

Emulsification yield related to formulation and composition variables as well as stirring energy*

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Abstract

The emulsification yield, i. e., the reduction of drop size when a surfactant-oil-water system is stirred, can be altered by changing: 1) the physicochemical formulation variables which are linked to the nature of the water, oil, and emulsifier, 2) the composition variables [surfactant concentration and water-to-oil ratio] and 3) the variables which characterize the mechanical energy supplied by the stirring device. After reporting the general trends found in previous research, the best compromise situations to attain a minimum drop size are located in a three dimensional formulation-composition-stirring space.

Key words: Emulsion, formulation, stirring, drop size.

Rendimiento de emulsión en función de la formulación, de la composición y de la energía de agitación

Resumen

El rendimiento de emulsión, que se puede estimar por la disminución del tamaño de gota al agitar un sistema surfactante-agua-aceite está regido por: 1) las variables de formulación físico-química que dependen de la naturaleza del agua, del aceite, y del emulsionante, 2) las variables de composición [concentración de surfactante, y relación agua-aceite], 3) las variables que caracterizan las condiciones de agitación. Después de describir las tendencias generales encontradas en investigaciones recientes, se especifican las condiciones para lograr el mínimo tamaño de gota en el espacio tridimensional formulación-composición-agitación.

Palabras clave: Emulsión, formulación, agitación, tamaño de gota.

Introduction

Emulsions are found in many natural and man-made products and industrial processes like polymerization, food conditioning, paint manufacturing, petroleum production, asphalt application, cosmetics and pharmaceuticals, etc. [1-2].

Emulsification is carried out in most cases by stirring a surfactant-oil-water (SOW) system. Water is generally an aqueous solution containing different electrolytes as well as other solutes. Oil refers to a nonpolar phase, such as hydrocarbons, natural triglycerides or their derivatives. The stabilizer, so-called emulsifier, is generally a

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surfactant or a surfactant-cosurfactant mixture. The efficiency of the emulsification operation is directly related to the drop size reduction that is attained at the end of a mixing-stirring process.

It is known that smaller drops can be attained by different means, as for instance by increasing the emulsifier concentration, by decreasing the interfacial tension, by stirring in a more energetic way or during a longer period of time. Some of these methods could be more or less effective depending of the case, and the emulsion maker has to rely on experience to decide how to combine the different effects to attain the best product characteristics. Most comprehensive studies, which are available in the literature, have been carried out either at constant formulation, constant composition or constant stirring conditions. This is essentially due to the fact that engineers involved in mixing-stirring technology do not know or do not care about physico-chemical formulation, whereas chemists or physical-chemists are not often concerned by hydrodynamics and mixing issues.

As a consequence none of the current approaches is satisfactory for the emulsion maker, and all are likely to hinder the effects of coupled and competitive phenomena, although these have been recently reported to be determinant in many instances [3-4].

Thus, an integrated phenomenological approach is to be preferred, in spite of the complexities inherent to the three types of variables. Starting with an overview of the formulation influence on emulsion properties at constant stirring [5-9] which has been known for almost two decades, the paper presents a new analysis of two variable coupling, i. e., formulation-stirring [10-11], composition-stirring, and relates it to the formulation-composition map [12]. It finally shows that a three-dimensional mapping of the emulsification yield as a function of the combined effects of the three types of variables at once, i.e., formulation, composition and stirring.

Physico-Chemical Formulation

Physico-chemical formulation concerns a set of intensive variables which are characteristic of the nature of the components, as well as temperature and pressure. It determines the phase

behavior, as well as interfacial properties such as tension or natural curvature. Although emulsions are systems out of equilibrium, the formulation is of paramount importance during the formation of an emulsion and its useful lifetime because it determines its properties [13], as will be discussed later on. This is because the emulsion persistence is very often long enough for the phases to approach or to reach physico-chemical equilibrium.

