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# Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 2. Effect of the Stirring Intensity on the Dynamic Inversion Frontier

Isabel Mira, Noelia Zambrano, Eric Tyrode, Laura Márquez, Alejandro A. Peña, Aldo Pizzino, and Jean-Louis Salager\*

FIRP Laboratory, Universidad de Los Andes, Mérida 5101, Venezuela

The stirring intensity has a complex effect on the catastrophic inversion of emulsions in the direction of change from abnormal to normal morphology. At both low and high stirring energy, the inversion takes place early, after a low amount of the internal phase is added and through the occurrence of a multiple emulsion. At some intermediate stirring energy, the inversion appears to be delayed and it takes place without the occurrence of multiple emulsions.

## Introduction

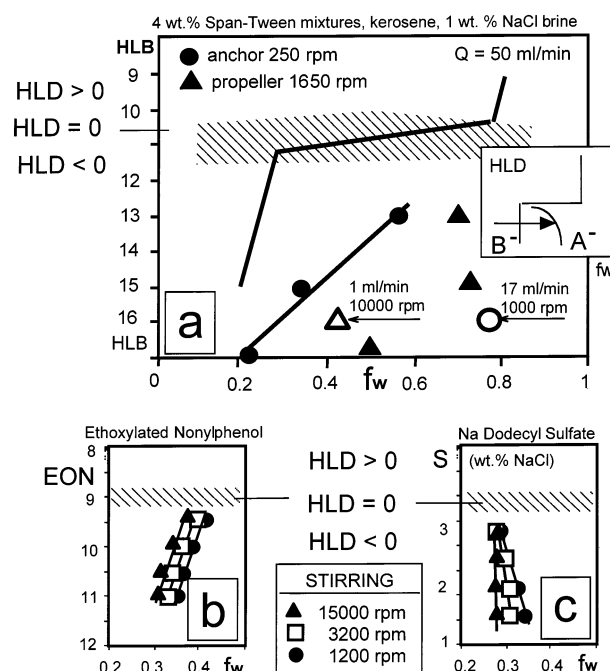
Dynamic inversion is the process in which an emulsion swaps its internal and external phases, with a morphological change from oil-in-water (O/W) to water-in-oil (W/O) or vice versa. Among the two inversion main types,<sup>1</sup> the one to be dealt with here is the so-called catastrophic inversion, whose name comes from its characteristics that mimic a catastrophe theory model, either the cusp<sup>2</sup> or the butterfly<sup>3</sup> depending on the degree of complexity which is desired. Such an inversion is produced by an increase in the internal phase content, in most cases with an increase in the number of drops, which end up touching and coalescing to become the new external phase. More details on these processes may be found in a recent review.<sup>4</sup>

The change from one type to the other often takes place rapidly (catastrophically) because it is opposed by a delaying phenomenon and is thus triggered at the "last" moment. This delay results in the formation of a hysteresis region in which the emulsion can be of one type or the other depending on its previous history. In practice, it is quite important to understand why and when the delay can be short or long. This point has received some attention in recent years, and some trends have been found concerning the effect of the surfactant concentration,<sup>5</sup> stirring energy,<sup>6,7</sup> phase viscosity,<sup>4,8,9</sup> and duration of stirring.<sup>10</sup> In part 1 of this series of papers,<sup>11</sup> the effect of the rate of addition of the internal phase on the catastrophic inversion from an abnormal to a normal emulsion type has been reported.

This second paper is dedicated to the effect of stirring energy, and it will explain the apparent discrepancies found in the literature.

## Basic Facts: Apparent Discrepancy

Figure 1 shows typical results in the hydrophilic part (HLD < 0) of a formulation–composition map. Different formulation scan variables are used, e.g., the HLB of a Tween–Span surfactant mixture (map a), the average number of ethylene oxide groups per ethoxylated nonylphenol molecule (map b), or the salinity of the aqueous



**Figure 1.** Formulation–composition maps showing the dynamic inversion line location as a function of the stirring energy for different systems.

phase in the case of a system containing dodecyl sulfate (map c). In all cases the three-phase behavior zone is indicated as a shaded region around optimum formulation at HLD = 0. The water/oil composition is indicated as the water volume fraction fw. In all cases the aqueous phase contains an electrolyte (NaCl) and the emulsion inversion from W/O to O/W is detected by an increase in the electrolytic conductivity. The addition of water to the original oil phase is carried out in a standard way in each experiment series, though not exactly the same for all plots. The inversion path follows the abnormal-to-normal direction ( $B^- \rightarrow A^-$ ), as indicated in the inserted schematic map. Each map indicates several inversion line branches that correspond to different stirring energies, produced by a change in the impeller or in the rotational speed.

