducts electricity.

$$f_{\text{Wef}} = \left(\frac{k}{k_w} \right)^{2/3} \quad (4)$$

where k is the emulsion conductivity and k_w the conductivity of the aqueous phase.

The rheomixer device [29] illustrated in Fig. 3, consists in a jacketed, non-baffled cylindrical vessel (with 70 ml of capacity) in which center is placed a U-type anchor impeller connected to the shaft of a RFS II rheometer (Rheometric Scientific, USA). The vessel is placed on a rotating turntable whereas the anchor is motionless; as such, the impeller is in relative motion with respect to the content of the vessel, and the torque produced by this motion can be measured to extract viscosity data.

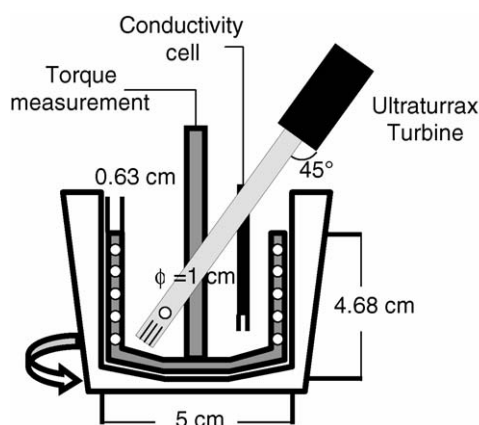


Fig. 3. Rheomixer device which provides stirring and mixing of the emulsion, and in-situ monitoring of both conductivity and viscosity.

The rotational speed of the turntable corresponds to an effective shear rate of 200 s^{-1} . The energy required for the emulsification and inversion process is provided by an Ultraturrax turbine (IKA DI 25 Basic/Dispersion Tool S25N – 10G, Germany) rotating at 9500 rpm. The presence of this stirrer in the vessel produces an additional torque on the anchor which is not accounted for in the Couette analogy method used to extract a viscosity-shear rate data from the non-conventional geometry [30]; therefore the viscosity data is reported in arbitrary units (a.u.).

The temperature of the system is controlled at 27 °C by circulating a liquid from a thermostatic bath through the jacket of the vessel. The conductivity is monitored with a CDM 210 conductimeter and a conductivity cell CDC 749 from Radiometer Analytical, France.

2.3. Phase behavior

The phase behavior of the surfactant-oil-water systems is studied by the so-called unidimensional scan technique [31], which consists in preparing series of systems with identical composition and formulation (same nature and amounts of surfactant, oil, aqueous phase, and alcohol) with the exception of the scanned variable. Thus, from one test tube to the next, the only difference is the value of the scanned variable, here the surfactant mixture composition and thus HLB, which is changed progressively.

The test tubes are closed with a screw cap. Then, they are gently shaken and left to equilibrate at 27 °C until there is not apparent change, typically 2 or 3 days. Then the phase behavior of the system is observed and eventual birefringent liquid crystals are detected by observation with a crossed polarizer filter device. The optimum formulation is chosen as the value of the variable that corresponds to the center of the three-phase behavior range [23].

In the present study the HLB of the Span80–NP9EO surfactant mixture is the scanned variable. Different HLB are attained by changing the proportion of the two surfactants, and using the linear average mixing rule between the base values as discussed previously.

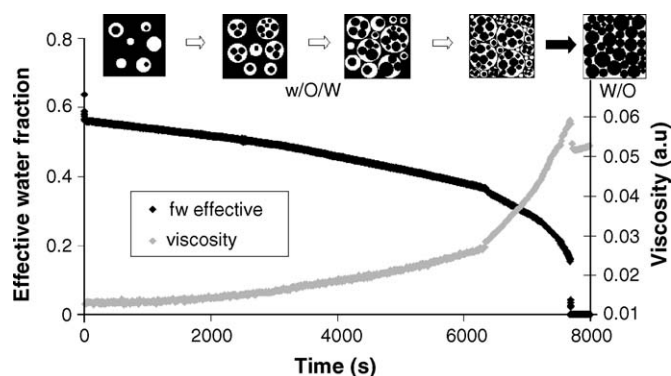


Fig. 4. Evolution of the properties (external W fraction f_{Wef} and viscosity) of a w/O/W abnormal emulsion ($fw = 0.6$) submitted to a continuous stirring protocol. Illustrations indicate the emulsion morphology evolution.

