

DYNAMICS OF NEAR-ZERO ENERGY EMULSIFICATION

Jean-Louis Salager, Ana Forgiarini, Juan Carlos Lopez, Shirley Marfisi, Gabriela Alvarez
Lab. FIRP, Universidad de Los Andes, Mérida, Venezuela

ABSTRACT Emulsification is generally carried out by introducing mechanical stirring in a two phase systems. However such methods are not always easy to apply and are often costly, particularly to produce the extremely fine droplets found in the so-called mini or nanoemulsions. The present talk deals with emulsification methods in which stirring has essentially no effect in the breaking mechanisms, which are based on one or several of the following dynamic processes: surfactant mass transfer, spontaneous emulsification, transitional or/and catastrophic phase inversion. They are all produced by interfacial transient events (most often under low-energy homogenization), either by putting into contact non-equilibrated phases or by changing the formulation, temperature, or the water-oil ratio of an equilibrated system. A unified approach is presented here on the basis of the generalized formulation concept, and it is shown to be a handy tool to design industrial processes such as polymer coating manufacturing, cutting oil concentrate dispersion or heavy crude oil emulsification.

INTRODUCTION

Emulsions are two-phase dispersed systems produced by some mechanism which allows the attainment of a dispersed transient state in which the free energy is higher than in the separated phase counterpart. In the free energy increase ($\Delta G = \gamma \Delta A - T \Delta S$) the entropy term is small and negligible unless extremely small droplets are formed, generally at a very low interfacial tension value, a situation which has been proposed as the key for the stability of microemulsions,⁽¹⁾ which are single phase systems, and consequently no emulsion, as far as we are concerned here.

It is worth remarking that the $\gamma \Delta A$ term, which is the work associated to the creation of surface during emulsification is in general much smaller, e.g. 1% and even 0.1%, than the actual energy supplied by an emulsifying device such as a turbine blender. As a consequence, it can be said that in brute force emulsification processes most of the supplied mechanical energy is generally wasted, i. e., transformed into heat. Moreover, as smaller drops are required, the drop breaking efficiency is more and more inhibited by the Laplace pressure which oppose elongation and builds up inversely to the drop size. The classical Grace plot (2) which shows how the critical Capillary or Weber number (ratio of viscous to capillary forces) varies as a function of the phase viscosity ratio, indicates that only axisymetrical elongational shear such as orifice homogenizator and ultrasonic stirrer allows to enter the submicron range, says the so-called mini or nanoemulsion realm, at the expense of a high energy cost. The present talk addresses the other cases of emulsification, in which the actually supplied energy is much lower and sometimes completely unrelated with the drop breaking process and only providing an overall blending of the system.

ZERO-ENERGY AND NEAR-ZERO-ENERGY EMULSIFICATION

In the labeling of the title, the term energy refers to mechanical energy, and it is true that emulsification can take place with no mechanical energy input. However, there is no possibility of producing a dispersed system, i.e., to create an area ΔA , if a free energy at least equivalent to $\gamma \Delta A$ is not supplied somehow to the system. The point is that this amount is essentially negligible with respect to the mechanical energy which is usually brought by a mechanical device. Nevertheless, mechanical energy, even a small amount such as $\gamma \Delta A$, is not absolutely required, since the energy supply can come from other sources, for instance the variation of chemical potential of a substance which passes from one phase to another for which it has a higher affinity.

In "zero-mechanical-energy" emulsification processes, the two-phase emulsion appears as the result of a spontaneous evolution of a morphology, often a single phase structure such as a microemulsion, when the formulation and/or composition are altered.

In "near-zero-mechanical-energy" emulsification process, the supplied mechanical energy participates in the breaking mechanism, which is considerably enhanced by the occurrence of very special situations in which the interfacial tension is close to zero or the effective shear is close to infinity, or both occurring simultaneously at the same time. In such cases the supply of more or less energy generally does not affect the resulting average drop size which is controlled by the formulation.