In map a, the low-energy stirring is provided by an anchor rotating at 250 rpm, which is essentially the minimum mixing energy required to produce a homo-

\* To whom correspondence should be addressed. Tel/Fax: (+58) 274-2402954. E-mail: salager@ula.ve.

geneous system at the macroscopic scale. In the same map, the high-energy stirring is provided by a high-efficiency twisted-blade propeller with axial and radial impulses rotating at 1650 rpm to provide incipient turbulence. It is seen in map a that the increase in the stirring energy tends to shift the dynamic inversion line toward a higher fw, i.e., a higher internal phase content at inversion. The effect is particularly marked at HLB around 15, which corresponds to the high stability of the O/W emulsion type in the  $A^-$  region. This trend has been reported in most of the studies dealing with the effect of stirring on the inversion, whatever the formulation conditions and the addition protocol, for emulsions containing an emulsifier,<sup>12–14</sup> as well as for dispersions without any surfactant.<sup>15,16</sup>

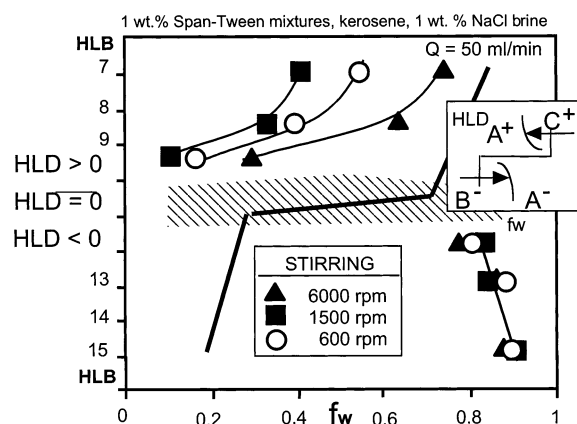
It is worth remarking that the anchor impeller would not contribute significantly to drop breakage but only to macromixing at the vessel scale. This means that with an anchor mixer some phase segregation can take place in some regions, resulting in a local water-to-oil ratio (WOR) quite different from the overall value. These nonhomogeneous zones are likely to play a role in the triggering of the emulsion inversion.<sup>12,17–19</sup>

The b and c graphs in Figure 1 are partial views of the formulation–composition map for systems submitted to a high intensity of stirring by using a high shear Ultraturrax turbine mixer, as discussed elsewhere.<sup>20</sup>

It is worth pointing out that even the 1200 rpm case provides a much higher shear than the 1650 rpm case in map a. Maps b and c are essentially similar, although one corresponds to a nonionic system and the other to an ionic one and they have different formulation variables. It is seen that in both cases a large increase in the stirring energy (from 1200 to 15 000 rpm) produces a slight shift of the inversion line toward a lower value of fw. This means that the delay from the standard inversion line is reduced as the stirring energy increases. This is a trend opposite to what was previously exhibited for low stirring energy cases. Moreover, the delay in the emulsion inversion in the opposite direction ( $A^- \rightarrow B^-$ ) is also reduced.<sup>21</sup> As a consequence, the hysteresis zone shrinks with an increase in the stirring energy, a trend which has been related to the attainment of an oil/water molecular “soup” at the limit of infinite stirring.<sup>21,22</sup> There is thus an apparent discrepancy between the trends observed at low and high stirring energy. If both trends are correct, a maximum delay should be found at intermediate stirring energy. This is investigated next.

## Experimental Procedures

In all of the experiments described in the following sections, a kerosene oil cut (EACN = 8.3) and a 1 wt % NaCl brine were used as the oil and aqueous phases, respectively. Blends of nonionic surfactants from the Tween and Span series from HLB = 4.3 to 15 were used at a concentration of 1 wt %. The different values of the generalized formulation HLD were attained by mixing surfactants as in part 1 of this series of papers, where other experimental details can be found.<sup>11</sup> Agitation was provided by a six-blade Rushton turbine (3 cm of diameter) placed in a 300 mL, 7.5 cm i.d. emulsification vessel fitted with four baffles. The stirring energy was supplied by an electrical mixer (Caframo model BDC6015). The temperature was kept constant at  $22 \pm 2$  °C. The inversion process was carried out at three different stirrer speeds: 600, 1500, and 6000 rpm.



