

EMULSIFICATION EFFICIENCY RELATED TO THE COMBINATION OF MECHANICAL ENERGY INPUT AND SYSTEM FORMULATION AND COMPOSITION VARIABLES

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Abstract. The reduction of drop size during emulsification may be favored by changing three types of variables: (1) the physicochemical formulation variables which are linked to the nature of the compounds [water, oil, emulsifier], (2) the composition variables that account for their relative proportions and (3) the variables which characterize the mechanical energy input conditions supplied by the stirring device. After reporting the general trends, the best compromise situations to attain a minimum drop size are located in the three dimensional formulation-composition-stirring space.

Résumé. La diminution de la taille des gouttes durant l'émulsification est favorisée par trois types de variables: (1) les variables de formulation physico-chimique qui dépendent de la nature des composés [eau, huile, émulsifiant], (2) les variables de compositions qui rendent compte des proportions relatives de ceux-ci, (3) les variables qui caractérisent les conditions et l'énergie d'agitation. Après avoir décrit les tendances générales, on précise les endroits où on peut atteindre une taille de goutte minimale dans l'espace tridimensionnel formulation-composition-agitation.

Key-words. emulsion, drop size, formulation, stirring, mixing efficiency

Emulsions are found in many instances of industrial processes like polymerization, food processing, paint manufacturing, petroleum production, cosmetics and pharmaceuticals etc (1). Emulsification is carried out in most cases by mixing a system containing two immiscible phases which are labeled as oil and water, and a stabilizer, so-called emulsifier, which is generally a surfactant or a surfactant-cosurfactant mixture. The efficiency of the emulsification operation is directly related to the drop size reduction which is reached at the end of the process. Experience shows that smaller drops can be attained in different ways, such as decreasing the surface tension, increasing the emulsifier concentration, reducing the dispersed phase viscosity, stirring in a more energetic way or during more time etc. Some of these methods could be effective or not depending of the case, which is an indication of their lack of universality. Most comprehensive studies have been carried out at constant formulation, constant composition or constant stirring conditions. However, such an approach exhibits serious drawbacks, because it is likely to hinder the effects of coupled and competitive phenomena, which have been recently found to be extremely important in some cases(2,3).

As a consequence, an integrated phenomenological approach is to be preferred, in spite of the inherent complexities to be dealt with. This paper is aimed at showing that recent advances in formulation engineering allow to reduce the difficulties to reasonable level, which may be handled through a three-dimensional graphical representation.

PHYSICOCHEMICAL FORMULATION EFFECTS

The effect of the physicochemical formulation variables can be brought together by using a generalized concept such as Winsor's R ratio or the Surfactant Affinity Difference SAD (4-6) or its Hydrophilic Lipophilic Difference (HLD) numerical equivalent (7,8) which defines the free energy of transfer of a surfactant molecule from oil to water phase. HLD may be expressed for nonionic surfactant systems by equation [1] that specifies the compensating effects of the formulation variables. A similar equation exists for ionic systems.

$$\text{HLD} = \alpha - \text{EON} + b \text{S} - k \text{ACN} + t \Delta\text{T} + a \text{A} \quad [1]$$

where

- α is a parameter which is characteristic of the surfactant lipophilic group
- EON** is the (average) number of ethylene oxide groups per surfactant molecule
- S** is the salinity of the aqueous phase in wt.% NaCl (or equivalent)
- ACN** is the number of carbon atoms in the alkane molecule (or equivalent)
- ΔT is the temperature difference with respect to reference (25°C)
- A** is the concentration (vol %) of alcohol
- k, t are constants characteristic of the surfactant type
- a, b are constants characteristic of the alcohol and electrolyte

HLD measure the relative affinity of the surfactant for the aqueous and oleic phase. At $\text{HLD} = 0$ the surfactant affinities are exactly matched, and a minimum interfacial tension is attained, sometimes in the ultralow range (< 0.001 mN/m) so that capillary phenomena virtually vanish.

It is now well established that as formulation is changed from hydrophilic ($\text{HLD} < 0$) to lipophilic ($\text{HLD} > 0$) conditions, whatever the variable used to produce the change in HLD, the emulsion inverts from oil-in-water (O/W) to water-in-oil (W/O) and the emulsion properties change according to Figure 1 scheme that sum up scores of experimental data (9-10).

The emulsion drop size is the result of a dynamic equilibrium between the effects that tends to decrease the drop size, and the ones that make the drop coalesce (11-12). As the $\text{HLD} = 0$ formulation is approached from both sides, the interfacial tension decrease favors the breaking process and thus a smaller drop size. However, the emulsion stability decreases as well, and drops are likely to coalesce at once upon contact near $\text{HLD} = 0$, which favors the opposite trend, i.e, a larger drop size. The first effect dominates far from $\text{HLD} = 0$, in the unshaded zones, whereas the second one prevails near it, in the shaded zone. This results in a complex variation of the drop size (2,13), which exhibits two minimums, one on each side of $\text{HLD} = 0$ as indicated by the tips of the arrow.

