

INFLUENCE OF PROCESS VARIABLES ON THE MECHANISM OF EMULSIFICATION BY INVERSION

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Abstract: Phase inversion of an abnormal emulsion is a low energy process used to produce a fine emulsion with viscous oils. Provided that the formulation conditions are appropriate, the continuous addition of a phase into another under continuous stirring, would result in the formation of a so-called abnormal emulsion which would invert at some point into a normal and stable one. The mechanism of inversion may involve or not the formation of a transient multiple emulsion, an occurrence which is of paramount importance in practice. The present paper reports the influence of process variables such as the addition rate, stirring, and vessel volume, as well as formulation on the type of inversion mechanism.

Keywords: Emulsification, Catastrophic phase inversion, intrinsic time, simple or multiple emulsion mechanism.

1. INTRODUCTION

Catastrophic phase inversion of an abnormal emulsion is a low energy process which is used in practice to produce fine droplet waterborne paints with particularly viscous oils such as alkyd, polyurethane or epoxy resin, silicone putty, foodstuffs or heavy hydrocarbon fuels. In such processes a surfactant-oil-water system is set so that the surfactant affinity dominates for the water phase, for instance by selecting a high HLB surfactant. (Yang and Zhao, 2000; Guérin, 1997; Salager *et al.*, 2002)

The water phase containing the surfactant is slowly added to the viscous oil phase under constant stirring. At first, a water-in-oil (W/O) emulsion is produced by the dispersion of the small amount of added water into the oil phase. This kind of emulsion is so-called abnormal because the physicochemical conditions would favor the formation of an O/W emulsion instead, but there is not enough water for this later to become the external phase. After some time the water droplets are numerous enough, typically when their volume fraction f_w attain 60%, and they come into contact; because of the formulation conditions, which do not stabilize this kind of dispersion, the water drops are likely to coalesce to form the continuous phase, while the oil is divided into drops. This is called a simple phase inversion from W/O to O/W morphology. (Mira *et al.*, 2003)

In some instances and because the formulation favors the formation of an O/W emulsion the drops of water in oil are deformed and an inclusion mechanism takes place in which small droplets of oil inside the water drops. This process result in the formation of a so-called multiple emulsion, in this case an o/W/O morphology in which the low case letter “o” indicates the most inner droplets inside the W drops which are dispersed in the O continuous phase.

The inclusion of the oil droplets tends to swell the W water drops and thus to increase their apparent volume. As a consequence the water drops are able to enter into contact at an early stage, e.g. when the water fraction is only 30% or so. The added phase volume fraction at which the inversion takes place is an important parameter in practice because it determines the actual internal phase ratio of the final inverted emulsion. For instance if the sought O/W emulsion must be concentrated, e.g. must contain more than 70% oil, the volume fraction of water f_w at inversion should not raise beyond 30%. Consequently the control of the mechanism, i.e. a simple inversion or one involving a multiple emulsion, is of great importance to carry out a practical process. (Tyrode *et al.*, 2003)

Previous studies have reported that a change in process variables is able to alter the type of mechanism, but no general correlation has been found (Tyrode *et al.*, 2003; Mira *et al.*, 2003; Zambrano *et al.*, 2003). The present paper presents the combined effect of the process variables to favor one of the other case.

2. INVERSION PATH ON A FORMULATION-COMPOSITION MAP

The general know-how on the effect of formulation and composition variables on the emulsion morphology has been represented in the generalized formulation-composition map indicated in figure 1 (Salager *et al.*, 1983). For the sake of simplicity the formulation is only related to the surfactant HLB, though it is known that in practice other formulation variables, such as the oil nature, the water stability, the temperature, etc. are able to contribute to the formulation change (Salager, 2000). The left map indicates the so-called standard inversion line, while the right one deals with the so-called dynamic inversion. As discussed in details elsewhere (Salager *et al.*, 2000), the dynamic inversion produced by adding (too much) of internal phase exhibits a memory phenomenon called hysteresis. In other words it does not take place at a fixed location, but depends on the direction of change, as indicated by the arrows.