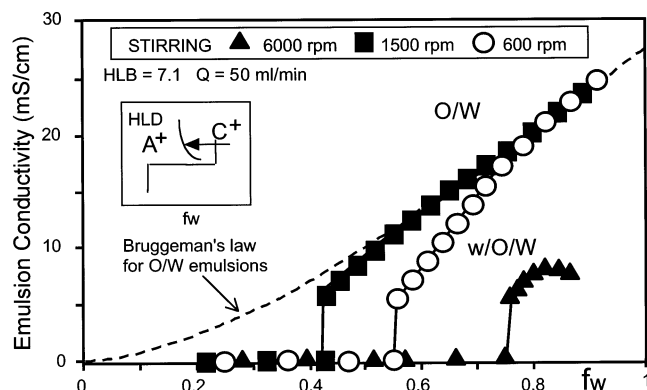
**Figure 2.** Formulation–composition map showing the effect of stirring energy on the location of the inversion lines.

As in part 1 of this series of papers,<sup>11</sup> emulsion inversion was induced by changing the WOR. Composition scans in the abnormal-to-normal direction of change were made for three HLD values below the optimal formulation condition ( $HLD = 0$  located at  $HLB = 10.5$ ) as well as for three HLD values above it. These scans were made by adding an aqueous phase to 240 mL of the oil phase contained in the emulsification cell for  $HLD < 0$  ( $B^- \rightarrow A^-$ ), or conversely for  $HLD > 0$  ( $C^+ \rightarrow A^+$ ). This means the emulsion aqueous volume fraction (fw) varied from 0 to 1 for the former ( $B^- \rightarrow A^-$ ) and from 1 to 0 for the later ( $C^+ \rightarrow A^+$ ). The aqueous or oil phase to be added continuously to the emulsification cell was pumped at a rate of 50 mL/min (residence time  $\tau = 4.8$  min) using a peristaltic pump (Cole Parmer). This addition rate was seen to result in a relatively long inversion delay at a 1500 rpm stirring velocity in part 1 of this series of papers. Because the 1500 rpm stirring velocity may be considered as intermediate, this is the right selection to investigate the desired effect. The volume in the emulsification cell during the inversion process was kept constant by withdrawing in a continuous fashion the excess volume. For each HLD studied, the same kind, proportion, and quantity of surfactants was contained in the two nonmiscible phases to be mixed. This was done in order to guarantee that the formulation and surfactant concentration of the emulsion formed in the emulsification cell remained the same throughout the process.

Phase inversion was detected by monitoring the electrical conductivity. Because the aqueous phase contains some electrolyte, an abrupt change in the emulsion conductivity is indicative of a change in the emulsion type from W/O to O/W, or conversely. The emulsion conductivity was measured by a digital conductivity meter (Orion model 150) with a RS-232-C serial port, which allowed to monitor and record the emulsion conductivity throughout the inversion process, thanks to an interfaced computer.

## Experimental Results

Figure 2 indicates the location of the inversion line at different stirring energies expressed as the rotational speed of the turbine (rpm). At  $HLD > 0$ , it is seen that the increase in stirring from 600 to 1500 rpm produces a shift to the left, i.e., increases the inversion delay. Then a further increase from 1500 to 6000 rpm produces the opposite shift; i.e., it reduces the inversion delay.



**Figure 3.** Emulsion conductivity variation as the O internal phase is added to conduct the inversion in the  $C^+ \rightarrow A^+$  direction at different stirring energy values.

There is thus a maximum inversion delay at the intermediate value of the stirring speed (1500 rpm). At  $HLD < 0$ , there is no significant effect of the stirring energy in the inversion location. In Figure 1a, a white triangle data point indicated that there is a shift to the left, i.e., a delay reduction, at very high stirring energy (10 000 rpm). Although it was with a different stirrer, this is qualitatively consistent with the previously mentioned trend of delay reduction in the high stirring range. The white circle data point in the Figure 1a map also indicates that a large delay is attained at intermediate stirring. From other experiments, it is deduced that the behavior at  $HLD < 0$  is essentially the same as it is at  $HLD > 0$ , although more insensitive to the studied factors in this and in the previous paper.

The discussion will thus focus on the results exhibited at  $HLD > 0$ , in which the conductivity measurement allows one to easily diagnose the morphology, which is not the case at  $HLD < 0$ .

Figure 3 indicates the change in conductivity of the emulsion along the  $C^+ \rightarrow A^+$  inversion path when oil is added to water at a formulation ( $HLB = 7.1$ ) that corresponds to the highest point in Figure 2 at  $HLD > 0$ . This is essentially the same case as that in Figure 4 in part 1 of this series of papers,<sup>11</sup> but this time the stirring energy is changed instead of the oil addition rate.

