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## MATERIALS AND INTERFACES

# Combined Effects of Formulation and Stirring on Emulsion Drop Size in the Vicinity of Three-Phase Behavior of Surfactant–Oil Water Systems

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As surfactant–oil–water systems approach Winsor III phase behavior, at the so-called optimum formulation, the interfacial tension decreases, thus allowing the generation of smaller drops upon stirring. On the other hand, the coalescence rate increases, thus favoring the formation of larger drops. The two opposite effects do not alter the drop size in the same way and result in a minimum drop size. Such a minimum drop size is found on both sides (for O/W and W/O emulsions) of optimum formulation, whatever the variable used to produce the scan. The location of these minima, which correspond to the most efficient use of the stirring energy to make small droplets, is found to be slightly shifted by a change in stirring energy.

## 1. Introduction

Emulsion properties such as type, drop size, stability, and viscosity, are known to be affected by the so-called formulation and composition variables, as well as by the mechanical mixing conditions. Once the type of the emulsion is determined, the second most important information is the size of its drops. Drop size produced during emulsification is the result of a dynamic equilibrium between two opposite phenomena, i.e., breakup and coalescence.<sup>1,2</sup> Hence, anything that affects one or the other is likely to change the drop size.

The mechanism dependence on formulation, composition, and stirring variables follows different patterns and keeps complex relations with each of them. For instance, increasing stirring energy makes the breakup process more efficient, but if the surfactant inventory is not large enough to satisfy the extra adsorption requirement, then the intensification in breakup would be worthless. On the other hand, changes in formulation can be programmed to reduce the interfacial tension value in order to favor the breaking efficiency.

Coalescence also depends on formulation, through the surfactant adsorbed layer that represents the main barrier for drops to approach, as well as through the thin film drainage.<sup>3,4</sup> The combination of all the previously mentioned variables and their programming in time and space allow the attainment of particular emulsion properties, in what may be called a product engineering optimization.

Attaining a minimum drop size is often a mandatory issue for ensuring the desired stability and rheological behavior in a profitable way. Increasing the stirring–mixing energy has been the most obvious way to reduce the drop size, until the handling of other factors such as formulation and composition allowed the attainment of better results at a lower expense of energy. Depending on the case, some industrial conditions cannot be changed and it becomes necessary to understand the whole phenomenology, and to be able to predict the combined effects of all the possible variables that influence the emulsification.

The formulation influence allows a reduction of the interfacial tension down to 1.0 or 0.1 mN/m just by introducing a surfactant. However, a much lower tension (<0.001 mN/m) can be attained at the so-called “optimum formulation”, a concept developed during the 1970s by enhanced oil recovery researchers, which is associated with the ultralow interfacial tension required to displace petroleum globules trapped by capillary forces in a porous medium.<sup>5</sup>

Such systems are related to a physicochemical situation in which the affinity of the surfactant is exactly equilibrated for both the water and oil phases. This formulation corresponds to a so-called Winsor III type phase behavior, which exhibits a microemulsion in equilibrium with excess water and oil phases. Numerous experimental works have reported the effect of formulation variables in terms of deviation from optimum conditions.<sup>6</sup>

It has been possible to establish a quantitative generalized variable, a so-called surfactant affinity difference correlation (SAD),<sup>7</sup> conceptually similar to Winsor’s *R* ratio,<sup>6</sup> which combines all the formulation effects. For ionic surfactant systems, SAD is a linear expression of the formulation variables:

$$\text{SAD}/RT = \ln S - k(\text{ACN}) - f(A) + \sigma - a_T(T - T_{\text{ref}}) \quad (1)$$

where *S* is the salinity in weight percent NaCl in water, ACN (alkane carbon number) is a characteristic of the oil,  $\sigma$  is a characteristic parameter of the surfactant, *f*(*A*) is a function that depends on the alcohol type and concentration, and *T* is the temperature. *k* and *a<sub>T</sub>* are constants. Correlation 1 applies for anionic<sup>8</sup> and cationic surfactants.<sup>9</sup> A similar relationship (eq 2) applies for polyethoxylated nonionic surfactant systems:<sup>10</sup>

$$\text{SAD}/RT = \alpha - \text{EON} + bS - k(\text{ACN}) - f(A) + c_T(T - T_{\text{ref}}) \quad (2)$$

where  $\alpha$  depends on the surfactant lipophilic group, EON is the average number of ethylene oxide groups per molecules, *k* and *c<sub>T</sub>* are constants.