Handling formulation issues is made difficult by the large number of components, which are included beyond the surfactant-oil-water ternary, such as co-surfactants, electrolytes or polymers additives. Additionally, most components are not pure substances, but mixtures of chemical species that could be as complex as a crude oil or that could contain as many different electrolytes as seawater. As a consequence, a systematic study could require thousands of research hours to be completed, even for a commonplace practical case. This is why formulation has been considered an art rather than a science. In the past half-century, researchers have tried to change this situation by quantifying formulation concepts and to assign to them some characteristic numerical value.

The empirical Hydrophilic-Lipophilic Balance (HLB) method was proposed 50 years ago by Griffin [14-15]. A few years later, Winsor [16] proposed a theoretical interpretation based on the molecular interactions of the adsorbed surfactant molecules at the interface and the neighboring oil and water molecules. This was an enlightening and pedagogical contribution as far as the physico-chemical understanding was concerned, but no numerical value was attainable. In the 60's Shinoda introduced the Phase Inversion Temperature PIT, i. e., an experimentally attainable parameter which takes into account all the variables [17]. In the late 70's studies on the enhanced oil recovery by surfactant flooding reached a complete description of the formulation effects, under the framework of correlations involving the effect of the oil type, electrolyte type and concentration in water, surfactant type, alcohol type and concentration, as well as temperature and even pressure [18-21].

More recently, these relationships were justified from a physicochemical point of view as

representative of the surfactant affinity difference (SAD), i.e., the free energy of transfer of a surfactant molecule from the oil phase to the water phase [22-24], as indicated by equation (1):

$$\text{SAD} = \Delta\mu_{o \rightarrow w}^* = \mu^{*w} - \mu^{*o} \quad (1)$$

where the μ^* are the standard chemical potentials.

For the sake of simplicity, SAD was later replaced by the Hydrophilic Lipophilic Deviation (HLD) which is SAD numerical equivalent when reference is taken at optimum formulation [25-26]. HLD has been recently shown to be experimentally attainable through the measurement of the partitioning coefficient P of the surfactant between excess oil and water phases of a Winsor's type III system [26-28] by HPLC or HPSEC analysis [29-30].

$$\text{RT HLD} = \Delta\mu_{o \rightarrow w}^* = \mu^{*w} - \mu^{*o} = \text{RT} \ln P = \text{RT} \ln \frac{C^o}{C^w} \quad (2)$$

HLD may be expressed for nonionic surfactant systems by equation (3) that specifies the compensating effects of the formulation variables and coincides with the early correlation for low tension attainment [31]:

$$\text{HLD} = \alpha - \text{EON} + b S - k \text{ACN} - \phi_A + c_T \Delta T \quad (3)$$

A similar equation (4) has been found for ionic systems, either anionic or cationic [32-33]:

$$\text{HLD} = \ln S - k \text{ACN} + \sigma - f_A - a_T \Delta T \quad (4)$$

where

- α is a parameter which is characteristic of the surfactant lipophilic group
- EON is the number of ethylene oxide groups per nonionic surfactant molecule
- σ is a function of the surfactant hydrophilic and lipophilic groups
- 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)

f_A and ϕ_A are functions of alcohol type and concentration

ΔT is the temperature difference with respect to the reference (25°C)

k , a_T , c_T are constants characteristic of the surfactant type

b is a constant characteristic of the electrolyte

The values of all these parameters are available for some systems in the literature [19-25, 31-34].

Physico-Chemical Formulation Effects on Emulsion Properties

HLD measure the relative affinity of the surfactant for the aqueous and oil phase. At 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, as sought in enhanced oil recovery processes [18].

It is now well established that as formulation is changed from hydrophilic (HLD < 0) to lipophilic (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) a change which is known as Bancroft's rule [35-36] because it essentially corresponds to what was enounced almost one century ago.

It is now well accepted that the emulsion properties change according to Figure 1 scheme that sum up scores of experimental data [3-11].