3. Results and discussion

Fig. 4 shows the variations of emulsion external W proportion f_{Wef} and viscosity during a typical phase inversion experiment induced by stirring only, from abnormal to normal morphology (in the $C^+ \rightarrow A^+$ direction of the bidimensional formulation–composition map) with a water content $fw = 0.6$.

The original emulsion (at $t = 0$) exhibits an external water content f_{Wef} , which is just slightly below its water content ($fw = 0.6$), i.e. it is essentially an O/W emulsion. As stirring goes on the amount of (W) external water decreases as a consequence of the inclusion of (w) droplets inside the O drops. The concomitant increases in viscosity also indicates the increase in internal phase (w + O) content of the w/O/W emulsion [32]. This trend proceeds slowly up to 7000 s. Then, the tendency accelerates and the sudden fall in f_{Wef} and in viscosity at 7600 s corresponds to the change in the morphology of the emulsion, from a water external type to an oil external one. At this point the swelling the oil (O) drops has increased the apparent dispersed phase volume up to the critical value at which the inversion is triggered [11,19].

When the experiment is repeated with variable water content, the inversion time is found to strongly depend on the (initial and actually constant) water content. The variation versus fw is quite non-monotonous, in both cases shown in Fig. 5, i.e. with and without 2-butanol co-surfactant. When the initial water fraction increases from 0.6 and 0.8, the inversion time increases, according to the expected trends [11,19]. The logical explanation for this trend is that the higher the initial water content (i.e. the lower the oil phase fraction), the longer the time it takes for the w water droplets to be included in a lower amount of oil drops. In other words, a higher swelling of the O drops by w droplets is required to attain the critical dispersed phase volume necessary to trigger inversion.

Fig. 5 diamond dot data indicate that in absence of co-surfactant, this trend unexpectedly reverses when the initial water fraction fw increases beyond 0.8.

In order to analyze the possible reasons for this reversal, the phase behavior of the system was studied, but due to the high sur-

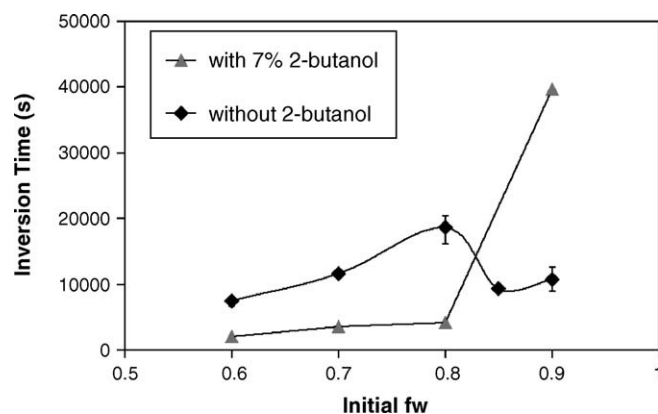


Fig. 5. Variation of the inversion time during a continuous stirring protocol of a w/O/W abnormal emulsion vs. the water fraction fw , in systems with and without alcohol cosurfactant.

factant content, mesophases were found and the exact location of optimum formulation was difficult to determine with accuracy. Nevertheless, the liquid crystal formation was definitely detected at fw 0.85 and 0.9 at the HLB (6) value corresponding to the systems studied in the inversion experiments.