FORMULATION AND COMPOSITION VARIABLES - PHASE DIAGRAMS

The chemical potential of a substance is usually written as :

$$\mu = \mu^\circ + RT \ln (a/a_{ref}) \quad [1]$$

where μ° is the value of the chemical potential in some reference state. Here "a" is the activity of the substance, which, for the sake of simplicity can be replaced by its concentration, provided that some conditions are met. This expression means that the chemical potential of a substance, which is the driving force to produce changes, depend on two terms: the first one (μ°) depends on the nature of the substance and on other components of the system, as well as temperature and pressure, which are all intensive FORMULATION variables, independent of the size of the system. On the other hand the second term ($\ln a/a_{ref}$) depends on COMPOSITION, which in the case of a simple surfactant-oil-water system are two independent concentrations values, usually the surfactant concentration (Cs) and the water-oil ratio (WOR).

Thanks to the enhanced oil recovery research drive of the 1970, a lot of experimental and fundamental work has been carried out, thus simplifying the job of the formulator, and a generalized formulation approach, along Winsor R ratio pionering concept (3) and Davies contribution proposal (4) is currently available as the surfactant affinity difference concept which is the free energy of transfer of a surfactant molecule from the water to the oil phase. (5)

$$SAD = \mu^{*O} - \mu^{*W} = \Delta\mu^*_{W \rightarrow O} \quad [2]$$

SAD can be expressed as a series of contributions of all the formulation variables involved in the system such as the surfactant head group (number of ethylene oxide group EON if nonionic), the tail group (α), if a n-alkane oil, its alkane carbon number (ACN), the aqueous phase salinity (S as wt% NaCl) and its temperature (T).

An adimensional expression of SAD, so-called HLD or hydrophilic-lipophilic deviation numerically express the deviation of the formulation from the so-called "optimum" formulation in which the surfactant-oil-water system exhibits three-phase behavior, i.e. Winsor III type, and minimum interfacial tension.(6) The term "optimum" comes from the fact that this is a formulation at which petroleum can be recovered efficiently in the so-called enhanced oil recovery processes.

$$HLD = (SAD - SAD_{ref})/RT = \alpha - EON - k ACN + b S + \phi(A) + c_T (T - T_{ref}) \quad [3]$$

Contrarily to HLB, HLD involves not only the characteristics of the surfactant, but also takes into accounts all the other compounds, as well as temperature and pressure, just as Winsor R, but in a quantitative way. Whenever $HLD < 0$ (respectively > 0) the surfactant affinity for the aqueous (respectively oil) phase dominates and at low surfactant concentration a Winsor I (respectively II) phase behavior is attained. At $HLD = 0$ a three-phase, microemulsion/excess oil and excess water system Winsor III phase behavior is exhibited.

This expression, its equivalent for ionic surfactant systems, and other complements or modifications to handle non-alkane oils, non NaCl electrolytes, surfactant mixtures and other cases are very useful in practice because (1) they describe the physicochemical conditions with a unique and single variable which means a considerable simplification in the handling of the problem, (2) they show that formulation could be altered in many ways with similar results, and (3) they quantify the compensating effects of the different variables. From now on the formulation will be handled only through HLD, whichever the actually used variable is, either temperature, EON or salinity which is used for changing the formulation of the system.

In the simplest surfactant-oil-water ternary system, two independent variables are required to describe the composition, e.g. surfactant concentration (C_s) and water-to-oil ratio (WOR). It means that the chemical potential (equation [1]) depends on three variables: one generalized formulation variable such as HLD, and two composition variables (C_s , WOR). In practice these are too many variables to plot any property, and one of them has to be dropped, or each of them at a time. This situation produced three kinds of diagrams, in which the phase behavior is plotted in fig. 1.