The emulsion drop size is the result of a dynamic equilibrium between two opposite effects: on the one hand those which tend to decrease the drop size, e. g., shearing or stirring, and on the other hand those which favor the coalescence between drops [2, 37]. As the HLD = 0 formulation is approached from both sides, the decreasing interfacial tension advantages the breaking process with a resulting smaller drop size. However, the emulsion stability concomitantly decreases, and drops coalesce instantly upon contact, which favors the opposite trend, i.e., a larger drop size. The first effect dominates far from HLD = 0, in Figure 1 unshaded zones, whereas the second

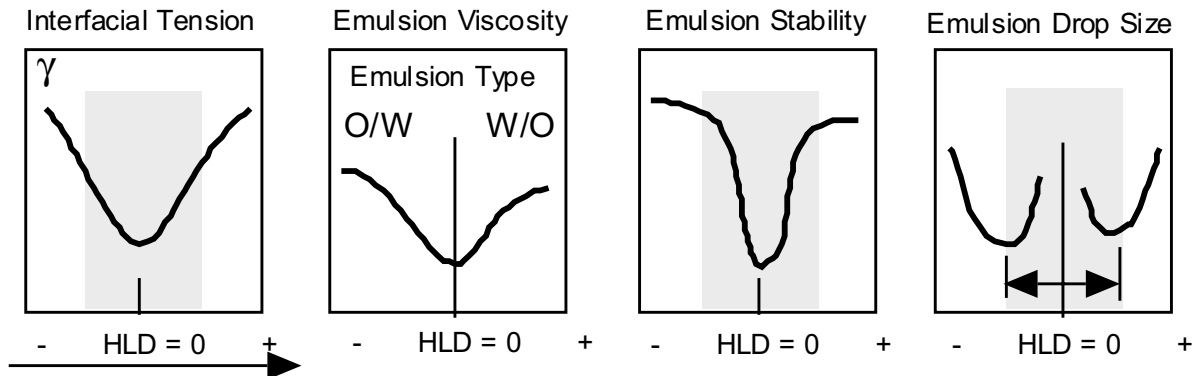


Figure 1. Interfacial tension and emulsion property variations versus formulation (as HLD) at near unit water-to-oil ratio.

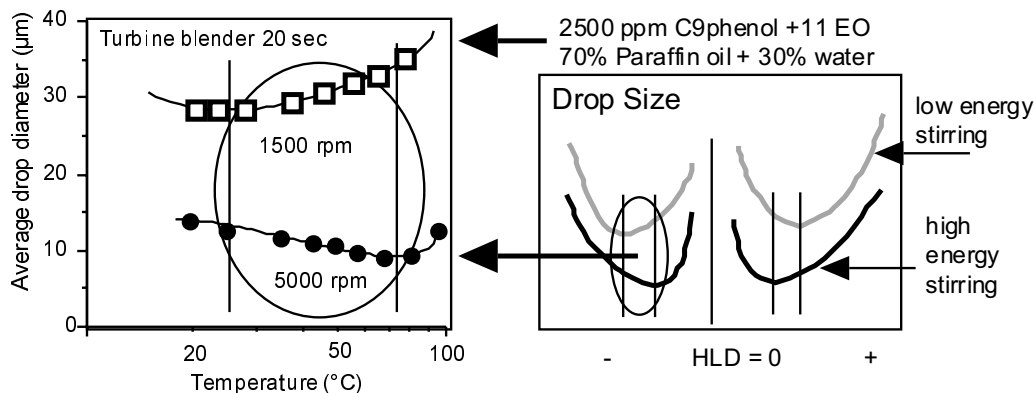


Figure 2. Coupled effects of formulation and mechanical energy on drop size.

one prevails near it, in the shaded zone. This results in a complex variation of the drop size [11, 38-39], which exhibits two minimums, one on each side of HLD = 0 as indicated by the tips of the double arrow in Figure 1 drop size plot.