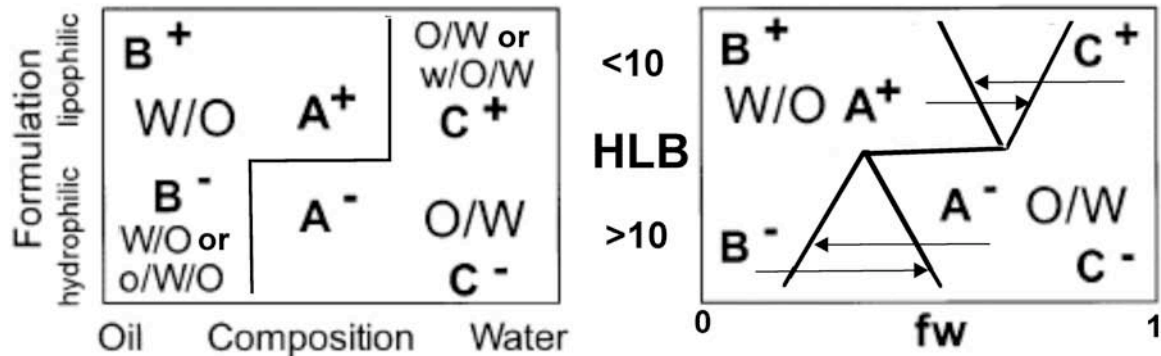


Fig. 1. Formulation-composition maps showing emulsion types in standard inversion (left map) and hysteresis behavior in dynamic inversion (right map).

The map is divided into six regions A, B, C with + and – signs, in which the attained emulsion exhibit specific properties. A⁻ and A⁺ regions correspond to stable O/W and W/O emulsions, respectively. C⁺ and B⁻ regions are so-called abnormal zones and are likely to exhibit multiple emulsions, w/O/W and o/W/O respectively. In these zones the most external emulsions, i.e. O/W and W/O respectively, are unstable.

In the phase inversion processes dealt with in this paper, an abnormal emulsion such as W/O (respectively O/W) in B⁻ (respectively C⁺) region is inverted into a normal O/W (respectively W/O) emulsion in the A⁻ (respectively A⁺) region, with an eventual occurrence of a multiple o/W/O (respectively w/O/W) emulsion as a transient morphology in the B⁻ (respectively C⁺) region before inversion takes place. Multiple emulsions are clearly detected by conductivity in the C⁺ region, and by other means such as viscosity variations (Allouche *et al.*, 2004) or backscattering (Pizzino *et al.*, 2007) in both C⁺ and B⁻ zones, though not with the same accuracy.

3. EXPERIMENTAL CONDITIONS

Abnormal emulsion inversion is carried out by adding water (respectively oil) in a W/O (respectively O/W) emulsion located in the B⁻ (respectively C⁺) region. The formulation is varied from very hydrophobic (HLB = 7) to very hydrophilic (HLB = 15) surfactant mixtures, with intermediate values, in particular HLB=9.6, which is hydrophobic but close to the so-called optimum or balanced formulation. Two vessel volume are used, e.g. 250 ml and 1000 ml to test the scale up, the stirring is carried out with a Rushton turbine at different velocities corresponding to a Reynolds number range from 20,000 to 100,000. The rate of addition of the internal phase Q is spanned over a tenfold range to vary the residence time in the emulsification vessel. The vessel is thermostated and is fitted with a sucking system, which maintains a constant liquid volume V. The mass balance may be expressed as:

$$Q fw_a - Q fw = V \frac{dfw}{dt} \quad (1)$$

Where f_w represents the water volume fraction in the emulsion at time t , and f_{w_a} is the water volume fraction in the added phase; V is the emulsion volume in the vessel, which is kept constant, and Q is the added phase volumetric flow rate. If the flow rate Q is constant and if the residence time τ is defined as $\tau = V/Q$, then equation 1 becomes:

$$\frac{f_w - f_{w_a}}{f_{w_0} - f_{w_a}} = \exp(-t / \tau) = \exp(-\theta) \quad (2)$$

where f_{w_0} is the initial value of f_w at $t = 0$. Depending upon the direction in which the composition scan is carried out, the f_w value will be equivalent or not to the dispersed phase volume fraction (f_{disp}) in simple O/W or W/O emulsions. At $HLB > 10$, when the initial phase contained in the emulsification cell is the oil phase and the added phase is the aqueous phase (path $B^- \rightarrow A^-$), $f_{w_0} = 0$, $f_{w_a} = 1$, and $f_{disp} = f_w$. In the opposite case ($HLB < 10$), when oil is added to the water phase (path $C^+ \rightarrow A^+$) $f_{w_0} = 1$, $f_{w_a} = 0$, and $f_{disp} = 1 - f_w$. In all cases the surfactant amount is assumed to be negligible in the total volume inventory. θ is a dimensionless time parameter called ‘‘intrinsic’’ time. Hence, for $HLB > 10$ case, f_o (the oil fraction, i.e., $1 - f_w$) is always, particularly at the inversion point equal to:

