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# 4 Emulsion Phase Inversion Phenomena

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## 4.1 INTRODUCTION

Emulsions are by definition dispersions of a liquid phase in another, which exhibit a certain stability, in most cases thanks to the presence of an adsorbed surfactant at interface. Hence, at least two immiscible liquid phases should be present to make an emulsion. As a consequence, the

phase behavior of the system made by the surfactant (S) and the two immiscible liquids, referred to as oil (O) and water (W) in a very general way, is of paramount importance [1].

As a general trend, it can be said that oil and water alone produce a two-phase system which leads to an unstable dispersion upon stirring. As surfactant is added to the oil/water binary, it tends to make the liquids more compatible, it reduces the interfacial tension and facilitates the emulsification, and often promotes a stabilization mechanism at a concentration level down to 0.3 wt% or even less. As far as the phase behavior is concerned, the added surfactant also tends to reduce the oil–water immiscibility gap, just as it would do with an increase in temperature, but this time through a so-called solubilization process associated with the presence of micelles and other self-association structures.

However, a large amount of surfactant, say 10 to 20%, is generally required to attain a critical point at which a single phase SOW system is obtained. As a consequence, it can be said that the surfactant concentration range over which two-phase systems are likely to occur and to produce reasonably stable emulsions is from less than 1 wt% up to 5 or 10 wt% and even more in some applications. This would be the range over which the phase behavior has to be scrutinized.

The emulsion type, either oil-in-water (O/W) or water-in-oil (W/O) or more complex morphologies, and therefore the type swap (so-called phase inversion), depends on many different variables, which can be classified in three categories: (1) field variables associated with the equilibrium state of the system, e.g., its phase behavior, also called **formulation** variables because they include the nature of the components as well as temperature and pressure; (2) **composition** variables which deal with quantities or proportions, for instance surfactant concentration and water/oil ratio; and (3) emulsification **protocol** characteristics which indicate the way the emulsion is made or modified, or how the formulation or composition are changed as a function of time or space.

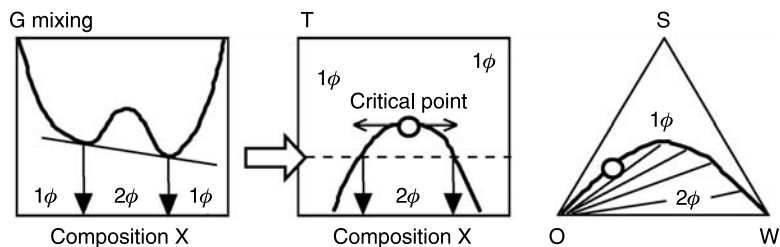
The attainment of an emulsion with given properties is a very difficult practical problem which often requires, firstly, a step by step disaggregation of the current information on the phenomena involved. This is the approach presented in the following section sequence: phase behavior of SOW systems at equilibrium, methods to reduce the number of independent variables and to pack them into a generalized formulation concept, emulsion types, standard inversion, and dynamic processes.

## 4.2 PHASE BEHAVIOR

Phase behavior is an equilibrium thermodynamic property which depends on the formulation variables, i.e., the nature of the different components, plus temperature and pressure. Since surfactants are amphiphilic substances with an affinity toward both water and oil, at high surfactant concentration the system usually exhibits a single phase behavior, but by dilution either by water, oil, or both, it splits in a two-phase behavior system, which is the proper kind to generate an emulsion upon stirring. Hence the boundary between the single and multiphase regions is of primary importance in practice, because it sets the limits to make emulsions.

### 4.2.1 TWO-PHASE BEHAVIOR

In what follows, the two immiscible phases are referred to as water (W) for the polar one, generally an aqueous solution, and oil (O) for the less polar or apolar one, which can be any non-water-soluble organic liquid from an n-alkane to a natural triglyceride or a polydimethyl siloxane polymer. In most cases, one of these phases contains the majority of the surfactant, as



**FIGURE 4.1** Phase behavior of binary and ternary systems.

a molecular solution or as a microstructure such as a micellar solution, a microemulsion, or a liquid crystal.

In the simplest case of mismatched mixture, i.e., a binary, the free energy function  $G$  (composition  $X$ ) exhibits at constant temperature and pressure two minima and the splitting between the corresponding phases reduces the overall free energy of the system according to the Maxwell convention (Figure 4.1, left graph).

The situation is often similar in a SOW ternary, at least at low surfactant concentration, e.g., the system splits into two phases, one of them closer to pure  $W$  and the other closer to pure  $O$ . The phase diagram of a binary versus temperature (Figure 4.1, center) has essentially the same aspect that the SOW ternary diagram (Figure 4.1, right), which means that the surfactant plays the same role as temperature in making the components compatible. As the amount of surfactant increases, the compatibility gap diminishes and the conjugate phase compositions get closer, until they merge at a so-called critical point, beyond which the system is monophasic. In a ternary SOW diagram the critical point is often located on one side because the tie lines are slanted, as in Figure 4.1's triangular plot indicating that the surfactant preferentially partition in one of the conjugate phases.

There are essentially two cases of two-phase behavior with SOW systems, so-called Winsor I and Winsor II (abbreviated  $W\ I$  and  $W\ II$  in Figure 4.3), [2] which correspond respectively to a surfactant-rich water phase in equilibrium with a surfactant-depleted oil phase or vice versa. In  $W\ I$  (respectively  $W\ II$ ) case the critical point (white circle in Figure 4.1, right graph) is located close to the  $W$  (respectively  $O$ ) vertex.

Two-phase systems would lead to different dispersion morphologies, the simplest ones being the so-called  $O/W$  and  $W/O$  types in which one of the phases is dispersed as drops in the other, which is continuous. More intricate morphologies like the so-called multiple emulsions, i.e., emulsion in emulsion, could theoretically become very complex although in practice there are essentially two cases, i.e.,  $o/W/O$  and  $w/O/W$ , in which the first lower case letter indicates the phase dispersed as droplets in drops, the next letter indicates the drop phase, and the last one the continuous phase. Multiple emulsions could be somehow considered as a mixture of both types of emulsions, and as such they might be found as intermediate morphology in inversion processes, as will be discussed later.

#### 4.2.2 THREE-PHASE BEHAVIOR

Three-phase behavior (Figure 4.2) is allowed by the phase rule for a true SOW ternary system, and any higher order multicomponent system, but it is very unlikely to happen by chance. However, it has to be considered in some detail because it is important as an intermediate between the two classical biphasic cases.



to M and thus a microemulsion, and may be called the “oil” phase since it is in equilibrium with W. Similarly, in the left two-phase lobe the splitting is between essentially pure oil O and a microemulsion (B) which may be called the “water” phase since it is in equilibrium with O. The paradox is that a look at the phase diagram confirms that “oil” A contains more water than “water” B. Hence, it is better to refer to this type of phase as a microemulsion and to label it as M, or Om and Wm as some authors do.

The bicontinuous structure of M means that its conductivity can be intermediate between those of water and oil, and this would make it very difficult to determine the dispersed system morphology type from conductivity measurements [11]. However, it does not matter very much, because in practice, three-phase W III systems result in extremely unstable emulsions, which do not persist more than a few minutes.

On the other hand, the extremely low interfacial tension associated with W III phase behavior probably generates a dispersed phase which is not made of drops but rather of threads which elongate in the direction of flow as soon as the system is submitted to shear [12]. This is essentially what was observed 30 years ago in enhanced oil recovery (EOR) methods by surfactant flooding [13].

## 4.2.3 VARIABLES THAT INFLUENCE THE PHASE BEHAVIOR

### 4.2.3.1 Variable Types

Extensive studies associated with the EOR research drive in the 1970s showed that the phase behavior of SOW systems depends on many different parameters [3]. The typical equation for chemical potential of a surfactant ( $\mu = \mu^* + RT \ln X$ ) indicates that it depends on intensive variables or field variables, so-called **formulation** variables, which are independent of quantities, i.e., the nature of the different components (at least SOW), as well as temperature and pressure, which all influence the standard chemical potential  $\mu^*$  of a surfactant in any phase.

There are also the extensive **composition** variables, like concentrations or proportions, which in the case of a ternary (three components, thus two independent composition variables) are generally taken as the surfactant concentration (represented here by X) and the water/oil ratio WOR.

### 4.2.3.2 Generalized Formulation

In real systems that additionally contain electrolytes and alcohols, the number of degrees of freedom is appalling. However, the extensive research work carried out to rationalize the observed findings has shown that the formulation effect can be gathered in a single parameter, either theoretical such as Winsor's R ratio of interaction energies [2,3] or experimental such as Shinoda's phase inversion temperature (PIT) [14], whose value command the phase behavior. This generalized formulation has been numerically expressed as the surfactant affinity difference (SAD) [9,10], which takes into account the numerical contribution of all formulation variables, including temperature and eventually pressure [15,16].

These are defined from thermodynamic equilibrium of the surfactant in the oil and water phases, using concentrations instead of activities, provided that the concentrations are low enough so that there is no micelle or other self-assembly structure [17].

$$\mu^O = \mu^{*O} + RT \ln[C_S^O/C^{*O}] = \mu^W = \mu^{*W} + RT \ln[C_S^W/C^{*W}] \quad (4.3)$$

$$\text{SAD} = \Delta\mu_{O \rightarrow W}^* = \mu^{*W} - \mu^{*O} = RT \ln[K_{OW}/K_{OW}^*] = RT \ln K_{OW} - RT \ln K_{OW}^* \quad (4.4)$$

where the  $\mu^*$  indicates the standard chemical potential of the surfactant in some reference state (superscript  $*$ ) at which the dimensionless concentration  $C/C^*$  is unity, with  $C^*$  to be defined later.  $K_{ow}$  is the partitioning coefficient of the surfactant between oil and water, and  $K_{ow}^*$  its value in the reference state. If the affinity is defined as the negative of the chemical potential of the surfactant in the reference state, the surfactant affinity difference (SAD) is the variation of chemical potential when a molecule of surfactant is transferred from oil to water, and it can be estimated from the measurement of the partitioning coefficient according to Equation 4.4. For the sake of simplicity the reference state is taken at the Winsor III three-phase behavior, so-called **optimum formulation** because it corresponds to the best formulation to displace petroleum in enhanced oil recovery techniques, and the surfactant concentrations in excess O and W phases, which are at or below the CMC, are taken as reference  $C^{*O}$  and  $C^{*W}$ , and  $K_{ow}^* = C^{*O}/C^{*W}$ . For ionic surfactants  $K_{ow}^*$  is essentially unity at optimum formulation [18] so that  $SAD = RT \ln K_{ow}$ .

However, this is not the general case and  $K^*$  may be different from unity, in particular if the surfactant CMC is quite different in water and oil, as for ethoxylated alkylphenol for which  $K_{ow}^*$  has been found to be about 30 [19–21].

Equation 4.4 has been recently expressed as a dimensionless parameter so-called hydrophilic–lipophilic deviation (HLD), some kind of “system HLB,” which measures the departure from optimum formulation [22,23]:

$$HLD = SAD/RT = (1/RT)\Delta\mu_{O \rightarrow W}^* = \ln K_{ow} - \ln K_{ow}^* \quad (4.5)$$

It was found that HLD may be written as a linear form of the different formulation variables, with essentially the same expression as the empirical equations proposed 25 years ago to attain the optimum formulation to produce an ultra-low tension for enhanced oil recovery. For ionic surfactant systems [18,24]:

$$HLD = \ln S - K \text{ ACN} + f(A) - \sigma + a_T (T-25) \quad (4.6)$$

and for ethoxylated nonionic systems [25]:

$$HLD = \alpha - \text{EON} - k \text{ ACN} + b S + \phi(A) - c_T (T-25) \quad (4.7)$$

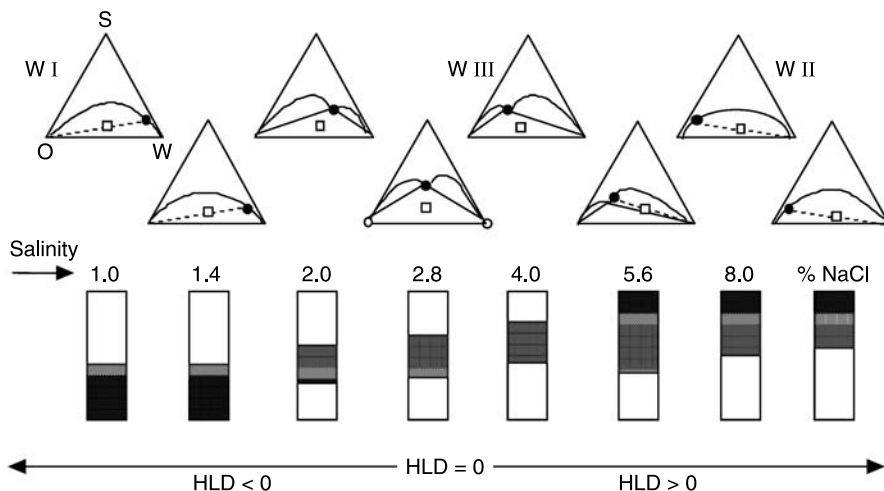
These linear expressions have been found to provide quite a good match [26], with the exception of the temperature term for ethoxylated nonionic systems, for which the effect is more complex than the linear variation proportional to  $c_T$  [22]. More detailed information on these correlations and their extension to many systems may be found in the literature [9–10,27–30].