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. This evidence shows why it is difficult to interpret experimental data when no clear understanding of the phenomenology is available.

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. 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.

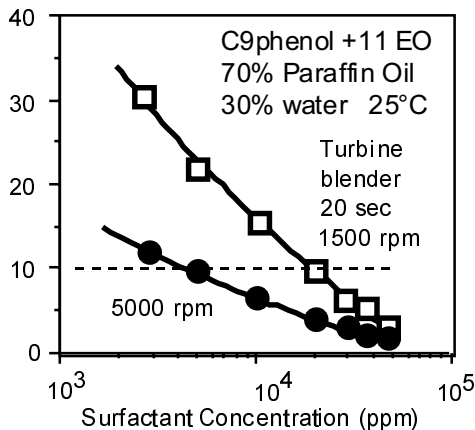


Figure 3. Coupled Effects of Surfactant Concentration and Stirring Energy on Emulsion Drop Size.

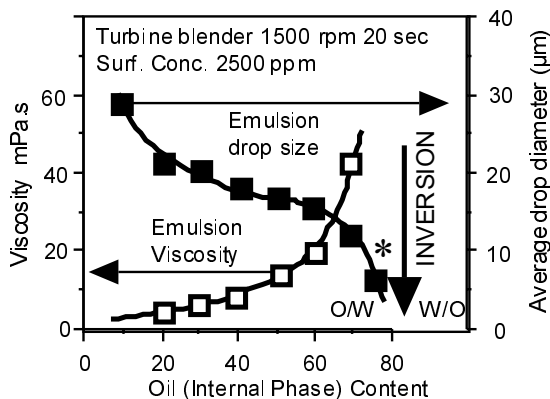


Figure 4. Influence of composition (water/oil ratio) on Emulsion drop size and viscosity.

In most practical cases the optimum strategy will be some intermediate compromise between not so low surfactant concentration and not so high stirring energy. For instance a 10 µm droplet size (dashed line in Figure 3) can be attained somewhere in between 1500 rpm and 20,000 ppm of surfactant or 5000 rpm and 5,000 ppm of surfactant.

Figure 4 indicates that the average drop size decreases, concomitantly to an increase in emulsion viscosity as the internal phase (oil) amount increases from left to right. When the internal phase ratio approaches the inversion value, the emulsion becomes extremely viscous, often viscoelastic and a high yield (indicated with an asterisk in Figure 4) is attained.

In this so-called High Internal Phase Ratio (HIPR) emulsification process [40-42], which has been industrially used to prepare cosmetics as well as heavy crude oil emulsions [40-42], the high viscosity of the concentrated emulsion is the key to an enhanced drop breakage mechanism [43] in regions where the formulation insure emulsion stability.

As indicated in Figure 4, this enhanced emulsification performance is attained near the inversion line, typically located at 70-80% internal phase content, where the emulsion viscosity is so high that only a low shear mixing can be applied. Nevertheless, this effect has been recently found [44] to hold at constant Reynolds number and at constant stirring energy input per unit volume of the system, i. e., independently of the variation of the emulsion viscosity.

Combining Formulation and Composition Effects in 2D Property Map

Early studies [45] indicated that the departure from Bancroft's rule was in many cases due to a water-to-oil ratio (WOR) very different from unity. Since formulation and water-to-oil ratio were likely to exhibit some crossed effect, the situation was analyzed by plotting the emulsion properties in a bidimensional map [46] as a function of the generalized formulation (HLD) and the water fraction as illustrated in Figure 5 left map, which schematically indicates the mapping of the emulsion type in the formulation-composition 2D space [12]. Many experimental maps backing this phenomenology have been published in the scientific literature in the past ten years [3, 12, 39, 47-55].