- (1) C_s -WOR diagram (at constant HLD), usually drawn as equilateral triangles
- (2) HLD- C_s diagram (at constant WOR) sometimes called "fish" diagram
- (3) HLD-WOR diagram (at constant C_s) sometimes called "X" diagram

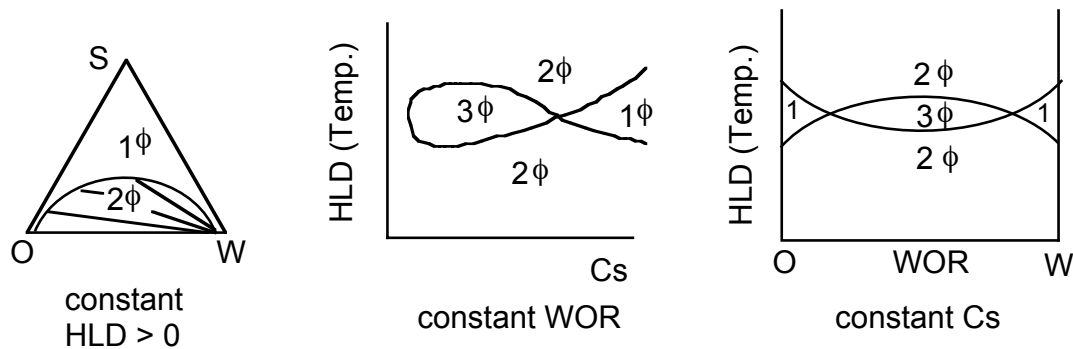


Figure 1: Phase behavior of ternary SOW systems in the three kinds of 2D diagrams.

Depending on what matters, some diagram is better than another. For instance, if a change of temperature is to be used, any of the two last cases, which involve HLD is useful, whereas such a change would have to be handled by a series of triangular diagrams.

If a quaternary system such as surfactant-alcohol-oil-water or a two-surfactant system is considered, things become more complex. The 2D triangle diagram becomes a 3D tetrahedron diagram, and in some cases a 2D cut is extracted from it, in which one of the vertices (at least) represents a pseudocomponent such as a surfactant/alcohol or a two-surfactant mixture. If the two components do not behave collectively, then a selective partitioning occurs (7) which is known to alter the composition in the phases and at the interface, and would produce a change in formulation. It has been shown that both C_s and WOR changes alter the partitioning of ethoxylated nonionics, (7) particularly low ethoxylation ones. Hence in this case composition variables C_s and WOR could also behave as formulation variables, a complex case, which cannot be put aside because it is very commonly used in practice. As a general rule, the severity of the partitioning effect increases as the species which make the mixture become different on a hydrophilicity basis.

Partitioning cases are particularly easy to detect in the HLD- C_s "fish" diagram in which the fish is slanted, i. e. the center line of the "fish" which corresponds to $HLD = 0$ changes with the surfactant concentration (figure 3). Similarly, the three-phase behavior band (around $HLD = 0$) in the HLD-WOR X diagram is also slanted. In the triangular C_s -WOR diagram the partitioning is not obvious, but it can be unveiled if the WI-WII phase behavior switches when the surfactant concentration changes.

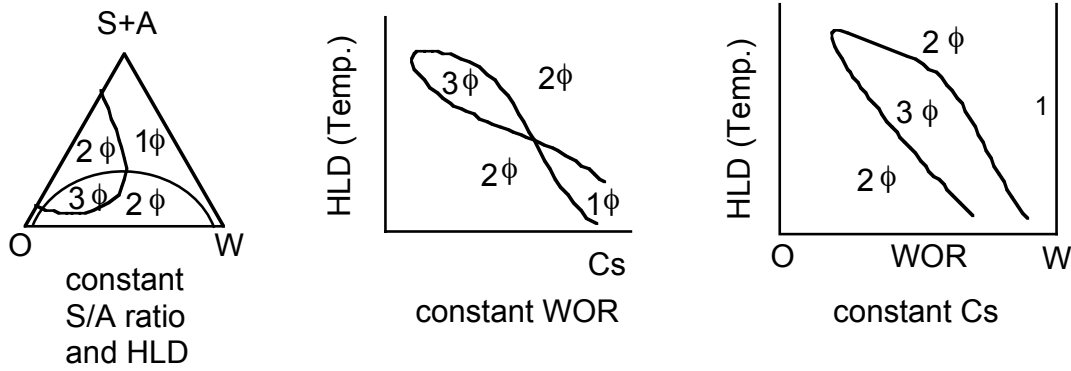


Figure 2: 2D-Diagrams in presence of fractionation of an amphiphilic mixture (surfactant-alcohol or two different surfactants)