$HLD = 0$  is equivalent to the case of unit Winsor’s R ratio or of a temperature equal to Shinoda’s PIT. In practice the formulation studies are carried out by changing a single formulation variable at the time, which is often the salinity of the aqueous phase for ionic systems, and the degree of ethoxylation (EON) or the temperature (T) for ethoxylated nonionics.

When the scanned variable in an ionic surfactant system is for instance the salinity of the aqueous phase (see Figure 4.3) at all other variables constant, there is a certain value of the salinity, so-called optimum salinity  $S^*$ , which correspond to W III phase behavior:

$$HLD = \ln S^* - K \text{ ACN} + f(A) - \sigma + a_T (T-25) = 0 \quad (4.8)$$

At salinity lower (respectively higher) than  $S^*$ ,  $HLD < 0$  (respectively  $> 0$ ) and a W I (respectively II) phase behavior is observed. At  $HLD = 0$  a W III phase behavior is found.



**FIGURE 4.3** Phase behavior of a SOW system along a formulation (salinity) scan.

If the scanned variable is the temperature with an ethoxylated nonionic system, then W III phase behavior is attained at a so-called optimum temperature  $T^*$ :

$$\text{HLD} = \alpha - \text{EON} - k \text{ ACN} + b S + \phi(A) - c_T (T^* - 25) = 0 \quad (4.9)$$

At temperature lower (respectively higher) than  $T^*$ ,  $\text{HLD} < 0$  (respectively  $> 0$ ) and a Winsor type I (respectively II) phase behavior is observed, i.e.,  $T^*$  is the PIT or the HLB-temperature of the system.

The advantage of HLD over any specific variable is that it gathers the numerical contributions of all formulation variables, and allows the calculation of compensation effects, a trade-off between variables, and the combined effects due to the concomitant variations of two or more variables.

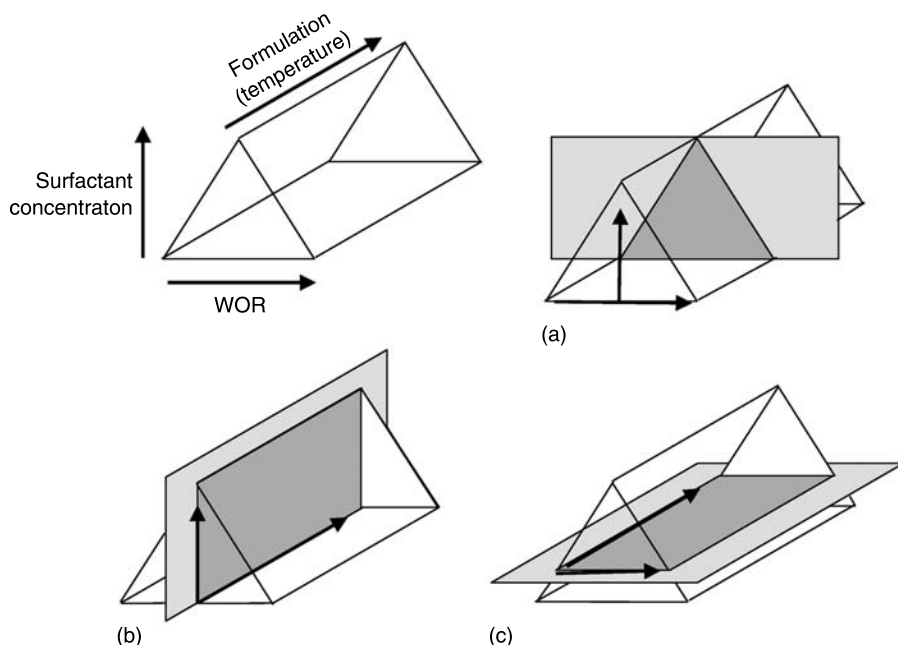
HLD is thus a single generalized formulation variable, whose value is associated with the phase behavior of the SOW system at equilibrium, and whose meaning is related to a free energy of transfer of a surfactant molecule from one phase to the other, thus having the same physicochemical meaning whatever the specific values of the variables.

In practice the use of HLD represents quite a reduction in the degrees of freedom, and for the most simple SOW ternary there are now **only** three independent variables to describe the system at equilibrium:

- HLD generalized formulation (nature of components plus  $T$  and  $P$ )
- Surfactant concentration
- Water/oil composition, e.g., WOR

#### 4.2.4 2D/3D REPRESENTATIONS OF PHASE BEHAVIOR

The handling of three independent variables implies a three-dimensional (3D) representation of the phase behavior and emulsion properties. This is not easy to deal with even in the simplest



**FIGURE 4.4** Different 2D cuts in the 3D formulation-WOR-surfactant concentration space.

case, and in real cases it can be unmanageable. Hence it is generally more convenient to use a two-dimensional (2D) cut of the 3D space.

There are three kinds of 2D cuts, illustrated in Figure 4.4:

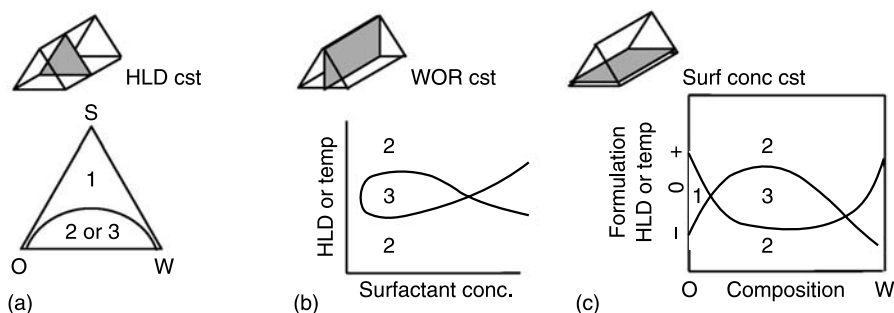
- At constant formulation it is a triangular phase diagram (a) with two independent composition variables, e.g., surfactant concentration and WOR.
- At constant WOR it is a surfactant concentration-formulation (or temperature) so-called gamma and fish diagram (b) for reasons that will become clear later.
- At constant surfactant concentration, it is the formulation (or T)-WOR diagram (c), so-called F-WOR or HLD-WOR.

All these diagrams have been used in practice to represent the phase behavior and emulsion properties, and each of them has some advantages and some drawbacks, and the selection of the best 2D representation depends on what matters more in each case.

Surfactant concentration is the variable which determines whether there is a single or a multiple phase behavior case. Since emulsions are multiple phase systems, surfactant concentration should be low enough for the system to split in two phases. Moreover, the surfactant concentration has in practice a higher limit in accordance to cost, toxicity, or environmental constraints. It has also a lower limit which is associated with a minimum performance. As a consequence, the surfactant concentration is often fixed in practice and little variation is allowed. Accordingly, the most significant of the two composition variables is often the WO proportion expressed as WOR or water or oil fraction.

The generalized formulation dictates the phase behavior, which can be seen as a preference of the surfactant for O or W. Nevertheless, the WO composition might also dictate a preference





**FIGURE 4.5** Phase behavior in the different 2D representations.

toward the phase which is present in higher proportion; indeed, if the WO proportion is 1% W and 99% O it might be difficult for all the surfactant to migrate to the W phase in spite of a strong affinity. Hence the WOR is the second most important variable, and the F-WOR diagram at constant surfactant concentration, i.e., (c) in Figure 4.4, is often the most useful in practice, as will be shown in the following.

Figure 4.5 shows the phase behavior maps in all types of 2D diagrams. The triangular diagram (a) allows the effect of surfactant concentration and WOR to be dealt with, but not the effect of formulation, nor temperature. As seen previously, depending on the value of the generalized formulation HLD, there are three basic types of diagrams, so-called Winsor types I, II, or III, but in practice real phase diagrams are much more complex, particularly if liquid crystals are likely to exist [31].

The center diagram (b) allows the combined effect of formulation (including temperature) and surfactant concentration to be dealt with [32]. The effect of the WOR is not easy to handle in this type of diagram because it results in an apparent change in formulation, e.g., a twisting of the fish, and there are very few detailed reports in the literature [33]. On the contrary this diagram is quite useful to study the temperature effect, in particular on the phase inversion, which depends on the crossing of the single phase region (1) and the eventual presence of liquid crystal phases in it [34,35].

Finally, the right diagram (c), sometimes called X-cut, allows the handling of problems in which the formulation (including temperature) and WOR are of paramount importance, which is the case of the different instances of emulsion inversion. Therefore, it will be the diagram chosen for dealing with the topic of the present chapter.

## 4.3 STANDARD INVERSION BOUNDARY

### 4.3.1 WHAT IS THE STANDARD INVERSION?

An emulsion is a system which is out of equilibrium from the point of view of surface area and its free energy can be reduced by shrinking the surface area, i.e., by the coalescence of the drops. If the two phases exhibit a difference in chemical potential due for instance to a difference in some concentration, a non-equilibrium situation of physicochemical nature arises, whose effects often drive a mass transfer between phases and are much more difficult to ascertain. Such transfer, particularly of surfactant or other amphiphilic molecules, can produce very complex phenomena

like spontaneous emulsification, which considerably impairs the interpretation of the experimental results. As a matter of fact, it was only when emulsification was systematically carried out from pre-equilibrated systems that it was possible to repeat experiments and to fully organize the phenomenology relative to emulsion inversion [36].

These complex cases will be dealt with briefly at the end of this chapter. In the present and following sections and unless otherwise specified, the SOW system is assumed to be the first left to equilibrate for some time, e.g., often no more than 24 to 48 h, so that the surfactant and co-surfactant partition into phases and, eventually, mesophases are formed. In such cases the phase behavior determined on the equilibrated system is unique and may be related with the basic Winsor cases (W I, II, III, IV), eventually with the additional presence of a mesophase generally noted as liquid crystal LC.

If the pre-equilibration is achieved, it is generally accepted that the formulation is able to favor one or other curvature, hence one type of morphology, when the emulsification energy is supplied. This trend has been presented in different ways such as the empirical Bancroft's rule [37,38], the intuitive Langmuir's wedge theory [39], the mechanical dual tension model [40], Davies' competing emulsions coalescence [41], or more recent and sophisticated approaches by Ivanov [42] or Kabalnov [43].

The second most important parameter to influence emulsion type has been found to be the WOR, and its effect, sometimes referred to as Ostwald's rule [44,45], has to be combined with the formulation rule.

In experimental practice, an equilibrated SOW system is emulsified according to a standard typical procedure, e.g., a turbulent stirring during 30 sec or 10 min in a mixing device, and its electrolytical conductivity is measured. Since the aqueous phase contains some electrolyte in most practical cases, the emulsion would conduct electricity only if the aqueous phase is continuous. From the conductivity value, the morphologies O/W or W/O could be established. Multiple emulsion and even more complex morphologies may be deduced from conductivity measurements, though not always in a simple way [11].

The standard inversion line is by definition the frontier which separates the W-external from the O-external emulsions. Since multiple emulsions may have an intermediate conductivity as well as bicontinuous microemulsions and LC, a conductivity cut-off has to be specified, sometimes with some difficulty in marginal situations.