SAD = 0 corresponds to an optimum formulation at which the system goes through a very low tension minimum.<sup>11–13</sup> In

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such circumstances the capillary phenomena essentially vanish and the deformation of the droplets becomes very easy. Therefore, the breaking process generates very small droplets. However, as optimum formulation is approached, the emulsion stability decreases as well, and the coalescence of the drops takes place upon contact. This phenomenon favors the opposite trend, i.e., the formation of larger drops.<sup>14–17</sup>

This minimum in emulsion stability has been associated with the trapping of the surfactant in the microemulsion phase at  $SAD = 0$ , which is a spontaneous process because the surfactant chemical potential in microemulsion is lower than in any of the other phases.<sup>18</sup> Other authors proposed that the quick coalescence results from the formation of a microemulsion or liquid crystal bridges between the drops;<sup>19</sup> more advanced theoretical arguments on film instability have been proposed, too.<sup>20,21</sup> As a consequence, the approach of optimum formulation results in two opposite effects, e.g., an easier breakup and an easier coalescence, which result in a minimum drop size at some distance of optimum formulation, where the best compromise between low tension and coalescence rate is attained.

A few studies have reported that fine emulsions are produced at some distance from the three-phase zone through different formulation scans. When temperature is used as the formulation variable,  $SAD = 0$  corresponds to the phase inversion temperature (PIT). Fine emulsions have been obtained at a temperature not far from PIT (2–4 °C below it). This procedure, which is called emulsification by the PIT method, has evolved into an industrial method for producing stable fine emulsions.<sup>22</sup> Temperature and salinity scan experiments also showed the existence of a minimum in drop size at some distance from optimum formulation.<sup>23</sup>

It has been found that emulsion drop size depends on both formulation and composition of the surfactant–oil–water system, as well as on the stirring conditions. A minimum in drop size on the Winsor I type side (oil-in-water (O/W) emulsions) was observed for different combinations of these variables. Another favorable situation was found at high internal phase ratio where the emulsions are extremely viscous, and often viscoelastic. However, this was not related to a formulation effect.<sup>24</sup> A recent work on emulsion inversion by the PIT method<sup>25</sup> showed the variation of emulsion viscosity through a temperature scan. Two maxima in viscosity were found on both sides of  $SAD = 0$  just at the boundaries of the three-phase region, as was reported in previous studies.<sup>17</sup> These viscosity maxima were coincident with the minima in drop size.

Until now it may have been said that, at constant stirring, a drop size minimum has been found in  $T$ , EON, and  $S$  scans, though in most cases only on one side of optimum formulation ( $SAD < 0$ ). The present paper shows the variation of the drop size over complete formulation scans for the first time, and reports the effect of the stirring energy and of the presence of mesophases.

## 2. Experimental Section

**Materials.** Ethoxylated nonylphenols with an average of 4, 6, 9, and 15 ethylene oxide groups per molecule were supplied by Seppic-France. These surfactants were found to exhibit the typical Poisson law distribution in the number of ethylene oxide groups per molecules. The anionic surfactant used was sodium dodecyl sulfate, reagent grade from Riedel de Haën. Kerosene is a gasoline cut with an equivalent alkane carbon number EACN = 9.5; that is, it behaves as an intermediate between nonane and decane. The EACN was determined from the attainment of an optimum formulation through the interfacial