STANDARD AND DYNAMIC EMULSION INVERSION

When a two-phase SOW system at equilibrium is submitted to stirring an emulsion is produced and its type can be estimated, and indicated in one of the 2D plots. The frontier between one type and the other is called the standard emulsion inversion line, and it divides the spaces into different regions as seen in figure 3. Each of these regions exhibits particular properties as far as drop size, stability, viscosity are concerned, and the formulator will seek the proper location for its application.

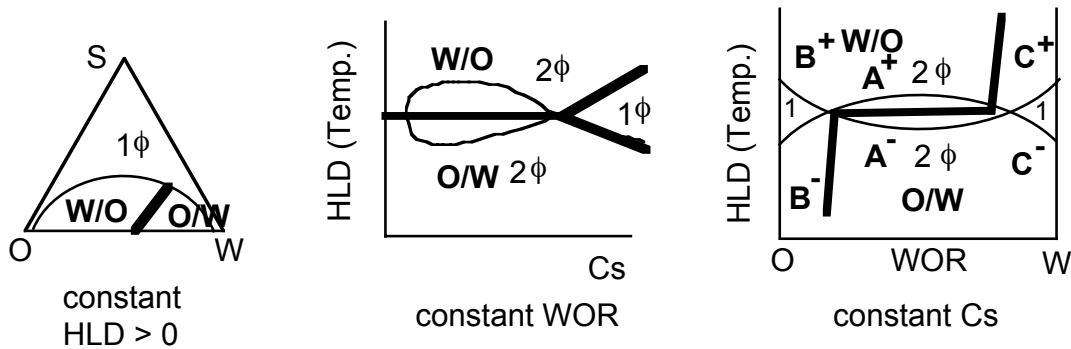


Figure 3: Standard inversion line in different 2D plots.

Formulation and composition variables can be changed to move the representative point of the emulsion from one location to another and to induce some change in emulsion properties, eventually crossing the inversion line so that the emulsion type switches. These are common practices in emulsion formulation engineering (8-9) and some of them which result in near-zero energy emulsification will be discussed next on the proper 2D diagram.

CASE #1 : TRANSITIONAL INVERSION (change in HLD at constant Cs and WOR)

This corresponds to a change in any of the variable affecting HLD, particularly temperature as it is the case in the PIT emulsification (figure 4), (10-15) but not necessarily since it can be performed with any other variables (16). The crossing of the HLD = 0 region is associated with the presence of a bicontinuous microemulsion or a liquid crystal, either as a single phase or in equilibrium with excess water and excess oil. During the crossing the phase behavior switches from WI to WII or vice-versa, and the surfactant-rich microemulsion changes continuously from aqueous to middle to oil phase, or

vice-versa, through a mass transfer process. Since the optimum formulation (HLD=0) corresponds to the maximum solubilization of oil and water, any slight displacement from optimum would result in a decrease in solubilization of oil or water. At some moment this would produce the exudation of an excess phase, under the form of small droplets. In most cases this droplets would coalesce at once since the near zero HLD region is intrinsically associated with extremely unstable emulsions. (17-19)