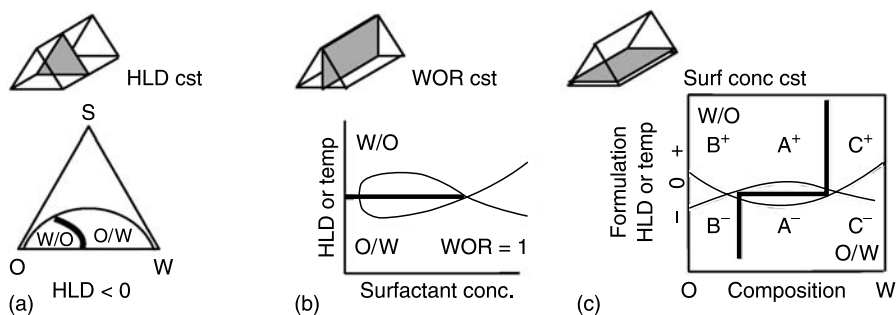
### 4.3.2 BIDIMENSIONAL MAPPING OF EMULSION TYPE

The standard inversion line can be drawn in the two-phase regions of any of the three types of diagrams shown in Figure 4.5, as indicated for typical cases in Figure 4.6. Some authors have used the triangular diagram whereas others, particularly those working with temperature as a formulation variable, have reported the fish type diagram [46–51].

However, the most convenient diagram is the formulation (or temperature) versus WOR diagram (c), because it deals with the two most significant variables as far as emulsion type is concerned. As will be seen later there is an additional and quite powerful reason, which is that the effect of all other variables is very simple and easy to systematize on this kind of map.

This diagram was introduced for studying nonionic systems in relation with the PIT concept [52] and then was systematically used with any of the formulation variables in the past twenty years [34,36,53–60].

To sum up the basic features of this F-WOR diagram, as found in the literature, it can be said that the formulation effect dominates unless the WO composition is too unequal, e.g., there is more than 70% of water or oil. The concept of disproportionate OW amounts might apply not



**FIGURE 4.6** Emulsion type mapping in the different 2D representations.

only to the system as a whole but also to the local situation and hence could depend on the way the emulsification is carried out, the shape of the vessel or stirrer, the position of the impeller etc. The excess of one phase over the other is essentially the same intuitive argument as Ostwald's rule related to the maximum packing (74% for most dense packing of equal spheres).

Generally speaking it can be said that the phase in smaller amount is more likely to be dispersed in the other than the reverse. It means that at high W (respectively O) content O/W (respectively W/O) emulsions are produced. In each diagram the region with high W and high O content, of more than 70%, exhibits a WOR-controlled morphology, whereas the formulation, i.e., the bending tendency, determines the type when the WOR is not extreme, e.g., from 30 to 70% of one phase.

Formulation-WOR maps have essentially the same aspects, whatever the formulation variable, e.g., salinity of the aqueous phase, surfactant hydrophilicity, temperature, pH, oil type etc. As seen in Figure 4.6(c) the standard inversion frontier (bold) exhibits an almost horizontal branch, which follows the optimum formulation ( $HLD = 0$ ) line in the central region of the map (from typically 30 to 70% of O or W), and two almost vertical branches located at about 30% W in the  $HLD > 0$  region and at about 30% O in the  $HLD < 0$  region. This results in a step-like shape of the inversion frontier illustrated in Figure 4.6(c) in which six regions are labeled: A, B, C to indicate the WOR, with + or - sign according to the HLD value.

The regions where Bancroft's rule applies, i.e., where the emulsion type is in accordance with the formulation (A+, B+ and A-, C-), are called **normal**, whereas the two regions in which the WOR imposes the morphology (C+ and B-) are called **abnormal** [36]. Abnormal regions are often associated with the presence of multiple morphologies, i.e. w/O/W in C+ and o/W/O in B-, where the lower case letter indicates the droplet phase dispersed in drops. Abnormal emulsions thus consist of a combination of both morphologies: the most internal emulsion (droplets in drops) follows Bancroft's rule and is thus normal, whereas the most external one is abnormal. It seems that this dual emulsion system is a way to settle the conflict between formulation and WOR effects.

In some cases, related to the fractionation of surfactant mixtures, the optimum formulation line (at the center of the three-phase behavior region) is slanted, and the "horizontal" branch of the inversion line essentially follows it and becomes slanted too [54,59]. In some other cases the vertical lines are not exactly vertical. However, if the formulation is taken as the deviation to three-phase behavior, i.e., the actual HLD value at each WOR, then the plot takes a stepwise shape, and this is the general phenomenology for essentially all known systems, even with very viscous resins [61–63] or very nonviscous "oils" such as supercritical carbon dioxide [64,65].

### 4.3.3 EFFECT OF OTHER VARIABLES

Many other variables have been reported to influence the emulsification process. For instance, the phase viscosity is an important factor since it is directly related to the efficiency of the stirring process. It is well known that if the phase viscosity ratio is very different from unity, the emulsification process efficiency could be considerably altered [66]. Because it can transfer momentum, the most viscous fluid tends to be the one to be put into motion under shear, and thus to become the dispersed phase, if no stronger effect prevails. As a consequence, a change in phase viscosity ratio can produce a change in emulsion standard inversion line, actually a shift in one of the vertical branches. The general trend when the viscosity of one of the phase is increased is that the central region corresponding to normal emulsions A+ (respectively A−), where the increased viscosity phase is the external phase, i.e., O (respectively W) in A+ (respectively A−), tends to shrink at the expense of the adjacent abnormal emulsion C+ (respectively B−) region [36,67–69].

Other variables have been shown to influence the position of the inversion line. For instance in many applications the surfactant concentration may vary in some range, and may be increased, in particular to produce a finer or more stable emulsion [70,71].

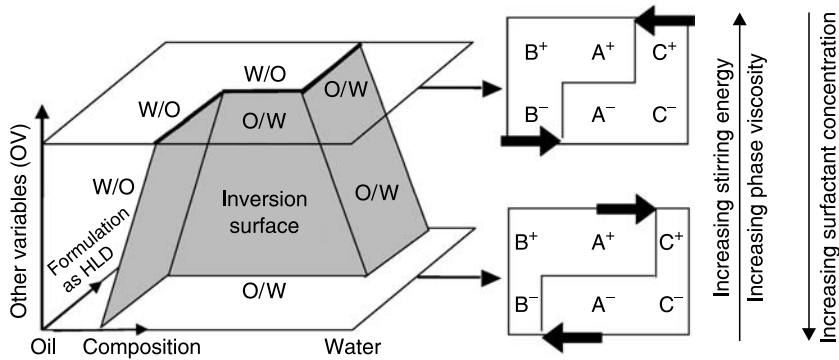
Hence, more surfactant should logically be associated with more command of the formulation variable, i.e., a wider A region range in a formulation-WOR map. This effect can be analyzed as well in a triangular diagram, in which it is obvious that an increase in surfactant concentration reduces the gap between the phases, until a limit, i.e., the critical point, is reached and above which there is a single phase and no emulsion. Such critical points (plait point in the triangular diagram in Figure 4.1, right graph) are on one side and at a low surfactant concentration in W I and W II types. In formulation-WOR diagrams the surfactant concentration changes the overlapping of the W I and W II regions which produces the W III region (see Figures 4.5 and 4.6). At high surfactant concentration the near optimum formulation region is associated with a single phase W IV behavior, a situation which may be used to produce phase inversion such as the PIT method, but implies a high surfactant cost.

Another parameter able to influence the standard inversion line is the stirring energy. The few available studies [72–75] show that an increased stirring energy tends to reduce the domain where formulation dominates, i.e., the A region. In the extreme extrapolated infinite stirring, the mixing is likely to dominate, because the formulation effect should fade as in absence of surfactant, and hence the phase in lesser amount will be dispersed in the phase of higher proportion. This is why the inversion line tends to the center ( $WOR = 1$ ) when stirring is increased in the triangular and F-WOR diagram. This may be quite important in practice, as for instance in the case of heavy crude oil fuel emulsions which contain 70% or more internal oil phase stabilized by a hydrophilic surfactant [76,77].

The representative point of these normal O/W emulsions are located in the A− region of the map close to the vertical branch of the inversion line. If such emulsions are pumped with a high shear device, e.g., a centrifugal pump, they are found to invert and this is due to the shift of the vertical branch toward the center of the map so that the representative point of the emulsion is now in the B− region.

The initial position of the impeller with respect to the original oil–water interface might result in a shift of the vertical branches of the inversion frontier which is easily related with a local WOR concept discussed elsewhere [78].

The effect of these extra variables (phase viscosity, stirring energy, surfactant concentration) can be rendered in any of the three types of 2D diagrams. First a diagram is experimentally built



**FIGURE 4.7** 3D mapping of emulsion type.

at a constant value of the third variable, then it is built again at another constant value, and so forth to produce a stacking of diagrams.

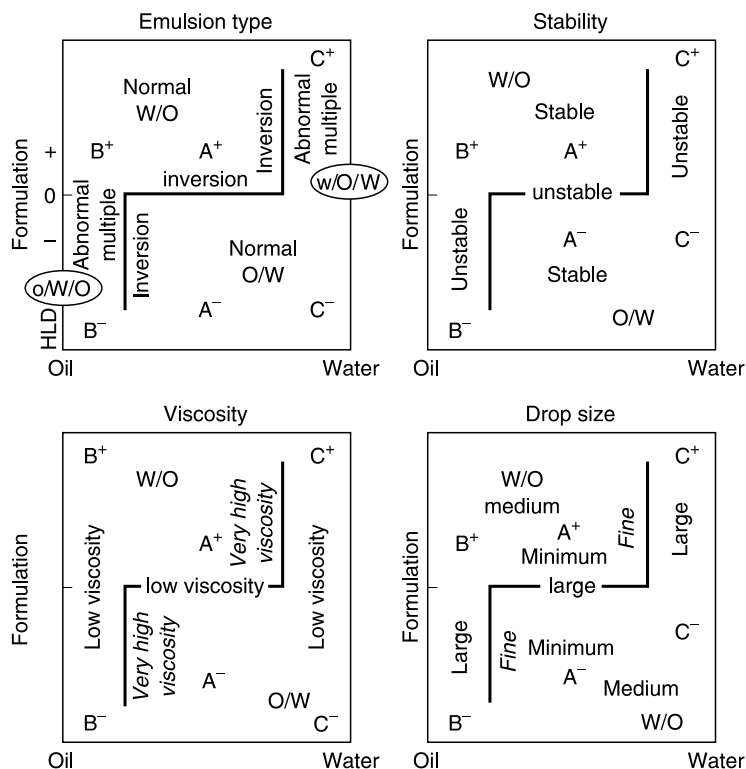
This generally produces a 3D diagram in which the extra variable is represented in the third dimension. This 3D diagram is particularly simple in the F-WOR plot in which the standard inversion line becomes a surface whose shape is illustrated in Figure 4.7.

It is worth remarking that a characteristic of the generalized formulation-WOR 2D map is that the central branch of the standard inversion frontier is unchanged by the variation of any of the other variables (indicated OV in Figure 4.7), and is always located at  $HLD = 0$ . As a consequence, the effect of any other variable is essentially to shift the vertical branches of the standard inversion line one way or the other, i.e., to increase or decrease the normal emulsion A range (right diagrams in Figure 4.7). This is quite advantageous because the qualitative effect of all other variables can be rendered by moving upward or downward in Figure 4.7's left graph, whose third axis (OV) accounts for the change, individual or combined, of other variables.

Hence, it can be said that all cases can be qualitatively treated in a 3D map in which the inversion surface exhibits the typical shape indicated in Figure 4.7, left graph, with the three axes representing (1) a generalized formulation variable such as HLD, (2) a WO composition variable, and (3) an “other effects” generalized variable OV. Although it is still an approximation, it is quite an improvement because it allows interpretations and elaborate predictions to be carried out, in particular about the relative position of the system with respect to the inversion. From what is currently known this simplification does not happen with the other diagram types, and this is why it is convenient to discuss dynamic inversion issues on the 2D and 3D diagrams involving HLD-WOR-OV.