Bruggeman's law is used as the reference to indicate the expected conductivity of the normal O/W emulsion in such a case. It is indicated as a dashed line in Figure 3.

$$k = k_w fw^{3/2} \quad (1)$$

where  $k$  is the emulsion conductivity and  $k_w$  the aqueous-phase conductivity (27.5 mS/cm).  $fw$  is the water fraction remaining in the system according to the mass balance. As the experiment proceeds in the  $C^+ \rightarrow A^+$  direction, more oil is added and  $fw$  diminishes. If the experimental value of the conductivity is lower than expected one from Bruggeman's law, this means that some of the water is not available to conduct electricity, which is evidence of the occurrence of a w/O/W multiple emulsion. The "horizontal" distance between the experimental point and Bruggeman's law line is an estimate of the "w" droplet water amount in the O oil phase of the multiple emulsion. On the other hand, the emulsion inversion from O/W to W/O is detected by a rapid fall in conductivity from about 5 mS/cm to essentially zero.

At first sight, Figure 3 indicates a trend which is compatible with data of part 1 of this series of papers: the shorter the inversion delay, the more likely the occurrence of w/O/W multiple emulsion and the higher the internal "w" content of the w/O/W, or the stronger the relative effect of the formulation over the opposite effect of the composition. Conversely, a long inversion delay seems to be associated with an emulsion type which passes from O/W to W/O almost without the occurrence of multiple morphology. This could be conjectured to probably be a general relation between the inversion delay and the emulsion morphology evolution because the factors involved are quite different and sometimes have opposite effects. This will be discussed in detail in a forthcoming paper.

It is worth remarking that the 6000 rpm case exhibits a low conductivity at a very early stage, e.g., at  $fw = 0.85$ , when the emulsion only contains 15% of oil. The corresponding conductivity value indicates that only 40% of the water is conforming to the continuous W phase. This means that more than half of the water (45% out of 85%) has been "encapsulated" into the oil 15%. This is indisputable evidence that the O oil drops contain 3 times as much water (as "w" droplets) than oil. This result indicates that a large amount of water immediately forms droplets that stuff and swell the oil drops as soon as the latter are formed. This will enlighten the forthcoming discussion on the inversion mechanism.

## Discussion

The experimental evidence of the existence of some intermediate stirring energy that produces a maximum delay in dynamic inversion tends to indicate that there are two competing effects, one dominating at low stirring and the other one commanding at high stirring energy. This intermediate value at which the opposite effects cancel out each other will be referred to as the "neutral" stirring condition because of the apparent trade-off and insensitivity associated with it. An analysis of the mechanisms involved in emulsion inversion will help to clear the picture.

**Low-Energy Stirring Regime.** When the stirring energy is much lower than the neutral value, the emulsified system is characterized by a high degree of macroscopic lack of homogeneity, with some segregated regions containing more water or more oil and thus with local WOR values which could largely deviate from the overall value. These localized deviations in composition are likely to produce regions with a few drops of oil in water or vice versa, i.e., a morphology differing from the whole system. Such an anomalous element of fluid could be denominated as an inversion seed, which could propagate or die away depending on the following circumstances.

If emulsion inversion is thought to involve an intermediate and transient zero interfacial curvature at some moment, it can be said that the lower the initial curvature is, the closer to the inversion condition the original system is and the easier it will be to invert it. Low stirring is associated with big drops, i.e., low curvature that could be easily reversed. Consequently, it can be associated with easy inversion, particularly if the inversion is favored by the abnormal-to-normal morphology change or by a large difference in the viscosity between the phases.<sup>10</sup> On the other hand, low-curvature interfaces are likely to suffer local deforma-



tion and local reversal of the curvature, particularly if favored by the formulation.<sup>23</sup>

This could be the key factor in the incorporation of droplets inside drops and the formation of a multiple emulsion. It seems that the natural tendencies corresponding to a low stirring energy regime favor the emulsion inversion and the occurrence of the multiple emulsion when there is a conflict between the formulation and composition effects on the curvature. In all cases, the change in the interface curvature, which could be random in the first place, should be stabilized later by the effect of formulation. The inversion under this regime is thus dominated by the formulation influence, which is always the case in the abnormal-to-normal direction of change. This interpretation accounts for the experimental data displayed by the 600 rpm case in Figure 3.