In order to eliminate the mesophases and to presumably shorten the equilibration time, 7 wt.% 2-butanol was added to the systems. This alcohol was chosen because it has essentially no effect on the formulation of the system, as its contribution in the Eqs. (1) and (2) $\alpha x_A = -0.16$ at concentration above 3%, i.e. close to negligible [23]. This alcohol has roughly the same affinity for the oil and water phase and it strongly co-adsorbs in the interfacial layer and dilutes the surfactant packing density, and consequently inhibits the formation of mesophase [21], reduces the viscosity and speeds up molecular transfer.

The phase behavior map shown in Fig. 6, indicates that the zone in which three phase behavior is found, and the corresponding optimum formulation line that corresponds to its center, are slanted.

This means that the actual formulation, i.e. the proportion of hydrophilic and lipophilic surfactant in the interfacial mixture, changes with the water/oil ratio. This peculiar behavior

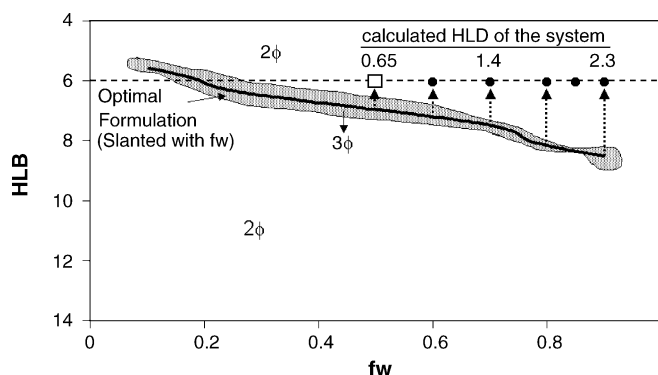


Fig. 6. Phase behavior of 7 wt.% Span80/NP9EO, 7 wt.% 2-butanol, 1 wt.% brine, kerosene as a function of formulation (mixtures of Span80/NP9EO) and composition (oil/water fraction). The black dots indicates the conditions for inversion experiments reported in Fig. 5 (Span80/NP9EO 80/20 and variable fw).

has been reported in the literature [20] with commercial non-ionic surfactants of the alkyl phenol type, which are mixtures of surfactant species with widely different hydrophilicities because the polyethoxylation mechanism results in a distribution of the number of ethylene oxide groups (EON) that approximately follows Poisson law [33].

It has been shown that the low EON oligomers (EON < 3) tend to partition preferentially into the oil phase, leaving the rest of the system, i.e. the water and the interface, with a higher content of high EON oligomers [34,35]. Such a partitioning results in a more hydrophilic composition at the interface [34].

It is known that at optimum formulation the surfactant hydrophilicity at interface is set whenever the oil, water, and temperature are fixed. This is what indicates Eqs. (1) and (2). When the water/oil ratio changes, the partitioning into the phases changes, as well as the equilibria with the interface. It has been shown that when the water content increases, the partitioning of low EON species into the reduced oil phase volume decreases with the corresponding migration of more lipophilic species to interface. As a consequence the interface tends to become less hydrophilic and a more hydrophilic overall mixture (higher EON or HLB) has to be used to compensate.

This is why the global formulation, i.e. the mixture HLB introduced in the system (as indicated by the ordinate in Fig. 6), is found to increase (downward to keep the direction of change of HLD indicated in Fig. 2) when the water content increases, as indicated by the slanting of the optimum formulation line in Fig. 6 [36].

The dots in Fig. 6 represent the systems with increasing fw from left to right. It is seen that at a constant Span80/NP9EO 80/20 surfactant mixture all representative points are located on a horizontal line at HLB = 6. However, this line does not correspond to a constant HLD formulation because of the fractionation phenomena. Instead it is seen that the increase in fw shifts the optimum formulation line away from the representative points.

In the corresponding A^+C^+ side of the map this means that the actual HLD of the systems represented by the dots in Fig. 6 becomes more lipophilic as dots are located farther to the right, i.e. as fw increases. Hence, as the water/oil ratio changes, an indirect formulation change occurs, i.e. an increase in lipophilicity, which may be estimated as follows.