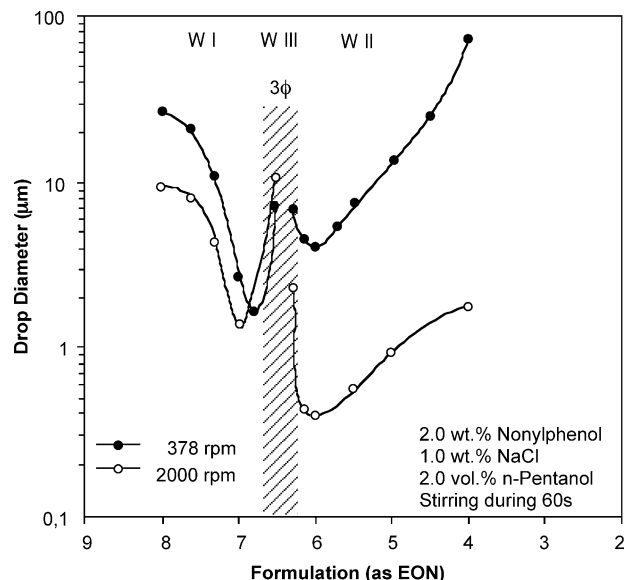


Figure 1. Variations of average drop size along an EON scan.

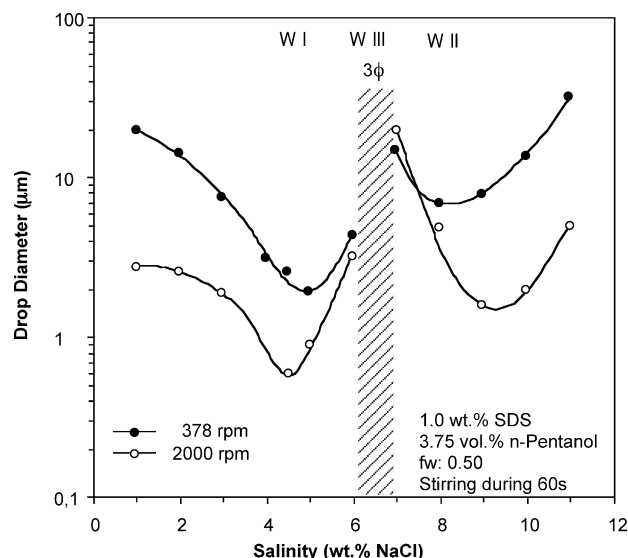
tension minimum.<sup>26</sup> 1-Pentanol (>99%) was supplied by Aldrich Chemical and NaCl was obtained from J. T. Baker.

**Phase Behavior.** A one-dimensional formulation scan was carried out for each system to locate the formulation that yields three-phase behavior. The anionic system formulation is changed by scanning the aqueous-phase salinity (NaCl), while an EON variation is used for nonionic systems. The surfactant–oil–water systems were placed in capped glass tubes. They were gently shaken from time to time during the first 2 h, and then they were kept at rest at constant temperature until equilibrium was reached, typically after 24 h. The phase behavior was observed along the different scans, and the three-phase zones were located. The presence of a liquid crystalline phase was detected by using an observation device with crossed polarizers.

**Emulsification and Droplet Size.** All concentrations are in weight percent except for 1-pentanol, which is measured in volume percent with respect to the whole system. Emulsions were prepared from preequilibrated systems, according to a standard procedure<sup>15,27</sup> using a water-to-oil ratio (WOR) equal to unity. High-energy stirring was provided by an Ultraturrax Turbine blender Model Ika-Werk DZM-1 at a rotation velocity above 1500 rpm. For low-energy stirring an IKA RW20DZM stirrer was used, typically in the 300–500 rpm range. All systems were stirred during 60 s at 25 °C, unless otherwise stated. Samples containing 50 mL of emulsion with formulations ranging from Winsor I to Winsor II phase behavior were prepared. The measurement of drop size was carried out immediately after emulsification by using a Malvern Mastersizer laser light scattering apparatus. The reported drop average diameter is the so-called  $D(V,0.5)$  average, i.e., the diameter below which half the volume distribution occurs. These results were corroborated by microscopic observations.