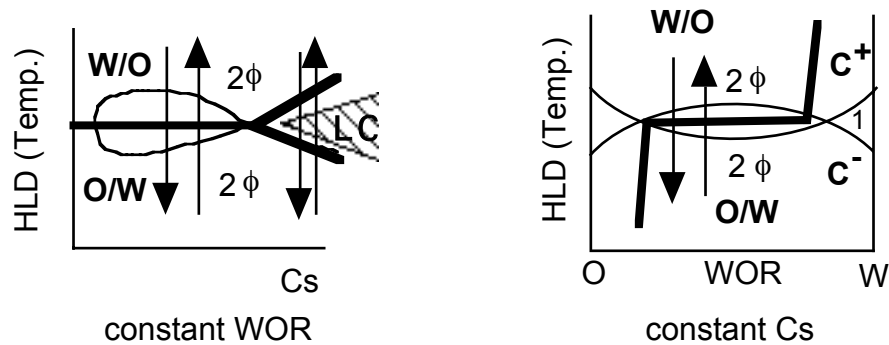


Figure 4: Path for transitional phase inversion

If coalescence could be prevented a fine emulsion would result. It is known to happen either because liquid crystal layers wrap the droplets (20-21) or when a quick change in HLD, e.g. a thermal or formulation quench, moves the formulation away from HLD = 0, so that the droplets wont coalesce.

The issue depends essentially on how the displacement away from HLD = 0 is carried out in practice and what could happen at this stage. It is not really known whether the conditions during the approach to HLD = 0 also matters as hinted by the commonly used back and forth change of temperature (22) and by the fact that some delay to inversion is found to vanish in presence of fast transferring molecules such as alcohol co-surfactant. (23)

CASE #2 : CATASTROPHIC INVERSION (change in WOR at constant HLD and Cs)

In the HLD-WOR plot, the standard inversion line exhibits two almost vertical branches at roughly 30 and 70% water or oil. In the central regions A+ and A- (see figure 3), so-called normal the emulsion type obeys Bancroft rule (i. e., the formulation effect prevails). In the B- (respectively C+) so-called abnormal regions there is not enough water (respectively oil) to make it the external phase, and an abnormal situation occur in which the emulsion type does not obey the formulation rule, being then the external phase the one in higher amount. Nevertheless, these abnormal emulsions often exhibit a multiple morphology with small droplets (of external phase) entering the drops. It can be said that the "inner" emulsion obeys the formulation, whereas the "outer" one obeys the composition (WOR). (24)

When a change in WOR shifts the representative points of the emulsion from one side to the other of one of these vertical branches, a so-called catastrophic inversion takes place. The name comes from the characteristics of the process, in particular irreversibility and delay, resulting in hysteresis, which is fairly well described by catastrophe theory.

Figure 5 indicates that the vertical branche is now replaced by two branches, each one corresponding to a direction of variation of WOR. The region in between belongs to one side or the other and is called an hysteresis zone. (25)

The change from abnormal to normal should be expected to be spontaneous, but it is not always the case and it can be delayed considerably depending of many factors. (26-28) Multiple emulsions are often found to be an intermediate stage in this inversion process, in which the "inner" emulsion tends to displace the original "outer" emulsion.

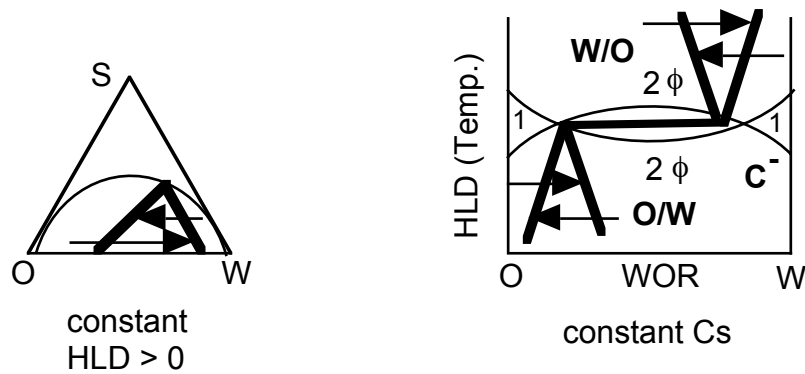


Figure 5. Dynamic inversion frontiers as WOR is changed.