### 4.3.4 IMPORTANCE OF 2D (HLD-WOR) AND 3D (HLD-WOR-OV) MAPS

The previous F-WOR 2D/3D maps indicating the location of the standard inversion frontier not only delimit the regions where one type of emulsion or the other is attained, but also allow the mapping of other emulsion properties such as stability, viscosity, and drop size. The typical property patterns associated with the different regions are beyond the scope of the present chapter and are thus only schematically indicated in Figure 4.8. More details can be found elsewhere [54,79,80].



**FIGURE 4.8** Emulsion property maps in a 2D formulation-WOR diagram. (Reprinted with permission from J.L. Salager. In: A. Chattopadhyay and K.L. Mittal, eds. *Surfactants in Solution*. New York: Marcel Dekker, 1996, pp. 261–295. Copyright (1996) Dekker.)

As far as the following discussion on emulsion inversion is concerned it is worth remarking here a few features exhibited by Figure 4.8 maps, which are determinants to understanding the phenomenology of dynamics. First of all, it should be noted that emulsions are very unstable near optimum formulation [43,81–84].

It was found that in all cases they coalesce very quickly close to  $HLD = 0$ , and their persistence may be shorter than the timescale of any manipulation or property measurement. Since optimum formulation is also associated with a very low interfacial tension which favors drop breaking, there are two opposite trends: rapid breakage and rapid coalescence which favor quick changes. It has been shown recently [85,86] that the combination of opposite tendencies tends to produce a minimum drop size on both sides of optimum formulation, i.e., at HLD slightly positive and HLD slightly negative, as indicated in Figure 4.8's drop size map.

On the other hand, it is worth noting that the high internal phase emulsions formed in each A region close to the vertical branch exhibit a high relative viscosity and in many cases pseudoplastic or viscoelastic rheology, which are favorable conditions for the formation of fine and monodispersed emulsions [87–89].

The different maps shown in Figure 4.7 confirm that the inversion frontier is of paramount importance because it delimits the regions where specific properties are attained. Hence, an eventual shift or alteration of the inversion frontier would be accompanied by a modification

of the property map, and thus can be used as a tool to custom-made emulsions. Up to now, it has been seen that “other” variables such as stirring energy, surfactant concentration, or phase viscosity could alter the position of the standard inversion frontier. In what follows, a new way to set the inversion frontier is discussed. It is associated with the displacement of the representative point of the emulsion in the 2D and 3D maps until the emulsion morphology changes, in a so-called dynamic inversion.

## 4.4 DYNAMIC INVERSION

### 4.4.1 EXPERIMENTAL DESCRIPTION OF DYNAMIC INVERSION

The standard inversion frontier indicated in Figures 4.6 and 4.7 is the limit between the regions where the HLD-WOR-OV conditions result upon stirring the pre-equilibrated SOW system, in a W/O or O/W emulsion in  $A+/B+$  or  $A-/C-$  regions, and eventually in a multiple morphology in  $C+/B-$  zones.

In a dynamic experiment one or more of the variables (HLD, WOR, or OV) is altered as time elapses, e.g., temperature is changed or oil is added, so that the representative point of the emulsion moves in the map. At some time the representative point of the emulsion might pass from one side to the other of the standard inversion frontier, and the question is to know whether the emulsion morphology changes, and eventually how. The answer is not simple and depends on many factors. In some cases the morphology change takes place instantly, as soon as the representative point trespasses the frontier, whereas in other cases, the original morphology is retained for some time, eventually for a long time, and it is said that the inversion is delayed, as if the emulsion were keeping the “memory” of its type.

Although dynamic inversion phenomena can be followed in the three types of maps, it has been mostly discussed in the HLD-WOR 2D map, in which the coordinates correspond to the two most important variables, as far as the phenomenon is concerned. In other maps (formulation–surfactant concentration or surfactant concentration–WOR) only one of the variables is able to trigger the dynamic inversion, while the other one (surfactant concentration) produces the formation of the emulsion through another mechanism similar to a nucleation process which will be discussed in the PIT method section.

Figure 4.9 indicates several paths of change in the HLD-WOR 2D map, most of them crossing the standard inversion frontier indicated as a bold dashed line. All these paths correspond to a change in variable value, such as the formulation (e.g., the salinity of the aqueous phase or the

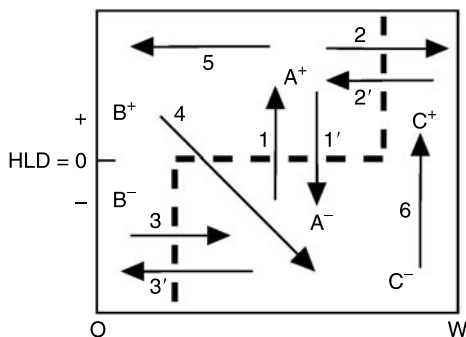


FIGURE 4.9 Paths of change in a formulation-WOR 2D map.

temperature), or the water/oil composition (e.g., by addition of oil or water), while the system is kept under stirring according to a specific procedure, whose characteristics are nevertheless determinant as far as the dynamic inversion is concerned.

For instance, path 1 could correspond to an increase in salinity of the aqueous phase of an anionic system, or an increase in temperature of a polyethoxylated nonionic system, at (essentially) constant WOR and surfactant concentration. On the other hand, path 2 could be representative of the addition of water to a W/O emulsion, whereas path 4 implies two concomitant changes, e.g., adding cold water to a nonionic W/O emulsion.

Paths like 5 and 6 do not cross the standard inversion line, and are not expected to result in an inversion, provided that all other variables are kept constant. However, the emulsion properties might be altered quite a lot to accommodate to the changes indicated in Figure 4.8 maps. For instance, along path 5 the W/O emulsion is “diluted” and its relative viscosity is expected to decrease, and along path 6 a O/W emulsion is likely to become a multiple w/O/W emulsion in which the O/W external emulsion would coalesce quickly.

The 1–1' (respectively 2–2' or 3–3') crossing of the horizontal (respectively vertical) branch of the inversion line would produce, if it occurs, a so-called **transitional** (respectively **catastrophic**) dynamic inversion, whereas a crossing like path 4 would be called a combined process. The labels come from the modeling of the inversion process by a catastrophe theory model, as discussed later.

#### 4.4.2 TRANSITIONAL INVERSION

Transitional inversion corresponds to a change in HLD at all other variables held constant, including WOR and surfactant concentration.

Historically, the first transitional inversion was reported by Shinoda and collaborators [14] in the 1960s when they introduced the concept of phase inversion temperature (PIT), as an improvement over the cloud point temperature and the HLB, and an intent to numerically describe a formulation concept. The phase inversion temperature was initially the temperature at which an emulsion containing a polyethoxylated nonionic surfactant switches from O/W to W/O. Afterwards, it was assimilated into the temperature at which the affinity of the surfactant changes from hydrophilic to lipophilic, an essentially coincident concept which was later relabeled HLB-temperature. The fact is that in most cases of temperature scans, the emulsion inversion takes place at optimum formulation, which is in this case an optimum temperature, and has been labeled  $T^*$  in Equation 4.10 when  $HLD = 0$ , and is called PIT in Equation 4.11, which is actually the same expression.

$$HLD = \alpha - EON - k ACN + b S + \phi(A) - c_T (T^*25) \quad (4.10)$$

$$(PIT - 25) = [\alpha - EON - k ACN + bS + \phi(A)]/c_T \quad (4.11)$$

Equation 4.11 indicates that PIT is a property characteristic of the SOW system. It is seen that it depends on the surfactant head and tail groups, the nature of the oil, the salinity of the aqueous phase, and alcohol type and concentration, as reported from experimental evidence by Shinoda and collaborators [90]. A straightforward calculation shows that the deviation from PIT is an expression of HLD according to the following relation, where  $c_T$  is not really a constant, but a weak function of the ethoxylation degree and temperature [22]:

$$HLD = c_T(T - PIT) \quad (4.12)$$

Temperature is a handy variable in the sense that it is fully reversible, and if evaporation is controlled, it can be changed at will at all other variables held constant. However, temperature



affects essentially all interactions and it is sometimes difficult to interpret the results in a simple way. Moreover, temperature exhibits a strong formulation effect for polyethoxylated nonionic surfactants, but much less for ionic or polyol-based nonionic ones like glycosides, for which other scanning variables are more helpful.

HLD may be changed by varying any other variable in Equation 4.10, whenever it is practically feasible to do so at constant WOR and surfactant concentration. Since a change in any of the other variables, but temperature, implies the addition or substitution of some substance, care has to be taken not to alter significantly the WOR and surfactant concentration, as well as other variables susceptible to alteration by a dilution process. In practice, high concentration solutions of surfactant or electrolytes are used not to significantly change the phase volumes. Alternatively, the added phases contain surfactant, oil, and water in constant amounts while the nature of some of them is changed, or the total system volume is kept constant by a suction device. It is worth noting that a slight change, say 20 to 30%, in WOR (around unity) or surfactant concentration (around 1 to 2 wt%) is generally not significant, and can be tolerated.

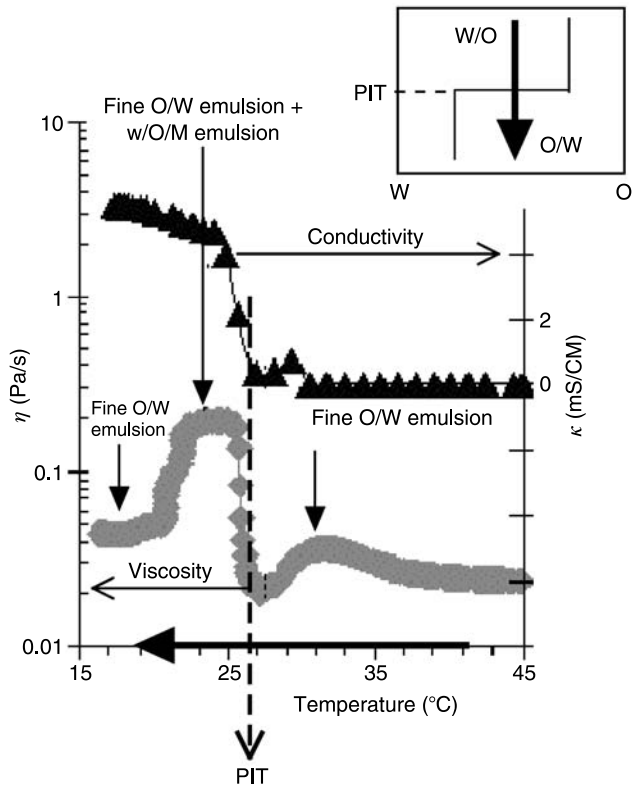
When the HLD is continuously changed along a path such as 1 or 1' in Figure 4.9 (near  $\text{WOR} = 1$ ) at constant surfactant concentration, and at a slow rate of change, the experience shows that the dynamic inversion takes place essentially at optimum formulation, i.e., at  $\text{HLD} = 0$ , whatever the variable used to produce the formulation variation. This is probably due to the fact that emulsions are very unstable near  $\text{HLD} = 0$ , so that any morphology would be destroyed quickly, while the morphology corresponding to the actual condition would be generated at once by the stirring, as if some constant renewal process were taking place. Consequently, a slight variation of formulation (including temperature) able to shift the sign of HLD would result in the inversion as indicated by the variation of emulsion conductivity and viscosity shown in Figure 4.10. The large variation of conductivity indicating inversion takes place at or close to  $\text{HLD} = 0$ , in the region associated with W III or W IV phase behavior [91]. In some cases an intermediate conductivity in this region could be interpreted as the formation of a dispersed system in which a bicontinuous microemulsion is the continuous phase.

The changes in emulsion viscosity at optimum formulation are associated with the change in morphology, and eventually in the emulsion internal phase ratio. The two viscosity maxima which appear in Figure 4.10 slightly above and slightly below PIT are related with the minimum drop size locations previously mentioned in Figure 4.8.

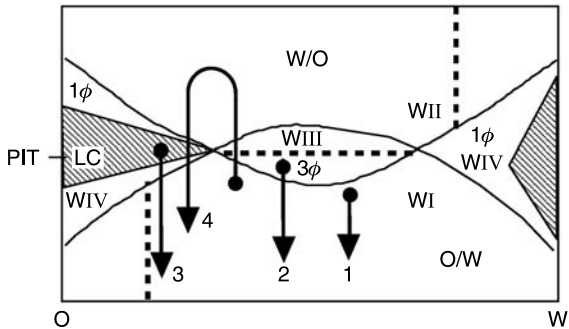
In some cases, the kinetics of morphology renewal and inversion might be slower than the formulation change, and a multiple emulsion resulting from some residual memory effect could occur just after trespassing  $\text{HLD} = 0$ . If the direction of change is appropriate, it is easily detected by a conductivity lower than expected for an O/W morphology and a viscosity higher than expected for the given WOR, as shown in Figure 4.10 from 26 to 23 °C [91].