$$f_o = 1 - \exp(-\theta) \quad (3)$$

Similarly for the $HLB < 10$ case:

$$f_w = 1 - \exp(-\theta) \quad (4)$$

4. RESULTS AND DISCUSSION

Figure 2 indicates the value of the added phase fraction (as f_o or/and f_w) at the emulsion inversion as a function of the dimensionless intrinsic time θ . All experimental points (Zambrano *et al.*, 2003; Mira *et al.*, 2003; Tyrode *et al.*, 2003; Rodriguez, 2007) are located along the mass balance equation (3) or (4), thus corroborating the assumption and experimental accuracy. Figure 2 (left) indicates that both hydrophilic and lipophilic formulation regions are able to produce inversion with a little or large added phase fraction, hence for a short or long intrinsic time, for a very wide range of formulation (HLB varying from 7 to 15). Figure 2 (right) plot shows that it is the same for a ten fold range of stirring energy expressed through the Re number. Hence it may be said that the actual regime does not depend directly on one of these parameters.

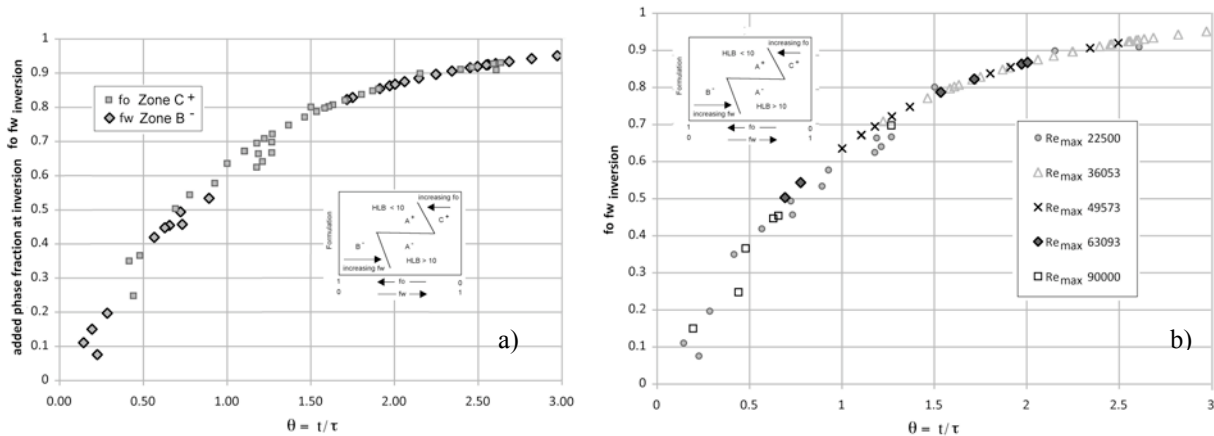


Figure 2. Inversion points (Added phase fraction vs. intrinsic time) a) for the two formulation groups (Zone C+ and B-) and b) for the different agitation regimes in function of Reynolds number.

Figure 3 indicates the data point for the C^+ region where the conductivity measurement allows to determine the nature of the mechanism, i.e. a direct inversion from O/W to W/O morphology, or the occurrence of an intermediate and transient w/O/W multiple emulsion. Although there is some evidence that the low intrinsic time region exhibit only multiple morphology cases, the two types are equally distributed on most of the time range, thus indicating that the mechanism is not directly related to the intrinsic time. Although the determination of the emulsion morphology cannot be determined for the B^- region by conductivity, it is known that the phenomenology is the same, thus it is not a limitation in the discussion validity.