The O/W and W/O emulsion type regions are separated by a bold line, so-called standard inversion line or locus, which exhibits a stair-like shape. In the central part of the map, where amounts of oil and water are relatively similar, the inversion line is horizontal, and is coinciding with HLD = 0 formulation, i. e., optimum formulation for low tension and three-phase behavior, as previously discussed. In this central region the formulation is the variable responsible for emulsion inversion, which occurs at optimum formulation, according to Bancroft rule and as al-

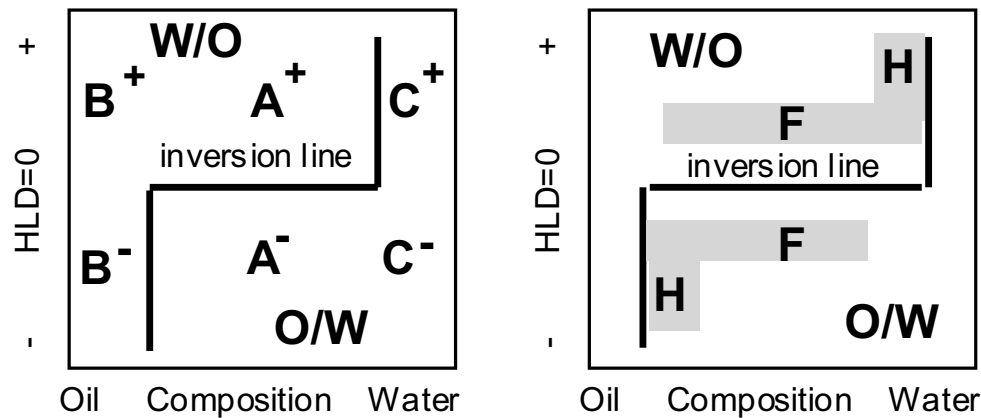


Figure 5. Bidimensional formulation-composition maps showing the emulsion types (left) and small drop zones (right).

ready seen in Figure 1. This central region is labeled "A" with a "+" (respectively "-") superscript to indicate the location above (respectively below) the optimum formulation line (HLD = 0).

The inversion also displays two lateral branches, which are essentially vertical, i. e., at constant oil-water composition, typically located at 25 and 75% of water. The low water content region is labeled "B" and the high water content one "C", both with the same superscript symbol as in the central region. The B^+ zone is the prolongation of the A^+ region, and there is no real boundary between them, but a simple change in WOR. The same occurs for the A^- and C^- regions.

Contrariwise, the C^+ and B^- regions exhibit distinct characteristics, which reflect the conflict between formulation and composition effects. The C^+ region is located at $HLD > 0$ and, according to Bancroft rule should correspond to the W/O emulsion type. However an O/W type is found in this region which is thus labeled as abnormal. Actually it is often a W/O/W multiple or double emulsion, in which small water droplets are located inside the oil drops, which are dispersed in a continuous water phase. The same is occurring in the B^- region, but this time the roles of the water and oil phases are inverted, and the multiple emulsion is of the O/W/O type. More information on these maps may be found elsewhere [56-57]. For the sake of simplicity it is enough to remark here that stable emulsions are found in the A^+ and A^- regions, respectively of the W/O and O/W types [12, 56].

It has been previously discussed that the effects of formulation on interfacial tension and emulsion stability result in the presence of a minimum drop size at some distance from $HLD = 0$ on both side of optimum formulation (Figure 1). On the 2D plot this minimum drop size extends parallel to the horizontal branch of the inversion line at $HLD = 0$ as the composition is changed. The corresponding zone where a small drop size is attained is indicated as a horizontal shaded band (F) in Figure 5 right map. On the other hand, it has also been shown (Figure 4) that small drop emulsions are attained at high internal phase ratio, near the inversion. The corresponding zones, which are located in both A regions close to the vertical branch of the inversion line, are shaded and labeled as H in Figure 5 right map.