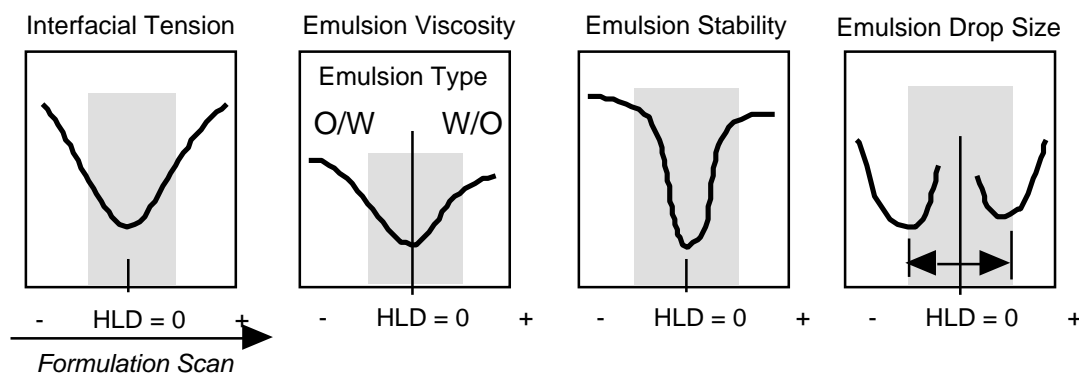


Figure 1. Interfacial tension and emulsion property variations versus formulation near $\text{HLD} = 0$.

COMBINING FORMULATION AND STIRRING EFFECTS

An increase in stirring energy generally tends to produce a decrease in drop size, because it affects more the drop breaking mechanism than the coalescence rate. Thus, an increase in stirring energy is expected to widen the region where the decreasing tension produces smaller drops. As a consequence, the location of the minimum drop is shifted closer to HLD = 0 when the mechanical energy input is increased, as indicated in Figure 2. In between the vertical lines that record the minimum position shift, the effect of the formulation on the drop size is one way or the other depending on the mechanical energy input.

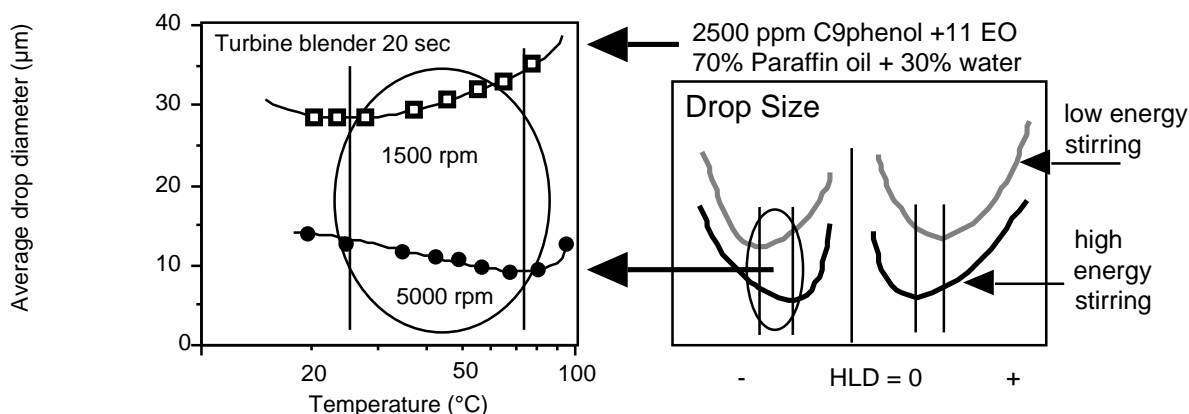


Figure 2. Influence of formulation and mechanical energy input on drop size.

COMBINING COMPOSITION AND STIRRING EFFECTS

The composition is also found to deeply alter the emulsification efficiency. Both an increase in surfactant concentration and an increase in stirring energy tend to produce a decrease in drop size as seen in Figure 3 right. However, the effects are not equivalent. Increasing stirring speed from 1500 to 5000 rpm is seen to be very significant at low surfactant concentration, whereas it has essentially no effect at 5% surfactant concentration.