First, it should be noted that the surfactant mixture that results in optimum formulation at fw = 0.5 is the one with HLB = 7, which correspond to 69% Span80 and 31% of NP9EO as calculated before. If in these reference conditions the surfactant parameters are $\beta_{\text{Span80}} = +23$ and $\beta_{\text{NP9EO}} = -16.7$, the mixture surfactant parameter is $\beta_{\text{optmix}(fw=0.5)} = +15.0$, and the HLD calculated after Eq. (2) is +0.65, which is a slightly lipophilic formulation corresponding to the distance of the square point (HLB = 6 and fw = 0.5) from the optimum formulation line in Fig. 6. For fw = 0.6, 0.7, 0.8 and so forth the distance tends to increase, as well as the HLD value. At fw = 0.9, the HLD of the surfactant mixture that results in optimum formulation is at an HLB = 8.5 mixture. Consequently, the experiment carried out at HLB = 6, is at a formulation which is about 2.5 HLB units more lipophilic. It is worth remarking that HLD unit and HLB units

are not exactly equivalent since the well-known formula

$$\text{HLB} = 20 \frac{44\text{EON}}{44\text{EON} + \text{MW}_L} \quad (5)$$

that relates the HLB of a polyethoxylated surfactant with its ethoxylation degree (EON) and the molecular weight of its lipophilic part (MW_L) is hyperbolic rather than linear. However, the use of the formula for ethoxylated nonylphenol ($\text{MW}_L = 220$) and close to optimum formulation (EON = 4.5) indicates that an increase in one EON unit from four to five, i.e. 1 HLD unit according to Eq. (1), results in an increase of 1.1 HLB unit. If this equivalent is used in the present case as a yardstick, it means that the formulation at the point represented by fw = 0.9 and HLB = 6, is HLD = +2.3 units, i.e. quite lipophilic.

It is well-known that there is a relationship between the generalized formulation (HLD) and the emulsion properties of surfactant-oil-water systems [37]. As reported by Salager et al. [6], and Miñana-Pérez et al. [20], a shift away from optimal formulation tends to increase, sometimes considerably, the stability of the emulsion, and this is a very general trend [37,38].

In the present case, enhancing the w/o inner emulsion stability makes it more competitive with respect to the O/W external one and thus, reduces the stirring time required to reach the critical dispersed phase content and trigger the inversion (Fig. 5). Additionally, the presence of liquid crystal in absence of 2-butanol would tend to increase even more the stability of the inner emulsion because of the gelification of the oil phase.

In order to diagnose the most important factor, the inversion experiences are repeated, but this time with 7 vol.% 2-butanol added to the systems. Fig. 5 reveals first that the inversion time is reduced by the addition of alcohol at low fw content (0.6–0.8), but that for the fw = 0.9 experiment, it is drastically increased.

The shorter time at low fw is probably related to the reduction in interfacial tension that favors the inclusion of droplets in drops.

As far as the lengthening of the inversion time at high fw is concerned, it is attributed to the elimination of liquid crystals that occur in absence of alcohol. This would increase the rate of escape of w droplets from the O drops according to Klahn et al. These authors reported that the escape rate is related to the drainage of the aqueous film between the internal droplets and the surface of the mother drop [39], whose stability could be greatly increased by the formation of liquid crystals [40].

4. Conclusions

When an emulsion inversion is carried out from abnormal O/W to normal W/O morphology (C^+ to A^+ regions) by continuous stirring only, it takes place through the evolution of a w/O/W multiple emulsion in which the external phase is continuously included as droplets in the dispersed phase drops.

The general trend is that the lower the initial dispersed oil phase (the higher the external water content), the longer the time required to incorporate enough water droplets into the oil drops to get them swollen enough to attain the critical dispersed phase fraction that triggers inversion. However, this trend could be unexpectedly reversed when the initial water content is increased

beyond 80%. This apparently anomalous result is attributed to an indirect shift in formulation toward more lipophilicity because of the variation of the interfacial surfactant mixture with the water/oil ratio, and to the formation of liquid crystals at high water contents and high surfactant concentration.

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