These trends may be considered as quite general for a transitional inversion, whatever the scanned variation variable, with very few exceptions which will be discussed later.

This inversion resulting from a temperature scan has been used as an emulsification technique so-called PIT emulsification method [90,92,93]. This term is, however, misleading because the essence of the method is not the emulsion inversion in itself but the production of the finest drop emulsion at one of the two “best” locations on one side or the other of  $\text{HLD} = 0$  (see “minimum” in Figure 4.8 drop size map) and the preservation of this fine drop size by some thermal or physicochemical quench. Such a quench essentially consists of a quick change in temperature or formulation to move the representative point of the emulsion far away from the instability zone, i.e., some distance inside the A+ or A- region, according to path 1 in Figure 4.11. The starting point might also be in the W III region as indicated in path 2 in Figure 4.11.



**FIGURE 4.10** Changes in conductivity and viscosity along a transitional inversion. (Reprinted with permission from J. Allouche, E. Tyrode, V. Sadtler, L. Choplin, and J.L. Salager. *Langmuir* 20: 2134 (2004). Copyright (2004) American Chemical Society.)



**FIGURE 4.11** Path for PIT method of emulsification to produce an O/W morphology.

Another kind of quenching may be accomplished by the formation of a lamellar liquid crystal layer to encapsulate the droplets [94]. In practice, this happens not as an inversion but as a change from a W IV single phase system to a W I or W II one, with some residual structured layer at the drop interface. A single phase behavior at optimum formulation is associated with a high

surfactant concentration in the system or in one of the phases, and it is often easier to attain at WOR different from unity, in one of the W IV “triangles” located at  $HLD = 0$  on the O and W sides (shaded in Figure 4.11). Figure 4.11 illustrates the several paths (1, 2, and 3) in which fine emulsions are made according to the PIT method, but without actually exhibiting any inversion. In path 3 the LC structure is likely to encapsulate the droplets formed when the representative point enters the W I region. Path 4, which crosses the inversion zone twice, is often cited [95], but this back and forth displacement is not really needed since the fine emulsion is produced just after the second crossing through the liquid crystal zone. It is worth remarking that the kinetics of changing temperature is of utmost importance [96].

#### 4.4.3 CATASTROPHIC INVERSION

When the WOR is changed by addition of a phase under constant stirring, this results either in dilution or in an increase in internal phase content, the latter one being the only case of interest, with two subcases: a change from normal morphology (A+ or A-) to abnormal one (C+ or B-) or vice versa.

In both subcases the increase in internal phase content results in an increase in the number of drops which then tend to get closer and closer to each other until they finally touch with one another.

It is worth noting here that the hexagonal close packing of identical rigid spheres, i.e., the most dense 3D way to stack spheres, accounts for 74% of the space volume. If the spheres are not identical, the packing could reach a higher percentage of the volume, but if the packing is random, as expected for an emulsion, the drops might start being in contact at a lower volume fraction, e.g., 60 to 65%.

If the emulsion is abnormal, the thin film between approaching drops is likely to break at once upon touching and the drops would coalesce quickly to become the continuous phase of the inverted emulsion. This would occur as soon as the drops are close enough for the contact to be highly probable, which could happen as early as 60% of internal phase content. In the previous figures the vertical branches of the standard inversion frontier were located at about 30 and 70%, which are typical values. Hence, the path from abnormal to normal morphology would cross the standard inversion frontier at 30%, whereas the previous discussion suggests that the critical packing for drop contact could be much higher, at about 60%. Consequently the contact occurrence and resulting inversion is likely to be delayed from 30 to 60% in the abnormal to normal morphology case.

Contrary to the previous case, the interdrop thin films in normal emulsions are expected to resist the contact, and the drops are not likely to coalesce instantly upon touching. As a consequence, normal emulsions can attain an internal phase content much higher than the hexagonal packing by deformation of the drops, sometimes so substantial that they result in polyhedral structures called biliquid foams. Therefore, the inversion from normal to abnormal morphology is likely to take place later than the typical 70% of internal phase content which corresponds to the location of the vertical branch of the standard inversion line.

The previous discussion based on fairly reasonable arguments points out that a dynamic inversion process due to an increase in internal phase content is expected to be delayed with respect to the position of the standard inversion line in all both subcases, i.e., in both directions of change. Experiments carried out in a variety of conditions of addition of internal phase show that, indeed, the dynamic inversion is always delayed, i.e., it takes place often well after the standard inversion frontier is crossed. The arrows in Figure 4.12 show the direction of change and the bold line passing at the tip of the black arrows indicates the point where the dynamic

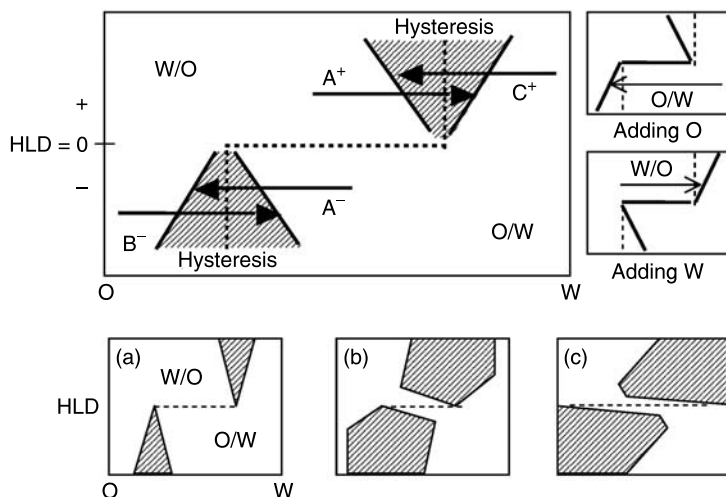


FIGURE 4.12 Catastrophic inversion 2D map (top) and typical cases of hysteresis regions (bottom).

inversion takes place. The region between the two dynamic inversion lines corresponds to one type of emulsion or the other depending on the direction of change. It is called an **ambivalent** or **hysteresis** zone, in which any of the two morphologies can occur, and thus belongs to the normal or abnormal region depending on the case.

This means that the extension of the regions, particularly the A<sup>-</sup> and A<sup>+</sup> normal ones, can be considerably modified by this so-called **memory** phenomenon, as well as the resulting emulsion properties associated with the regions [22].

The shape and extension of hysteresis regions might vary from case to case, and seems particularly dependent on the protocol by which WOR is changed, as discussed later. Figure 4.12 (lower graphs) illustrates different typical hysteresis patterns drawn after experimental data. Very close to HLD = 0 (dashed line in Figure 4.12, lower graphs) the emulsions produced are very unstable and the experimental data from different sources exhibit discrepancies. However, it is probable that the delay vanishes in this region, where any morphology change would take place as in a transitional inversion process, that is reversibly [97].

Since the handling of the experimental procedure could result in hysteresis regions with very different shape and extension, controlling this feature is of primary importance as far as the emulsion ultimate properties are concerned.

The issue can become more complex if the initial abnormal emulsion is, as often the case, a multiple emulsion. In effect the droplets which are inserted in the drops tend to swell them, hence to apparently increase the dispersed phase content, and to reduce the drop-drop distance. Consequently, the interdrop contact in the abnormal outer emulsion is more probable and the inversion will take place earlier, particularly if many droplets become inserted in drops.

As far as the droplets-in-drops inner emulsion is concerned, it is a normal emulsion according to formulation and the droplets are not likely to coalesce upon contact. If the conditions are appropriate this inner emulsion would resist coalescence and hence more and more droplets would be inserted in drops, which end up so swollen with droplets that they could reach the 50 to 60% critical packing condition to coalesce. In such cases inversion could take place after a small amount, say 10%, of the added phase is incorporated, i.e., even before the standard

inversion frontier is crossed at about 30%, with a puzzling apparent anticipation instead of delay with respect to the standard inversion frontier.

Things could turn out even more complex because multiple emulsions frequently evolve when they are submitted to continued stirring. In effect, the competition between the inner and outer emulsions is the result of the opposite mechanism: drop breakup and coalescence. Since the inner emulsion is more stable than the outer one, the former tends to increase at the expense of the latter. As a consequence, and just because of the stirring process, and without adding any phase, more and more droplets are incorporated in the drops as time elapses [98]. Hence the volume of the drops tends to increase and at some point the packing reaches the critical value and the inversion takes place.

Catastrophic inversion has been reported in triangular diagrams for very few systems, most of them with *n*-butyl monoglycol ether, which is not really a surfactant, though its behavior seems to be a fair model [46,47]. On the other hand, fish diagrams have been used to interpret transitional inversion by a change in temperature with ethoxylated nonionics, particularly *n*-alkyl polyglycol ethers [99]. In both kinds of diagrams the surfactant concentration axis's only important use is to locate the tri-critical point, and no effect of WOR can be followed. Hence, these later diagrams are essentially equivalent to 1D plots as far as the information is concerned.

#### 4.4.4 BASIC MODELING AND INTERPRETATION

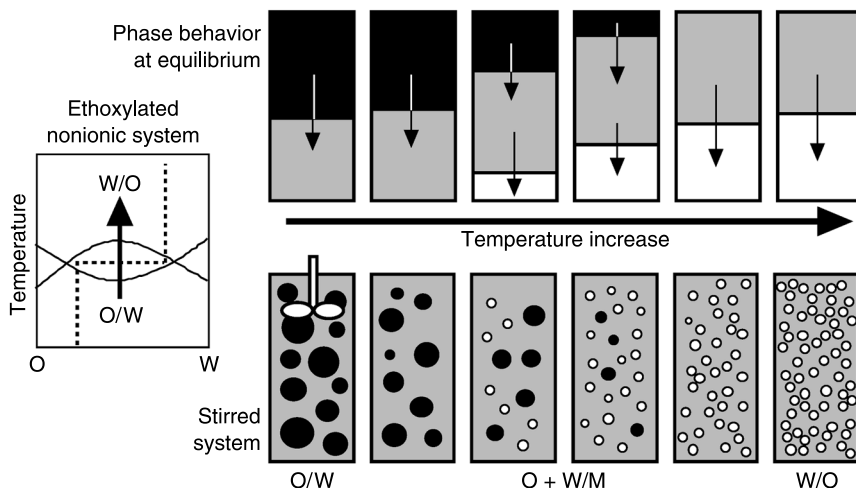
From the experimental evidence discussed in the previous paragraph, it is seen that the characteristics of the transitional and catastrophic inversions are quite different.

##### 4.4.4.1 Mechanism of Transitional Inversion

Transitional inversion is associated with a swap in phase behavior at equilibrium, and if the time scale of change is slow enough, mass transfer takes place during the process and equilibrium is approached at all times. Experimental evidence indicates that close to optimum formulation, surfactant diffusional mass transfer between phases is particularly quick [100,101] and on the other hand a complete transfer is not required for the emulsion morphology to change [102]. Moreover, the presence of alcohol cosurfactant seems to speed up the kinetics effects [103] and the low tension prevailing close to optimum formulation insure the transient formation of small drops, i.e., high interfacial area of transfer, even if stirring is not very energetic. Finally the very quick coalescence rate provides mixing which favors convective transfer.

At optimum formulation the phase behavior is either a single phase microemulsion (W IV) or a three-phase one (W III), whereas it is diphasic (W I or W II) at HLD slightly different from zero. Hence, the crossing of the  $HLD = 0$  region involves a change in the number of phases, whose analysis provides an interpretation of the mechanism of transitional inversion.

Figure 4.13 illustrates the case of a temperature scan with a polyethoxylated nonionic system at  $WOR = 1$  and a surfactant concentration which is about half what is required to attain the single phase behavior at optimum formulation. When the temperature is increased, the phase behavior changes from W I ( $T < PIT$ ) to W III ( $T = PIT$ ) and W II ( $T > PIT$ ) as indicated in the upper scan. If the temperature change is slow enough, the mass transfer, which proceeds quickly in the optimum formulation region, essentially maintains the phases in a pseudo-equilibrium state, and from left to right the microemulsion phase takes up oil and releases water. If the system is stirred, as shown in the lower scan, the dispersed phase is the one containing most of the surfactant, i.e., the microemulsion. At low temperature the emulsion is O/W, and as temperature increases, the external phase microemulsion (gray phase) takes up oil and the oil drop size decreases.