Combining Formulation, Composition and Stirring Effects

Thus each A region contains two strips where a small drop size is attainable. However, it is worth noting that both strips are associated with particular emulsion properties, which have to be handled with care in a manufacturing process. The F strips are located relatively near optimum formulation, which is a low stability region. As a consequence this location could be interesting as a temporal situation while the emulsion is made, followed by a formulation change to move the emulsion characteristic point in the center of the A regions where a good stability is warranted.

On the other hand the H strip can be a risky situation in an industrial process, since a small formulation error might trigger the emulsion inversion, with catastrophic consequences in most practical cases. However, this ambush can be avoided by shifting away the vertical branches of the inversion line, either by increasing surfactant concentration [58] or by decreasing the stirring energy or duration [59], which both result in the change indicated by the arrows in Figure 6 left graph.

The combination of the formulation, composition and stirring energy effects is exhibited in the 3D diagram shown in Figure 6 right plot, which indicates the variation of the 2D map along the stirring energy axis. The shaded volumes are the regions where the drop size is expected to be minimum on each side of the inversion line. Each of these regions may be divided into two bands, labeled H (high internal phase ratio) and F (formulation best compromise) as in Figure 5.

The corner where H and F regions are overlapping could be particularly favorable to attain extremely fine drop emulsions according to a very recent study [60]. However, this location is too near $HLD = 0$ to provide a good stability and again it could 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, in what may be called a quench process, one of the so-called unit operations in emulsion formulation engineering [60].

Very recent investigations indicate that local or transient stirring and mixing conditions may be used to affect the emulsion type [61], or to customize or fine tune the drop size distribution [53-54], as in the case of bimodal emulsions tailored to exhibit a particularly low viscosity and Newtonian rheological behavior, even at high internal phase content [62-65]. Even more complex cases are to be dealt with systems, which are emulsified by mass transfer or phase inversion [66-68], which is often associated to spontaneous emulsification [69] or with more or less retarded equilibration, depending on the formulation [70].

Conclusion

Attaining a smaller drop size during emulsification is not inevitably a matter of raw force and high stirring energy. Combining the effects of formulation (HLD), composition (WOR), and stirring energy can reach most efficient drop size reduction. Actually, the smallest drop size is not attained by high-speed stirring (which tends to limit the extension of the favorable $HIPR$ region), but by the slow mixing of viscous concentrated emulsions, or by phase inversion.

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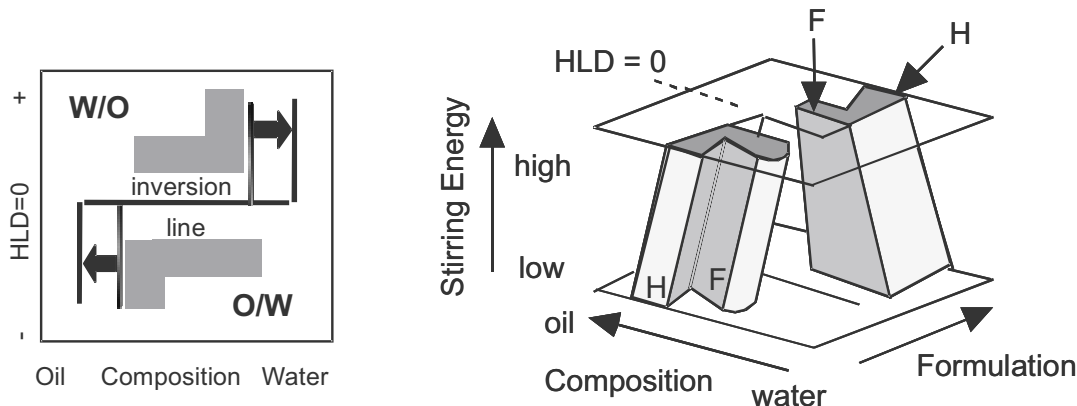


Figure 6. Changes in the 2D map when stirring is altered are plotted in a 3D map. Shades indicate the volumes where small drop size is attained.

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