In some extreme cases the addition of 10% aqueous phase to oil allows to make a 90% internal oil in water emulsion which could be diluted afterward. The formation of emulsion, which is a very early inversion, might be due to the transfer of surfactant or to the viscoelastic rheology which enhances the shear, but the fact is that in spite of being still unclear it is used in making alkyd, silicon and epoxy resins worldwide. (29-30)

In the normal to abnormal morphology change, the triggering of the inversion is found to depend on the rate of change, in particular to the way the internal phase is added to the emulsion. If the internal phase is added slowly and continuously, the inversion is often delayed so much that the emulsion becomes a viscoelastic high internal phase ratio dispersion. In such viscoelastic media, a slow motion stirring produce a fracture emulsification process in which the shear, i.e. the ratio of some velocity to some distance, can become extremely high because the distance is reduced to the fracture gap. (31) It is the typical case of the drop of oil added to a bowl of mayonnaise, which is emulsified with three or four turns of a spoon. This emulsification process is not a zero-energy one but the mechanical energy yield is so high that it deserves to be classified as a near-zero energy case. The fracture emulsification process tends to result in a monodispersed emulsion, a characteristic which is welcomed to reduce Ostwald ripening but which might result in unwelcome increased viscosity.

CASE #3 COMBINED HLD – WOR CHANGE

If the crossing of the inversion line is carried out by concomitantly changing both HLD and WOR some hybrid can be attained in the region where transitional and catastrophic regimes overlap in the HLD-WOR map. A recent study (32) showed that the exact location of the path is critical, and that the smallest drops are attained when the crossing is at HLD slightly different from zero, not at HLD=0, nor far away. This slightly off optimum formulation (path 3 in figure 6) seems to correspond to the point of best compromise between a low tension (which eases the drop breakup) and not so fast coalescence (33-34). In any case these small droplets have to be saved from growing by some thermal or physicochemical quenching.

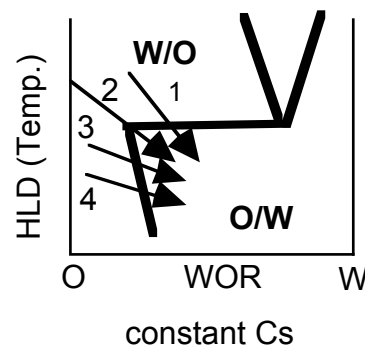


Figure 6. Combined transitional/catastrophic inversion

CASE #4 INDIRECT OR INDUCED HLD – WOR

When dilution, i.e. WOR change, results in fractionation, that is HLD change, an induced HLD-WOR coupling could take place. In such a case the WOR change might induce a transitional inversion as if it were a HLD change. This is one of the most commonly used, though most complex way to make miniemulsions with systems containing commercial surfactants which produce liquid crystals. (35-37) As in a voluntarily combined WOR-HLD change (case #3) the followed path is critical, and has to be finely tuned for a low tension region with L3 liquid crystal phase region to be crossed.

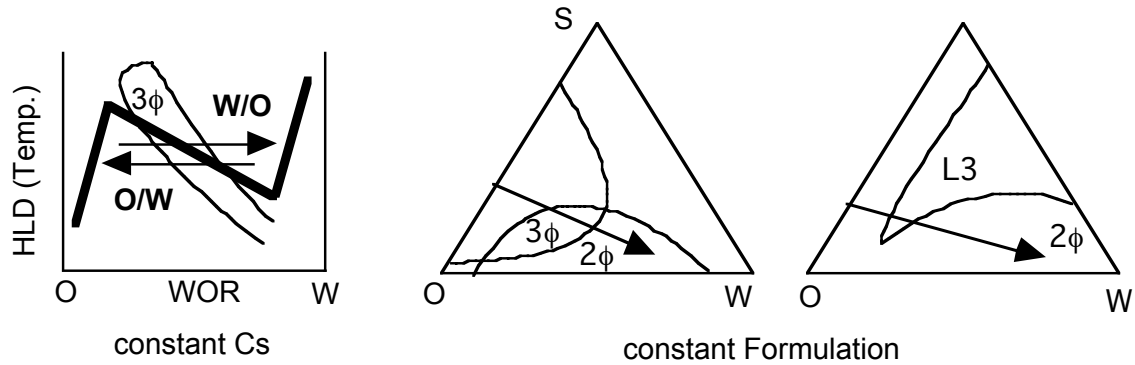


Figure 7. Coupled HLD-WOR variation produced by a WOR change.