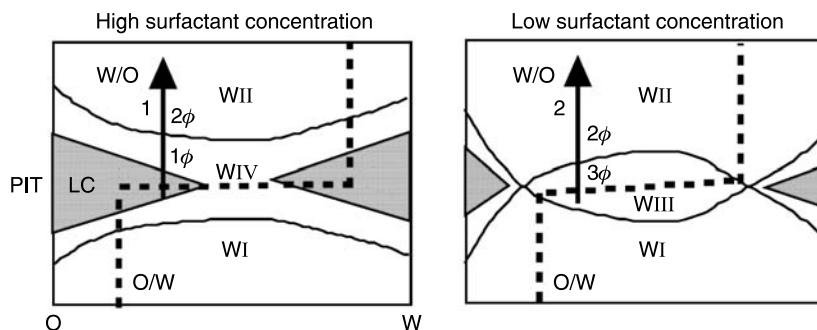


**FIGURE 4.13** Phase behavior at equilibrium and emulsion evolution in a transitional inversion process.

At some point close to PIT the microemulsion is in equilibrium with two excess phases, which means that the microemulsion is exuding tiny water droplets by some nucleation process and, consequently, the emulsified system contains oil drops and water droplets. As the temperature increases further, the microemulsion swallows more and more oil from the drops and expels more and more water as droplets, until a temperature higher than PIT is reached at which the microemulsion has incorporated all the oil and the emulsified system is now of the W/O type as tiny water droplets in oil. This mechanism corroborates that the transitional inversion is not really an inversion but a continuous change of the content of the external phase, from water to oil in the Figure 4.13 case. This mechanism is obviously reversible and can take place exactly in the same way in the other direction, provided that the assumptions of quasi-equilibrium are met.

The water droplets are particularly small because they are formed by a nucleation process produced by the splitting of a single phase. However, close to optimum formulation the droplets are likely to coalesce very quickly if something is not done to prevent it. As previously mentioned, there are essentially two practical tricks to keep the fine emulsion. The first one consists of applying a thermal [104] or physicochemical quench, i.e., to quickly change the value of HLD away from zero as soon as the droplets are formed, in the Figure 4.13 case to increase HLD by at least one unit, e.g., by increasing the temperature 20°C or so, or by adding a small amount of lipophilic surfactant or cosurfactant. The second clever procedure is to use a system in which the phase behavior at optimum formulation includes or consists of a lamellar liquid crystal able to encapsulate the droplets and prevent their coalescence. This second alternative requires a high surfactant concentration, e.g., at least 10 to 15%. At such a concentration or maybe a little higher, the phase behavior at optimum formulation is likely to be monophasic (W IV), eventually with a LC zone in it (path 1 in Figure 4.14). In this case the emulsion comes from a nucleation process which is expected to produce tiny and relatively monodispersed droplets if the quench process is efficient in inhibiting their coalescence.

In contrast, at low surfactant concentration the phase behavior at optimum formulation is W III and no liquid crystal is usually found along the followed path (path 2 in Figure 4.14). The volume of the microemulsion in such a three-phase system is probably small, e.g., 10% or less,



**FIGURE 4.14** Transitional inversion at high and low surfactant concentration.

hence the stirring of the system is likely to produce an emulsion whose morphology may be quite complex and sometimes results in some intermediate conductivity changes which are often difficult to interpret. Since the tension is low, any stirring, even at low energy, might be enough to disperse water-in-oil or vice versa. This is another drop formation process, this time due to stirring, and most often associated with the formation of larger drops, because of the inherent instability prevailing in this region. Consequently, at low surfactant concentration the inverted emulsion often exhibits a bimodal drop size distribution, the smaller droplets coming from the nucleation process and the larger ones from the stirring [71,96].

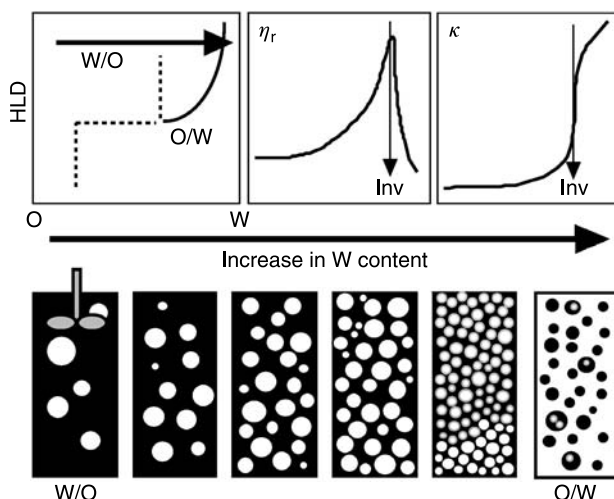
Although this bimodality may be corrected by controlling the stirring and quench processes, an increased surfactant concentration is often unavoidable.

#### 4.4.4.2 Modeling of Catastrophic Inversion

Catastrophic inversion is triggered by the addition of (too much) internal phase to an emulsion submitted to stirring. Main features involve the possibility of two states (O/W and W/O), sudden jump, irreversibility, hysteresis, divergence, all characteristic of the so-called cusp catastrophe [105]. An even better match can be provided by a higher order catastrophe model, so-called butterfly [106], which accounts for the HLD, WOR, and surfactant concentration effects on both the phase behavior at equilibrium (with a Maxwell convention of multistate overall minimum) [107] and emulsion inversion (with a maximum delay convention of local minimum seeking). A full account of these models may be found elsewhere [106], and it is enough to say here that catastrophe theory supplies an elegant nonconventional qualitative model to interpret a complex physical process. The fact that the same potential allows an interpretation of both the phase behavior and the emulsion inversion corroborates that some link exists between them, in spite of the fact that thermodynamics and kinetics are usually independent [108,109].

Trials to reach a quantification of the experimental data with a catastrophe theory model have achieved limited success, particularly through the use of coordinate change [46,110], but they failed to provide a deeper insight on some aspects [111].

Kinetic models on emulsion inversion were proposed a long time ago [41]. They are based on the competitive coalescence rate of the two types of emulsions, the most stable one leading to the prevailing morphology. These models can match the influence of both by the formulation and WOR and lead to a more rational description from the physical point of view [75]. However, they



**FIGURE 4.15** Catastrophic inversion from normal to abnormal morphology (A+  $\rightarrow$  C+). Variation of emulsion relative to viscosity, conductivity, and drop distribution.

have failed to provide a good description of some emulsion inversion basic features such as irreversibility and hysteresis.

Consequently, it may be said that the description of emulsion inversion still relies on experimental data, with a large variety of cases depending mostly on the experimental protocol.

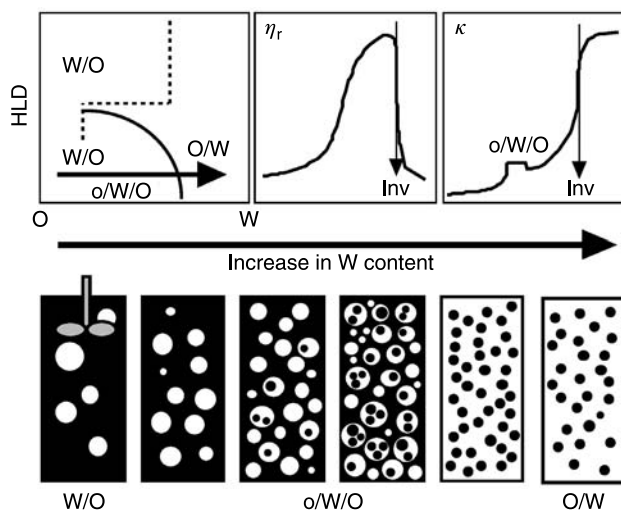
Figure 4.15 illustrates the case of catastrophic inversion from normal to abnormal morphology, produced by the addition of water to a W/O emulsion in conditions in which  $HLD > 0$ , at constant surfactant concentration. As water is added under continuous stirring it is dispersed into drops, which become more numerous and closer to each other. When the amount of water attains some critical packing, say about 65 to 70%, the drops start touching, but coalescence is not expected to take place upon contact because the location in the map (A+ region) corresponds to stable emulsions (see Figure 4.8). Hence, the internal phase amount continues to increase and at some W content, say 75 to 85% depending on the drop size distribution, drops are likely to become distorted. At some higher W content, which depends on the applied shear and on the performance of the surfactant, the interdrop films would break up and drops would coalesce to produce a continuous W phase, resulting in the inversion of the emulsion into a O/W abnormal morphology of low internal phase content, sometimes with a few residual droplets in drops.

In some cases the resistance of the interdrop film is high enough to hamper their rupture in the conditions of shear, and the normal emulsion does not invert (see Figure 4.12, lower right case). Actually the inversion likelihood is essentially set by the experimental protocol, and the fact that high internal phase content emulsions become viscoelastic and cannot be handled like a fluid any more.

It is worth noting that this extreme situation is not uncommon, as is the case of mayonnaise or cold creams. Moreover a viscoelastic emulsion may be a quite useful medium to increase the slow mixing emulsification performance in a variety of cases ranging from cosmetics and foods to heavy crude oil fuels [76].

Figure 4.16 illustrates the case of catastrophic inversion from abnormal to normal morphology, produced by the addition of water to an oil phase in conditions in which  $HLD < 0$ , at constant





**FIGURE 4.16** Catastrophic inversion from abnormal to normal morphology (B- → A-). Variation of emulsion relative to viscosity, conductivity, and drop distribution.

surfactant concentration. When water is added upon stirring of the oil phase, a W/O dispersion results since the water content is very low at first in this B- region. Nevertheless, it is worth noting that the formulation favors an O/W morphology, which means that the W/O type is abnormal and that W drops are prone to coalesce upon contact. Because the stirring device applies some kind of shear on the W drops, these can be elongated or flattened, and the formulation might locally favor the curvature leading to the O/W morphology. This process generally results in the formation of “o” droplets inside the W drops, i.e., the attainment of an o/W/O multiple emulsion, by a mechanism so-called inclusion [98,112–114]. If many “o” oil droplets are included in the W drops internal coalescence can take place [115], or the mechanism opposite to inclusion, so-called escape process, might happen too [116].

It is worth noting that the “o” droplets inside the W drops are not expected to coalesce upon contact since they are the normal type according to the formulation. Hence, the inclusion mechanism is expected to proceed, and eventually result in a high internal phase content o/W inner emulsion. This “stuffing” of W drops with “o” droplets produces their swelling and the apparent (W+o) drop volume increases (much) faster than predicted from the water content, since the volume of “o” droplets might be much larger than the W drops one. As a consequence, the W drops get closer and their contact might take place at a very low water content, e.g., 15% instead of the typical 50 to 60% critical value of the internal phase content at which an abnormal emulsion drops start to coalesce to trigger the inversion.

Since the critical W drop volume can be attained with more or less swollen W drops, the crucial and determining issue is to know what to do to favor or not the swelling of the W drops during the process, i.e., how to favor the formation of a multiple emulsion, a topic which will be discussed in the next section.

When the W drops come into contact and coalesce to form the continuous phase, the small oil droplets are released, and often result in an O/W nanoemulsion, which is quite stable according to the location of the HLD-WOR map. On the other hand the oil films of the continuous O phase

in the pre-inversion emulsion break up to form another category of drops, whose size depends on factors such as the film thickness, the interfacial tension, the WOR, the shear etc. Consequently, the inverted emulsion could exhibit a drop size bimodal distribution that accounts for this dual emulsification process [71].

As a conclusion it may be said that protocol is of the utmost importance because it can alter the conditions of mixing and the resulting effects on the emulsion. This is why dynamic inversion concepts are much more complex than standard inversion issues, but are also much more flexible for custom-made emulsions [117].