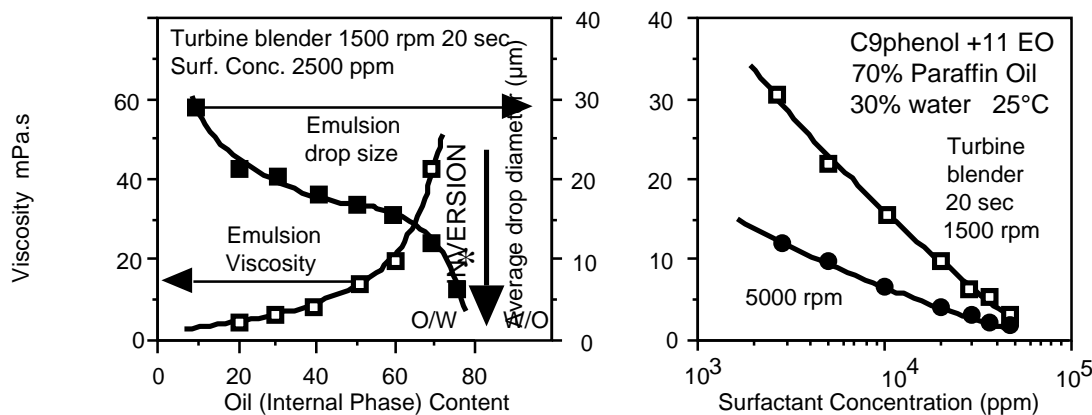


Figure 3: Influence of composition (water/oil ratio and surfactant concentration) on emulsion drop size

In the so-called High Internal Phase Ratio (HIPR) emulsification process (14), the high viscosity of the concentrated emulsion is the key to an enhanced drop breakage mechanism in regions where the formulation insure emulsion stability. As indicated by (*) in Figure 3 (left), this enhanced emulsification performance is attained near the inversion line, typically located at 70-80% internal phase content.

COMBINING FORMULATION, COMPOSITION AND STIRRING ENERGY EFFECTS

This would appear to be inconvenient in an actual production process, because of the catastrophic consequence of the emulsion inversion in most practical cases. Nevertheless, the position of the inversion line could be shifted in the generalized formulation-composition map as indicated in Figure 4, where a decrease in stirring widens the span of the HIPR region (shaded) in the direction of the arrows or conversely (15). Increasing the surfactant concentration result in the same shift than decreasing stirring energy (16).

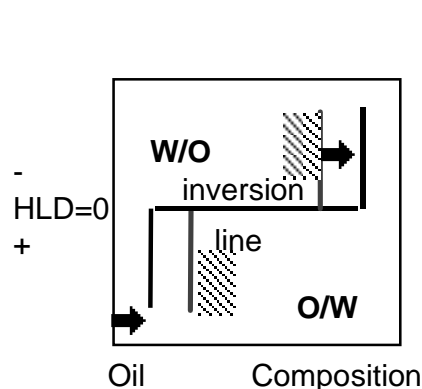


Figure 4: Effect of a decrease in mechanical energy input on formulation-composition map

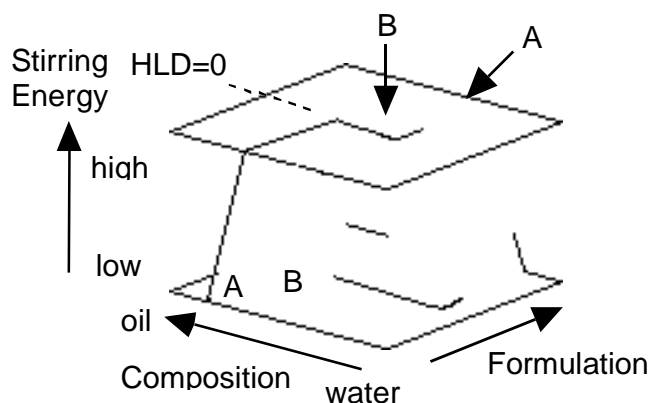


Figure 5: Regions where the conditions favor the production of small drop emulsions

The combination of the formulation, composition and stirring energy effects may be exhibited in the three dimensional diagram shown in Figure 5, that shows the volume regions where the drop size is minimum on each side of the inversion line. Each region may be divided into two bands, labeled A and B, where the emulsification efficiency is maximum: the high internal phase ratio region (A) which is near the inversion line as shown in Figure 3 left case, and region (B) about the drop size minimum located at some distance from HLD=0 as seen in Figure 2.

The corner where regions A and B are overlapping could be particularly favorable to attain extremely fine drop emulsions. However, this location is too near HLD=0 to provide a good stability, and it must be used only as a transient state for emulsification. As soon as the emulsion is made, the HLD must be shifted away far from HLD=0, for instance by changing temperature or by changing formulation. Oil/water content can be also adjusted, after the emulsification process is carried out in the favorable HIPR conditions.

Local or transient stirring and mixing conditions may be used to customize or fine tune the drop size distribution (13-18), as in the case of bimodal emulsions tailored to exhibit a particularly low viscosity and Newtonian rheological behavior, even at high internal phase content (19).

CONCLUSION

Producing a smaller drop size in an emulsification operation is not necessarily a matter of raw force and high mixing energy. Most efficient stirring can be reached by combining the effects of formulation (as expressed by a generalized parameter HLD, composition (surfactant concentration and water/oil ratio), and stirring energy. Actually the best size reduction cases are not attained by high speed stirring (which tends to limit restrict the favorable HIPR region), but by the slow mixing of viscous concentrated emulsions.

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