It is worth remarking that this implies to work out a lot of previous phase behavior studies to make sure that the phase diagram to be used contains the proper features, and this may be a tough problem. (30, 38-40)

As a matter of fact this kind of emulsification is essentially the same than the transitional one, but with a change of formulation which one does not directly control, but which results from the coupling between WOR and HLD.

In this case, as in all transitional cases, the scale of a microemulsion domains is much smaller than the resulting droplets found even in the best case of PIT. It means that during the single-phase/two-phase transition process hundred or thousands of domains get together to form a droplet as illustrated in figure 8. This is not a real coalescence process since the domains are not individual droplets, but some kind of rearrangement in which the surfactant layer that separates the domains shrinks and a droplet appears.

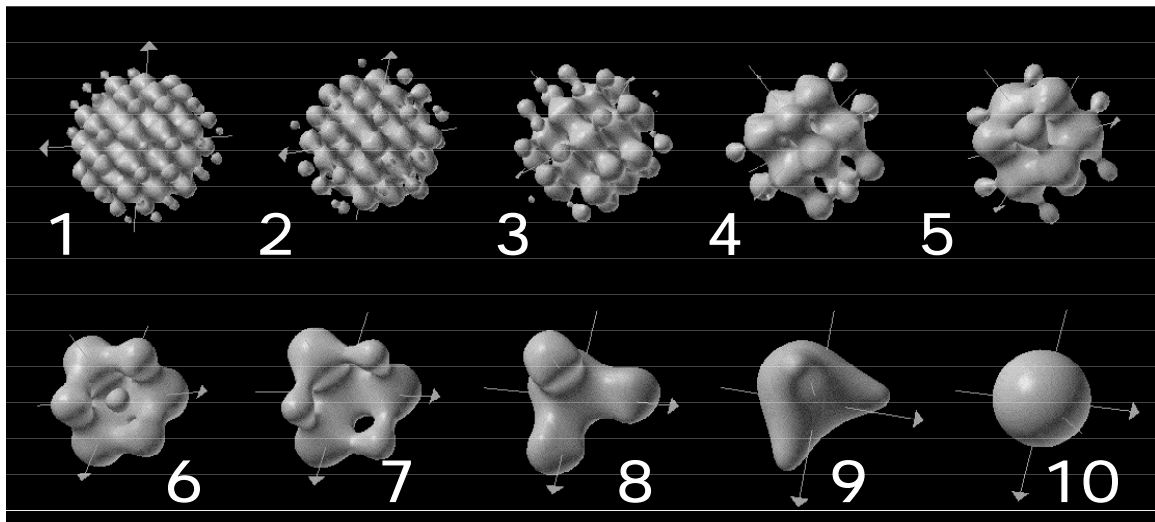


Figure 8. Possible evolution of a portion of a bicontinuous microemulsion into a droplet.

It is not known for sure what makes the final droplets smaller or larger, and a lot of work has to be done in order to understand it. The first hint can be brought by other phase separation processes such as nucleation or cloud point phenomena. It is well known that the rate of change, which influences the dynamic process at the molecular level is what influences most the size of the cluster in which the molecules are collected into the seed fragments of separated phase. This phase separation case could be view to be similar to an aggregation mechanism of colloid particles into a fractal whose shape and size depends on the limiting mechanism (reaction-balistic-diffusion) and the aggregation mechanism (molecule-cluster or cluster-cluster). At least the variables which are likely to affect theses mechanisms could be tested as candidates to control the final emulsion drop size.