**High-Energy Stirring Regime.** Contrariwise, a highly energetic stirring will result in the breakage into tiny droplets, which exhibit a high curvature and a large surface area. The drop and eddy scale is reduced, and transport phenomena are sped up because surfactant diffusion from the bulk is partly substituted by convection, with a resulting quicker surfactant adsorption at the interface. A quicker surfactant adsorption means favoring formulation effects and normal morphology, and it could be attained by a higher stirring energy<sup>21</sup> as well as a higher surfactant concentration,<sup>5</sup> in the abnormal-to-normal direction of change. This means that the normal curvature, as well as the formation of droplets in drops, is going to be favored. The stuffing of droplets inside the drops produces the swelling of the latter and increases their volume and their probability of collision and coalescence. On the other hand, the high turbulence is likely to increase the drop collision rate and thus also contribute to an increase in their probability of coalescence into a continuous phase. This interpretation matches the experimental data in the 6000 rpm case shown in Figure 3 that display a multiple emulsion occurrence and early inversion.

If the stirring energy is increased to infinity, the result should be some kind of molecular soup with extremely small drops of both phases, in which case the continuous phase is the one whose drops coalesce more quickly.<sup>22</sup> This refers to the coalescence of the abnormal emulsion drops during the abnormal-to-normal direction of change. This competitive kinetic model was the basis of a different approach to interpret emulsion inversion, which was proposed a few years ago<sup>7,14,24</sup> after Davies original concept based on the HLB scale,<sup>25</sup> i.e., on formulation issues that somehow quantify Bancroft's rule.

**Middle-of-the-Road Cases near Neutral Stirring.** From the previous discussion, it can be said that at a low stirring energy the produced shear is not sufficient to bend the interface one way or the other and that surfactant diffusion and adsorption will induce the interfacial curvature. On the other hand, at high stirring energy the surfactant is transported by convection so close to the surface that it can adsorb almost instantly, and again its effect dominates the situation.

None of these extremes would apply at or near the intermediate so-called neutral stirring conditions. The drop diameter is neither large nor very small, just small enough to exhibit a curvature which is difficult to reverse. On the other hand, the mixing in the bulk phase is not energetic enough to convey by convection

the surfactant molecules very close to the interface. Still a lot of slow diffusion would have to take place before the surfactant adsorbs at the interface. This means that the most internal droplets could coalesce because of the lack of surface coverage. As a consequence, multiple emulsions are not so likely to occur. As a result, the drops will not be stuffed by droplets and their apparent internal phase content due to swelling will not be so high, and collision between drops would be more unlikely, and even less probable because of a lower energy input.

The near-neutral stirring energy case is thus expected to exhibit less multiple morphology, as well as less coalescence between the drops, and thus a longer delay before inversion takes place. This interpretation coincides with the experimental data exhibited in the 1500 rpm case in Figure 3.

**Balance of the Effects.** The results reported in this paper and the previous one<sup>11</sup> have shown that the  $HLD < 0$  zone is exhibiting a large degree of insensitivity with respect to the studied factors, i.e., the rate of addition and stirring energy. It was mentioned that the surfactants in the  $HLD < 0$  region correspond to (20 EO) ethoxylated sorbitan esters, sometimes with several oleic tails, i.e., high molecular weight substances, when compared to the sorbitan monoesters used at  $HLD > 0$ . This was also the case in the  $HLD \geq 0$  zone at  $HLB = 9.6$ , in which a large proportion of Tween 85 was used. In all of these cases, the delay before inversion was found to be quite large, and according to the previous discussion, this could be now associated with a slow migration and adsorption of the high molecular weight surfactant during the breakup-coalescence process that takes place when the system is stirred. If this reasoning is correct, this means that the near-neutral stirring case might happen over quite a wide range in the case of high molecular surfactant. The relative insensitivity of the inversion line location in the  $HLD < 0$  zone is thus not surprising. On the contrary, it is an additional argument to back up the proposed explanation.

## Conclusion

The stirring energy has a dual effect on the location of the emulsion catastrophic inversion line in the abnormal-to-normal direction. At some intermediate value of the stirring energy, a so-called neutral condition, a maximum delay before inversion is displayed with little evidence of multiple morphology. This delay decreases when the stirring energy either increases or decreases. An almost nondelayed inversion is attained at very high or very low stirring, and it is associated with the occurrence of multiple emulsions. The intermediate stirring value seems to depend on other conditions such as the surfactant molecular weight and the inversion protocol.

## Acknowledgment

The authors acknowledge the financial backing from the Venezuelan National Research Council (CONICIT Agenda Petroleo Grant) and from their University Research Council CDCHT-ULA.

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Received for review July 17, 2002

Revised manuscript received October 25, 2002

Accepted October 29, 2002

IE020535W