## 3. Complete Formulation Scan (Nonylphenol EON and SDS Salinity)

Figures 1 and 2 indicate the variation of the emulsion drop size at constant stirring along a formulation scan. In Figure 1 the surfactant is a mixture of commercial ethoxylated nonylphenols whose average number of ethylene oxide groups per molecule (EON) is changed by mixing different species with close ethoxylation degrees. All these systems contain 1-pentanol to avoid the formation of mesophases as will be discussed later.



**Figure 2.** Variations of average drop size along a salinity scan.

The shaded zone corresponds to three-phase behavior, i.e., a microemulsion middle phase in equilibrium with excess water and excess oil phases, which takes place around optimum formulation at  $EON = 6.5$ . The surfactant mixture  $EON$  increases from right to left so that the generalized formulation  $SAD$  increases from left to right as generally taken in the literature, and in order to match the direction of increasing  $SAD$  used in other figures. It is seen that, when the formulation approaches optimum from both sides, the drop size first decreases and then increases in the very vicinity of the three-phase region.

The accepted explanation for this minimum drop size at some “distance” from optimum formulation is a competition between two opposite effects. The general phenomenology found for the effect of  $SAD$  on drop size applies over a wide range of water-to-oil ratio ( $WOR$ ) and with all formulation variables.<sup>23,24,28,29</sup>

As the formulation approaches optimum, but is still away, the tension decreases whereas the coalescence rate remains essentially constant. As a consequence, the low tension favors the breaking and the drop size tends to decrease. As the formulation becomes very close to optimum, the coalescence rate becomes very fast, and even if smaller droplets are produced because of an even lower tension, the dynamic equilibrium between rupture and coalescence is now shifted in favor of coalescence and the drop size tends to increase.

As a matter of fact, the measurement of drop size is carried out quickly after emulsification to avoid a change in drop size prior to analysis. The dilution of the emulsion sample with distilled water (for O/W) and liquid paraffin oil (for water-in-oil (W/O)) is made within 10 s of the end of the emulsification process. Once the emulsion is diluted to about 1:1000, the coalescence probability becomes very low because drops are far from one another, and the stirring of the cell is enough to avoid settling. Repeated trials indicated that this quick dilution technique results in an average drop size that is reproducible to within 5% accuracy. If a longer lag time is permitted, the drop size might tend to increase. However, the changes in drop size close to optimum formulation are so large, e.g., 1 order of magnitude, that the trend is perfectly defined.

In Figure 1 the minima in drop size are located at formulations that are very close to the boundary of the three-phase region. This is consistent with the presence of stable emulsion that sometimes occurs just outside the three-phase region.<sup>14,17</sup> In Figure 2, which describes a salinity scan with an anionic

surfactant system, the exhibited trends are the same, and a minimum drop size is attained on both sides of the three-phase region. However, the location of the minimum seems to be farther from the three-phase region, and again this is consistent with the fact that in this kind of system the high stability region of both O/W and W/O emulsions is farther from the three-phase region.<sup>18,27</sup>

Actually, it is worth noting that the “apparent distance” from optimum formulation might be just a matter of scale. If the common  $SAD$  scale is used to compare cases, the location of the minimum with respect to optimum formulation can be estimated by using anionic and nonionic expressions of  $SAD$ .<sup>30</sup>

For instance, for the 378 rpm data in Figure 1, the distance between the minima is about 0.8  $EON$  unit, i.e., 0.8  $SAD$  unit. In Figure 2, a salinity change from 4.8 to 8 is found between the two minima, which in terms of Neperian logarithm of salinity is about 0.5  $SAD$  unit. Hence, the minima in Figure 2 are actually closer to optimum formulation than those in Figure 1. Comparisons with values reported in the literature about the location of the minimum drop size in a temperature scan<sup>22,25</sup> points to an approximate  $SAD$  deviation of about 0.2 unit between the minimum and the PIT, thus 0.4 unit between minima.