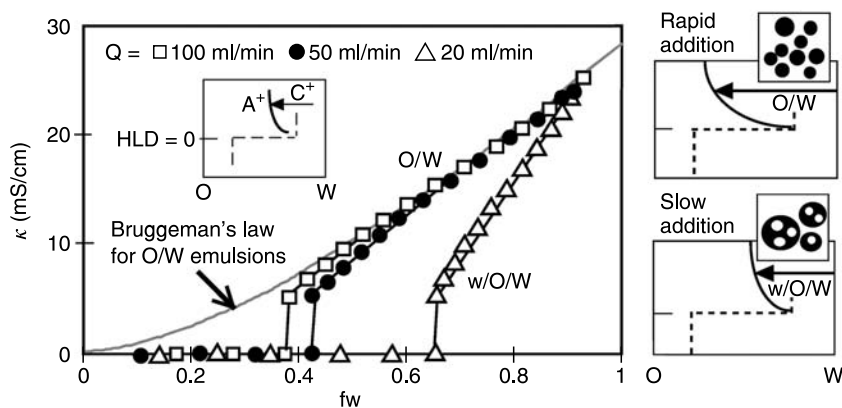
The next section is dedicated to the presentation of some trends or recent advances which have been identified as probably long-lasting in spite of the little amount of information available to support them.

#### 4.4.5 RECENT ADVANCES IN DYNAMIC INVERSION

##### 4.4.5.1 Catastrophic Inversion

Several recent studies were dedicated to discovering the influence of the dynamic (catastrophic) inversion protocol under continuous addition of one of the phases [69]. Most experiments were followed by conductivity monitoring in the case of inversion from abnormal O/W or w/O/W morphology (C+) to normal W/O type (A+), but the results seem to be valid as well for the inversion from B- to A- which was followed by rheological monitoring [12,118] since conductivity does not contribute much information.

As the rate of addition of internal phase increases, the dynamic inversion is delayed according to the conductivity variation shown in Figure 4.17 [119], in which the addition of oil to water (A+  $\leftarrow$  C+) results in a displacement from right to left, until the inversion from W-external to O-external takes place at 35% O for a low (20 ml/min) addition rate and at 63% O for a high (100 ml/min) addition rate. Figure 4.17 also shows that in the case of a high addition rate, the conductivity follows Bruggeman's law, which means that the abnormal emulsion is a simple O/W morphology. In contrast, in the case of a slow addition rate, the conductivity of the abnormal



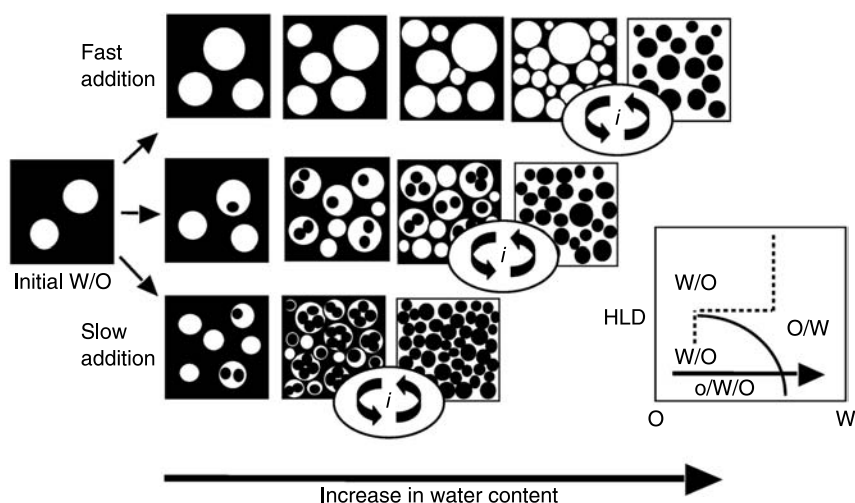
**FIGURE 4.17** Effect of addition rate of internal phase on catastrophic inversion from abnormal to normal morphology (A+  $\rightarrow$  C+). (Reprinted with permission from N. Zambrano, E. Tyrode, I. Mira, L. Marquez, M.P. Rodriguez, and J.L. Salager. *Ind. Eng. Chem. Res.* 42: 50 (2003). Copyright (2003) American Chemical Society.)

emulsion is much lower than expected from Bruggeman's law, indicating that the emulsion is a w/O/W multiple morphology.

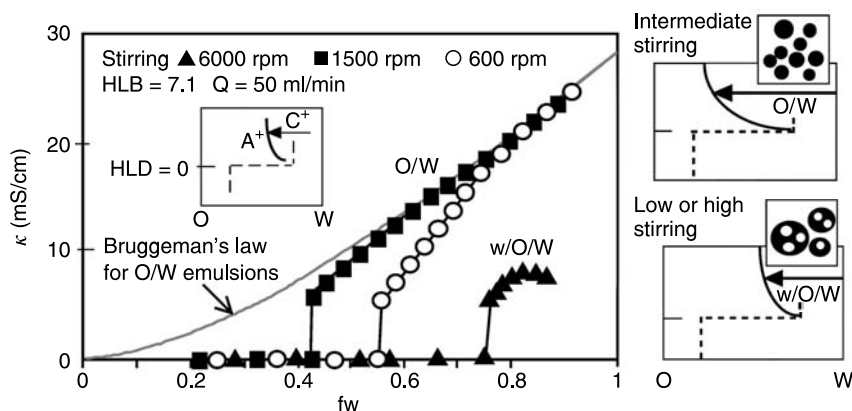
The interesting result in Figure 4.17 is that the conductivity at inversion is the same in all cases, i.e., the one which corresponds to 35% of external water, whether the drop phase consists either of pure oil or a w/O emulsion. This 65% of internal (drop) phase volume seems to be the critical packing at which the abnormal to normal inversion is triggered in this case [12,98,120,121]. It is worth remarking that the inversion takes place at a earlier time (after 2.3 min versus 5 min) if the addition rate is quicker (100 ml/min versus 20 ml/min) and essentially no multiple emulsion is produced. However, the inversion times are not in the same proportion as the addition rates, and the added amount of internal phase at inversion is much lower when a multiple emulsion is generated; consequently the resulting inverted emulsion would exhibit a higher internal phase amount and a higher viscosity.

This is particularly important for the emulsification of resins (epoxy, alkyd, silicone viscous polymers) in an O/W emulsion [57,122]. In this case water is added to the viscous oil at  $HLD < 0$  as shown in Figure 4.18. The conductivity measurement is of no use to detect pre-inversion phenomena and only shows the occurrence of multiple or simple emulsion after inversion. Before inversion the emulsion morphology has to be monitored by other means such as its viscosity [118]. Fast addition produces a delayed inversion from W/O to O/W morphology with large drops, whereas a slow addition results in the formation of an intermediate o/W/O emulsion which inverts to a high internal phase content O/W emulsion with fine drops. Drop size was found to depend on the addition rate, because of the different mechanism illustrated in Figure 4.18, as well as stirring energy [57].

In practice the slow addition can be substituted by the addition of a small quantity of internal phase (say 10%) to start making a multiple emulsion followed by the uninterrupted stirring of the emulsion after the addition is stopped [118]. The continuous stirring shear tends to produce both types of dispersion but the favored morphology is the one which corresponds to Bancroft's rule,



**FIGURE 4.18** Influence of addition rate on the catastrophic inversion from abnormal to normal morphology (B → A-). (Reprinted with permission from E. Tyrode, J. Allouche, L. Choplin, and J.L. Salager. *Ind. Eng. Chem. Res.* 44: 67 (2005). Copyright (2005) American Chemical Society.)



**FIGURE 4.19** Effect of stirring energy on catastrophic inversion from abnormal to normal morphology ( $A^+ \rightarrow C^+$ ). (Reprinted with permission from I. Mira, N. Zambrano, E. Tyrode, L. Marquez, A.A. Peña, A. Pizzino, and J.L. Salager. *Ind. Eng. Chem. Res.* 42: 57 (2003). Copyright (2003) American Chemical Society.)

i.e., the inner emulsion. As a consequence, the multiple emulsion evolution under continuous stirring is always toward the inclusion of more droplets into drops until the critical packing is attained. This means that slower addition is equivalent to longer stirring and more inclusion [12,118,123]. It also means that an abnormal emulsion is likely to invert, soon or later, if it is stirred long enough in an appropriate way.

The influence of the stirring intensity is more complex because it deals with two opposite effects [73]. Figure 4.19 indicates that when the stirring intensity increases from slow mixing (600 rpm) to high Couette shear (1500 rpm) the inversion is first delayed, then at a high turbulent regime (6000 rpm) it takes place sooner. As indicated in Figure 4.17 the lower addition of internal phase at inversion is associated with the formation of a pre-inversion multiple emulsion.

There is thus an intermediate stirring condition for which the delay is maximum, but its attainment is not yet related to some specific situation, though it has been shown to depend on other variable values. Hence, in some cases an increase in stirring would produce a delayed inversion [72], and in other cases just the opposite [56]. The two opposite influences, starting from the intermediate case in which no multiple emulsion forms, are probably (1) the long stirring duration associated with slow stirring intensity which favors the formation of a multiple emulsion as in the slow addition case, and (2) the excessive shearing at high stirring rate which is able to break down even the droplets inside the drops.

It is worth noting that in all three cases shown in Figure 4.19 the critical packing at inversion, indicated by the conductivity value, is the same (5 mS/cm) as in Figure 4.17 for the same SOW system but different protocols. However, it should be pointed out that the critical packing to trigger the inversion from abnormal to normal morphology has been experimentally found to vary with the formulation, i.e., the HLD value. The general trend is an increased delay, sometimes up to 90% of internal phase content as  $HLD = 0$  is approached [12,97], although it should end up vanishing at  $HLD = 0$  for the sake of continuity. Two explanations, which are not completely satisfactory, have been proposed. The first is related to the existence of fibrous dispersion instead of spherical drop emulsion, because of the low interfacial tension and permanent renewal of the dispersion by a breakup and coalescence of fast equilibrium [12]. The second is the existence of only a transitional inversion mechanism close to optimum formulation [94]. It should be noted that

in practice it is very difficult to carry out foolproof experiments on emulsions close to  $HLD = 0$  because of their extreme instability [113], hence this actual mechanism might not be settled soon.

Another issue which has been addressed is the scale of the WOR variation in a stirred system, i.e., the micromixing, and the introduction of the local WOR instead of the global one. In a system containing equal amounts of oil and water, the position and fluid mechanics action of the stirrer has been found to influence the emulsion type, particularly if the convection pattern produces a thrust of one of the phases into the other, thus resulting in a local WOR value quite different from the overall one. Hence the apparent (global WOR) position of the catastrophic branches of the inversion line is shifted right or left depending on the difference between the global and local WOR. This shift can be harnessed to produce a multiple emulsion with a dual stirring process [78].

This notion of local WOR is probably linked to the very onset of emulsion inversion, since the position of the catastrophic inversion in both directions has been found to be dependent on the way the internal phase is added. Reported inversion studies used a variety of addition protocol from continuous flow to lump-wise aliquot addition. A recent study [124] has pointed out that incipient inversion might require, particularly in the normal to abnormal direction, a local excess of added phase of some extension and persistence. This can be attained either by adding a large aliquot or using a fast continuous addition rate at high stirring or a smaller aliquot or a slower continuous addition rate at lower stirring, so that the heterogeneity does not dissipate so quickly.

Nevertheless, it is yet to be demonstrated that a spatial and temporal WOR heterogeneity could be the key starting point of catastrophic inversion.