CASE #5 SINGLE PHASE SEPARATION INTO TWO PHASES

When a change is such that the binodal curve (i.e. the frontier between single and two phase behaviors) is attained a phase separation takes place. This can happens in different ways, either by diminishing C_s , or by changing WOR or HLD (particularly temperature as in cloud point phenomenon). (41) This does not result in small drops, unless some supersaturation region occurs, as in spontaneous emulsification by diffusion and standing. (42)

CASE #6 FAR FROM EQUILIBRIUM EMULSIFICATION PROCESSES

Most of the previous transitional mechanism dealt with situation in which an equilibrated SOW system is somehow perturbed, particularly from the point of view of its formulation, so that a slightly out-of-equilibrium driving mechanism takes place. But in most previous cases the change is reversible and relatively easy to control. This is not the case when two phases, which are very far from equilibrium are put into contact. In far from equilibrium situations, very large concentration or tension gradients would produce macroscopic motion and sometimes actual mixing, through mechanism we will include in this category of far-from-equilibrium spontaneous emulsification, which are treated in details elsewhere. (43-45)

Traditionally three main mechanisms have been proposed for spontaneous emulsification: (1) interfacial turbulence, (2) diffusion and stranding, and (3) negative interfacial tension. The so-called interfacial turbulence takes place as local interfacial tension gradients are formed throughout the liquid-liquid interface. This is found when an alkaline aqueous phase is put into contact with an oil phase containing carboxylic acids. The in-situ formation of carboxylate soaps results in a very low tension in some places and drives fluid motion.

Second, diffusion and stranding happens when one of the components of a phase has a very strong affinity for the other and quickly partitions to it. This happens for instance when an alcoholic beverage containing ethanol and anethol (anis oil) is mixed with water, with an instant formation of a cloud of tiny oil droplets. If the solubilization of oil is insured by a surfactant/alcohol mixture, swollen micelles are stripped from one component, break up and release the solubilized content of the micelles as droplets. This is related is used many self-emulsifiable concentrates of pesticides, cutting oils and other applications.

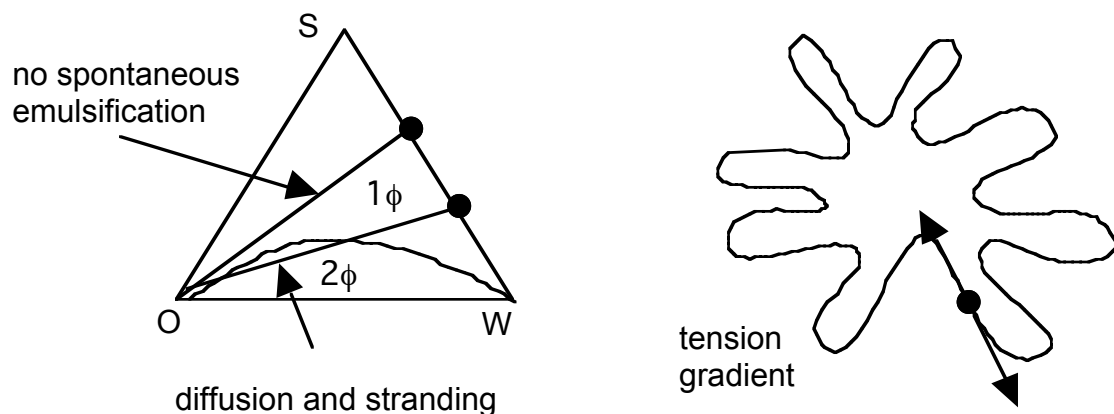


Figure 9. Spontaneous emulsification depends of the exact path followed by the system.

Third, it is conjectured by some authors that the tension can become negative at least in a transient way, but it is still the matter of controversy, as discussed recently. (43)

It is worth remarking than in a recent review on spontaneous emulsification (43) some new mechanisms are reported and discussed, such as drop or liquid crystal explosion, which is related to intense instabilities driven by concentration and tension gradients. As a matter of fact, it is worth pointing out that the effect is even stronger when the tension is very low.

CONCLUSION

There are obviously many ways to make an emulsion with a very little amount of mechanical energy. However none is as straightforward that the brute force method in which the process variables can be controlled easily.

In spite of that, a lot of near-zero energy emulsification process are carried out in practice and it is believed that this trends will continue as the main features of slightly out-of-equilibrium or far-from-equilibrium mechanism are understood.

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