Although these values depend on other factors such as stirring energy, as will be seen in the next section, they indicate that the minimum is rather “close” to optimum formulation, although it seems that it must be outside the three-phase region.

#### 4. Effect of Stirring

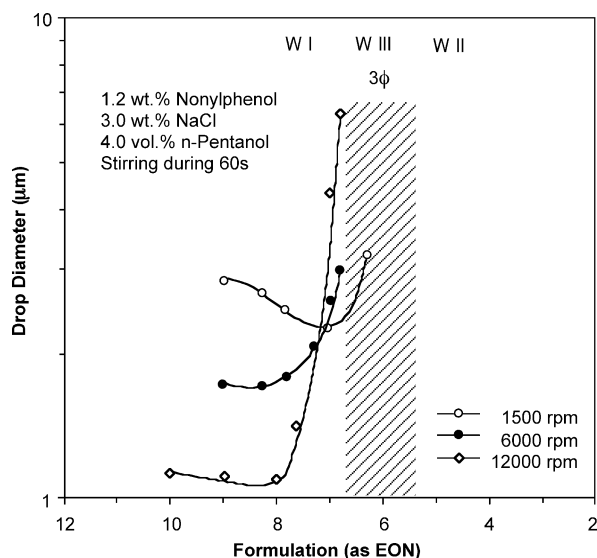
Stirring obviously has an effect on both breakup and coalescence, since it provides the shear to elongate the drop before breaking and also provides the inertia to gather drops and help them coalesce. Since an increase in stirring energy is not expected to have exactly the same effect on these opposite phenomena, it is likely to shift the dynamic equilibrium, i.e., the location of the minimum, one way or the other.

A simple reasoning could first lead to think that an increase in stirring would mainly magnify the rupture mechanism, with a resulting decrease in drop size. This is what can be seen in Figures 1 and 2 when the rotational speed of the stirring device is increased from 378 to 2000 rpm. The power consumption ( $\rho N^3 D^5$ , where  $\rho$  is the density,  $N$  the rotational velocity, and  $D$  the impeller diameter) increases about 600 times. Hence, it is no wonder that the average drop size decreases consequently. It is worth noting however that the decrease in Figure 1 is much more pronounced for the W/O emulsions ( $EON < 6.5$ ) than for the O/W ones, probably because the regimes, particularly the surfactant concentration effect, are different, as discussed elsewhere.<sup>24,31</sup>

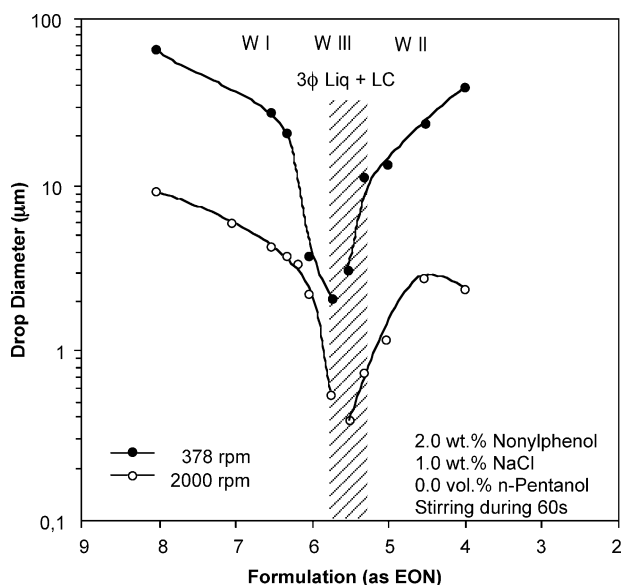
On the contrary, the variation of the drop size in Figure 2 is almost symmetrical. Figure 3 indicates the variation of the average drop size on the O/W side only, but for a considerable variation in stirring energy. Again the drop size tends to decrease when the stirring energy is augmented, and in the 12 000 rpm case very tiny droplets at the boundary of the nanoemulsion range are attained.