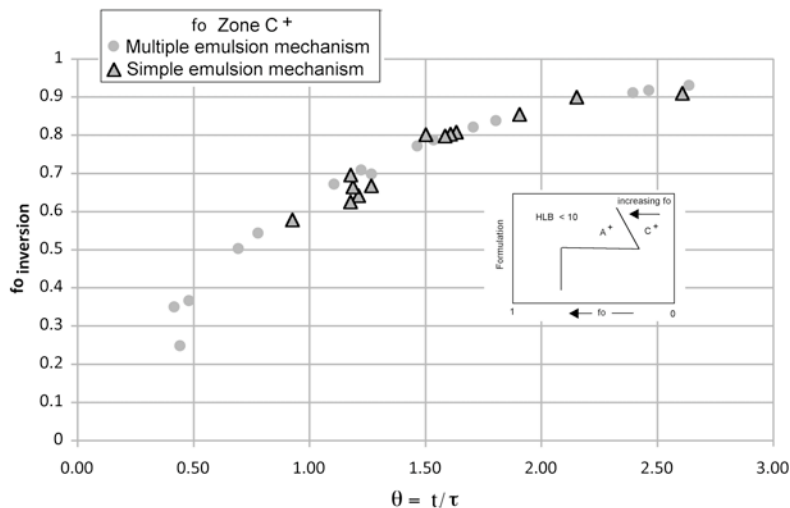


Figure 3. Inversion points for the simple and multiple emulsion mechanism in the C+ region.

Before going further, it is worth noting that the intrinsic time tends to increase when the addition flow rate increases or when the stirring energy decreases, both effect producing a weaker local mixing, hence an increased probability of the occurrence of a small region where the added phase could exhibit a volume large enough to behave as a seed of the future continuous phase. For a given intrinsic time, these changes would result in an easier inversion, i.e. an inversion taking place at a shorter actual time t , although the added internal phase fraction at inversion could be greater. This means that there should be some relationship between the stirring energy and the time required to produce the inversion.

Figure 4 shows the correlation between the stirring energy indicated as the Re number and the intrinsic time, with an indication of the two mechanisms, i.e. white dot data points for the simple inversion from O/W to W/O, and black ones for the cases involving an intermediate multiple w/O/W emulsion.

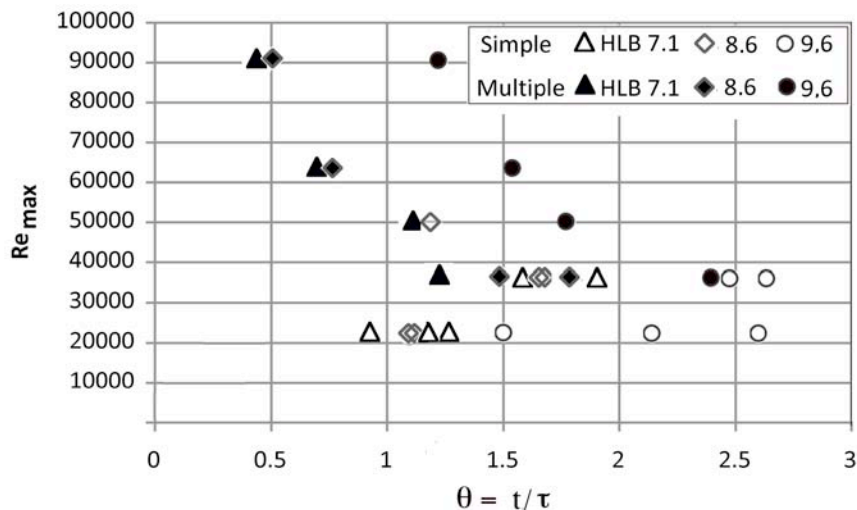


Fig 4. Phase inversion mechanism related with Reynolds number and intrinsic time for the three formulation values of HLB in the C+ region.

This figure indicates the same trend for the three tested formulation cases on the hydrophobic formulation side. At low intrinsic time, hence “quick” inversion, there is a strong influence of the stirring. The more energetic the stirring the shorter the inversion time, as expected from the above argument. The data points are essentially the same for the formulations relatively far away from optimum (HLB = 7 and 8.6). Whereas there is an even stronger effect for the formulation close to optimum, probably due to the lower interfacial tension which allows for an even easier drop breaking process that make tinier drops, thus difficulting the enclosing of w droplets in O drops.

In all formulation cases the low Re region is associated with a simple inversion mechanism beyond a certain value of the intrinsic time about unity.

5. CONCLUSION

Hence it may be concluded that the most critical parameter, as far as the attainment of a multiple emulsion mechanism is concerned, is probably the combination of a high stirring energy with a low intrinsic time, i.e. a low addition rate or a high residence time (also attained by a high volume), all features favoring a better micromixing, and thus avoiding unmixed zones that could act as a seed for the inversion to take place directly.

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