Figures 1–3 indicate a second trend; i.e., the minimum location tends to drift away from optimum formulation as the stirring energy increases. This is an experimental result which seems to be quite general from the data that have been collected, although it might appear to be somehow counterintuitive. In effect, an increase in stirring energy is expected to favor the breakage step rather than the coalescence; hence it would tend to extend the zone where the drop size decreases, and





**Figure 3.** Effect of stirring energy on variation of average drop size with formulation.



**Figure 4.** Effect of absence of alcohol on variation of average drop size versus formulation.

consequently to shift the minimum toward optimum formulation. The experimental evidence shows that the opposite occurs. It may be conjectured that an increase in stirring tends to increase both the breaking and the coalescence, and if the main effect of breakage is to get smaller droplets, these smaller droplets are more numerous and closer, and hence eventually more likely to coalesce. Moreover, the increased surface area of the droplets makes it more difficult for the surfactant to adsorb instantly and protect them from immediate coalescence.

### 5. Effect of Structure or Alcohol (Liquid Crystal vs Microemulsion)

Figure 4 indicates the variation of the emulsion drop size in the absence of alcohol for the two cases indicated in Figure 1. The difference is that in the latter case the emulsion drop size does not rise as optimum formulation is closely approached. Instead, emulsions formed in the three-phase region appear to exhibit a smaller drop size in the conditions of measurement.

The obvious conclusion is that the coalescence mechanism does not take place anymore at or close to optimum formulation, or at least not so fast.

This may be explained by the double role of alcohol in the interfacial palisade. The first effect of 1-pentanol on formulation is well-known,<sup>10</sup> and in this case it contributes to add a lipophilic cosurfactant contribution at interface. Therefore, removing 1-pentanol produces a shift of the optimum EON for three-phase behavior toward a lower value, e.g., 5.7 instead of 6.4. This shift however is unlikely to alter the coalescence. The removal of the alcohol has another effect; i.e., it reduces the disorder that was produced at the interface in the adsorbed layer by short-chain pentanol molecules inserted between surfactant molecules. At optimum formulation, the interfacial curvature is known to be zero, and as reported by Winsor 50 years ago,<sup>32</sup> the structural alternatives are either a lamellar liquid crystal or a bicontinuous microemulsion. The removal of the alcohol could possibly result in the formation of lamellar liquid crystals, if the surfactant concentration is large enough. It was found that the 2 wt % surfactant concentration level without alcohol results in a mixture of both structures, i.e., microemulsion and lamellar liquid crystal (LLC). Evidence of birefringence was observed at EON = 5.5, indicating the presence of LLC in the system. As a consequence, a single or multilayer liquid crystal is probably formed around the emulsion droplets and prevents them from coalescing immediately.<sup>33–35</sup>

As a matter of fact, the formation of a LLC layer around droplets is an essential quench feature in producing mini- or nanoemulsions by the PIT emulsification method.<sup>36,37</sup> It is worth noting that the tiny drops attained in the three-phase region are not due, at least totally, to a zero energy phase separation process<sup>38</sup> but almost certainly to an even lower interfacial tension. In effect the increase in stirring energy results in a decrease in droplet size in the three-phase behavior region, with essentially no change outside it, evidence that there is probably little effect of alcohol on the low tension value.

### 6. Conclusions

The proper selection of the formulation and stirring conditions could help in making the finest possible emulsions. The best formulation seems to be at some "short distance" from optimum formulation, on both O/W and W/O sides, provided that a quick change in formulation (or temperature), referred to as a physicochemical quench, is immediately applied to stabilize the generated fine emulsion.

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