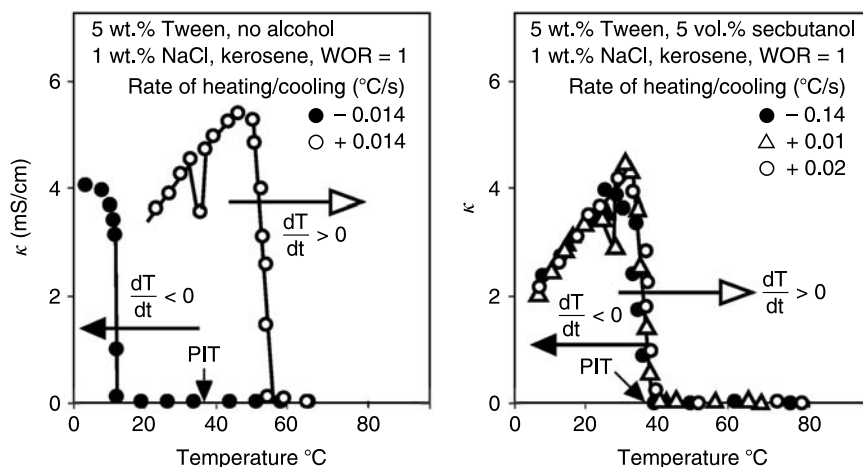
As a general rule of thumb, it can be said that in the case of inversion from abnormal to normal morphology, anything that promotes the development or persistence of a spatial or temporal WOR heterogeneity tends to (1) inhibit the formation of multiple emulsion, (2) tends to delay the inversion in the sense that a higher amount of added internal phase is required, (3) but tends to shorten the time scale at which inversion is likely to take place. Consequently, a slow addition would result in the formation of multiple emulsion before the inversion, which would take place after only a small amount is added. In contrast, in the normal to abnormal direction a slow addition is not expected to result in a multiple emulsion but to produce a simple normal morphology, but inversion is delayed, sometimes to an extremely high internal phase content, and in some extreme cases it never takes place (Figure 4.12, lower right).

#### 4.4.5.2 TRANSITIONAL INVERSION

As was discussed in the previous sections, transitional inversion takes place when the generalized formulation is close to optimum, i.e., when the simultaneous low interfacial tension and high instability result in a pseudo-equilibrium between drop breakdown and coalescence. However, a high rate of formulation change or a reduced equilibration rate might defeat these assumptions [125].

PIT experiments carried out at different rates of temperature change were recently reported [126] to show a delay of transitional inversion in both cooling and heating directions (see Figure 4.20, left). The rate of change was also reported to alter the delay, which was noteworthy, say more than  $20^{\circ}\text{C}$ , in some cases. The system contained a mixture of surfactants, among them high molecular weight ethoxylated sorbitan trioleate, which is not likely to diffuse rapidly. The addition of sec-butanol cosurfactant was found to eliminate the delay (Figure 4.20, right) whatever the rate of change, a result which is consistent with its role of speeding up equilibration processes, as shown in other kinds of experiments [100,103].

The conductivity record along a transitional inversion path often exhibits irregularities, particularly excessive conductivity values which are not due to random errors of measurement.

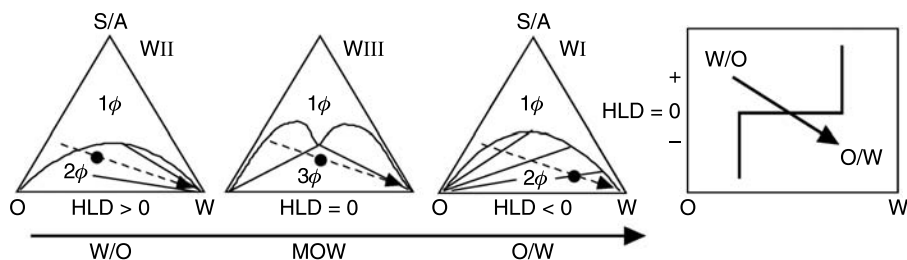


**FIGURE 4.20** Transitional inversion with and without delay (Reprinted with permission from L. Marquez, A. Graciaa, J. Lachaise, J.L. Salager, and N. Zambrano. *Polym. Int.* 52: 590 (2003). Copyright (2003) John Wiley and Sons.)

Such conductivity bumps, as seen in Figure 4.10 at 29 °C, takes place at surfactant concentration above 10%, and are likely to be associated with the presence of lamellar liquid crystals which confer a significant, though still low, conductivity [51,127–129]. Because of the fast dynamic balance between breakup and coalescence, any alteration of one of these opposed effects might result in a large alteration of the drop size. This is the case of the presence of a liquid crystal at the drop interface at the moment the drop is generated either by shear or by nucleation. Because of the proximity of  $HLD = 0$ , the liquid crystal likely to exist is of the zero curvature lamellar type, which takes time to be formed or to dissolve. Hence the liquid crystal should be pre-existent to the formation of the drop. If the drops are formed by stirring, the LC might be in either phase, but since the formulation (Bancroft rule) favors the surfactant-rich phase as the external phase, the LC should be in it. When the drops come from a nucleation due to a change in formulation, the W IV region containing LC is somehow crossed during the process. Obviously, the time scale of the LC region crossing is of utmost importance for the formation and layering of LC at the drop interface [94]. Slight variations in the starting point and in the formulation or temperature protocol of change result in a considerable change in drop size [35,96] because of their effect on the kinetics of formation of the protective layer around the drops. On the other hand the stirring seems not to have any effect on drop size [57].

#### 4.4.5.3 Inversion Produced by Combined Formulation-WOR Variation

Transition and catastrophic mechanisms are not always easy to separate in real cases. In some instances both formulation or temperature and WOR are changed simultaneously in order to cross the inversion line in some slanted way (path 4 in Figure 4.9). This is very easy to realize in practice, e.g., by adding a phase with a composition or temperature which alters the formulation. Depending on the exact position of the crossing of the inversion frontier, it is the transitional or catastrophic branch which is mainly crossed, with the intermediate case of crossing just at the corner where transitional and catastrophic regimes overlap. Experimental evidence [130] indicates



**FIGURE 4.21** Transitional inversion produced by adding water in the case in which it results in a formulation change.

that very slight variations in such corner paths produce huge variations in the resulting drop size after inversion.

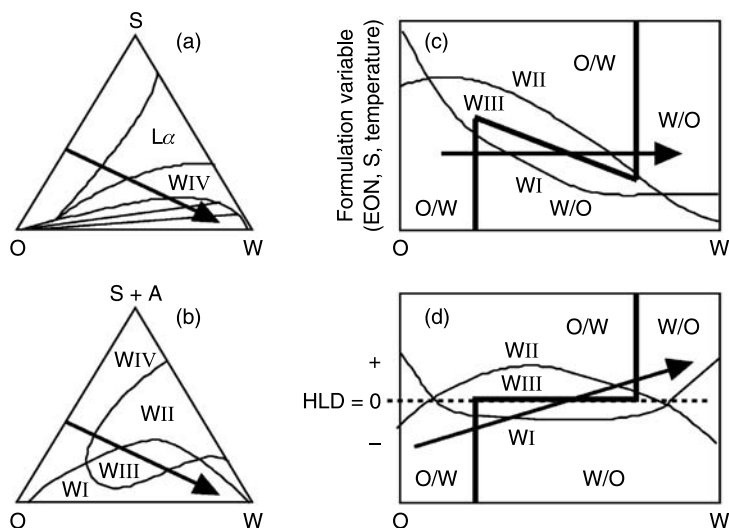
In most cases the mixed concomitant variations of formulation and WOR, and sometimes surfactant/cosurfactant concentration, is not voluntary, but comes from the protocol. For instance, the addition of one phase can result in different effects which are likely to change the formulation. The first one is a dilution effect, e.g., adding water to an electrolyte or alcohol solution, which would result in a formulation effect through the  $S$  and  $f(A)$  term in HLD expression. In practice it means that the composition change results in a simultaneous formulation change, or in other words a diagram change as illustrated in Figure 4.21 for the case of dilution with pure water of a system containing an aqueous brine and some slightly lipophilic alcohol. As water is added, the path of the representative point in the ternary diagram heads to the  $W$  vertex along the dashed arrow. However, the salinity decrease and the resulting dilution of alcohol both tends to decrease the HLD value, which results in change of ternary diagram type  $WII \rightarrow V III$  or  $IV \rightarrow WI$  transition accompanied by the  $W/O \rightarrow O/W$  emulsion inversion.

In a HLD-WOR diagram, the change in both the water content and formulation would result in a slanted path indicated in Figure 4.21 (right map), with the same transitional inversion result, but with a much more straightforward interpretation.

In most cases the phase behavior SOW ternary diagram is more complex than any of the classical Winsor types, and exhibits liquid crystal region (Figure 4.22(a)) [131–138] or/and complex variation due to the selective partitioning of different amphiphiles, e.g., surfactant mixtures [139] or surfactant and alcohol [140], as in Figure 4.22(b), in which case the increase of surfactant + alcohol tends to increase HLD [141].

Such a selective partitioning [139] results in the slanting of the three-phase band and thus of the optimum formulation line in a F-WOR diagram (Figure 4.22(c)) [52–54,59,142]. In the case illustrated, in which the formulation variable could be, for instance, the surfactant EON, the salinity of the aqueous phase or the temperature, a dilution with water along the arrow generates a path that crosses the inversion line three times: first a catastrophic inversion from abnormal to normal morphology, then a transitional one from normal to normal, and finally another catastrophic inversion, but this time from normal to abnormal. Provided that the crossing of the “vertical” branches could be delayed, additional twisting of the frontier could result, with an apparently whimsical morphology sequence if the proper diagram is not available to interpret the data [143].

It is worth noting that if the formulation is expressed as HLD (at any value of WOR) the optimum formulation becomes the horizontal line at  $HLD = 0$ , but now it is the path which is



**FIGURE 4.22** Complex inversion processes produced by adding water.

slanted, because the change in WOR changes the formulation, i.e., the HLD value, as illustrated in Figure 4.22(d). As a consequence the crossing features are essentially the same.

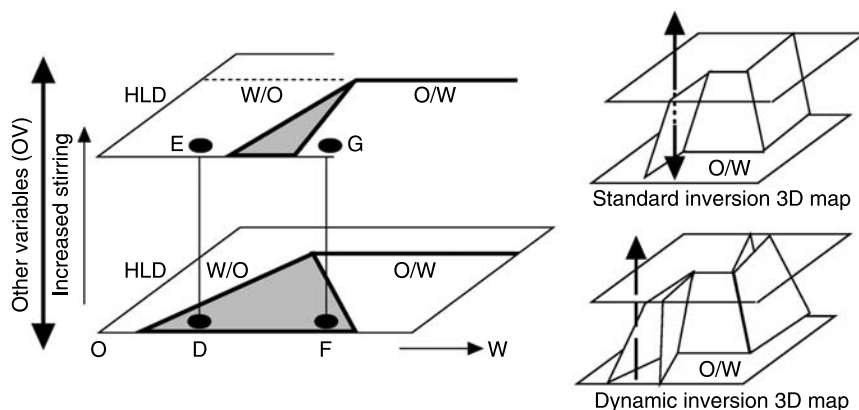
In real complex phase behavior cases such as in Figure 4.22(a) and (b), the path of dilution by water (arrow) could cross liquid crystal [133,144] or microemulsion regions or both and could result in emulsification by phase inversion or more complex mechanisms such as spontaneous emulsification [145–147], if the rate of change is rapid enough for non-equilibrium transfer processes to take place. Several such processes have been reported and are used in practice [142,148,149].

#### 4.4.5.4 Inversion Produced by Other Variables in 3D Representation

Protocol variables such as internal phase addition rate or stirring energy were found to alter the location of the dynamic inversion produced by a WOR change, which results in the shifting of the catastrophic branches of the inversion line in a 2D F-WOR map.

This shift may probably be represented as well in a 3D map if the change is now along the direction of the third variable, i.e., vertically in Figure 4.23 plot. However, it seems that the only case to have been reported of such an inversion is the effect of increased stirring on Orimulsion®, a fuel substitute marketed by Venezuela National Oil Company. This product is an emulsion of heavy crude oil-in-water emulsion containing 70% of extremely viscous hydrocarbon dispersed as 10 to 20  $\mu\text{m}$  drops, which has to be transported by pipeline for over 300 km from the emulsification plant located in the oil field to the tanker embarking terminal. Pumping by high shear devices such as centrifugal pumps has been reported to produce an increase in drop size and to end up in emulsion inversion [150]. Since the emulsion is located in the A– region very close to the “vertical” branch of the inversion line, an increase in stirring reported to shrink the A– region and the hysteresis zone as well [72] would pass the F-WOR representative point of the emulsion on the other side of the frontier, i.e., in the B– region. According to Figure 4.23 notation, the O/W emulsion at point D (at low stirring) inverts into a W/O emulsion at point E





**FIGURE 4.23** An increase in stirring energy may or may not produce emulsion inversion. (Reprinted with permission from J.L. Salager, L. Marquez, A. Peña, M. Rondon, F. Silva, and E. Tyrode. *Ind. Eng. Chem. Res.* 39: 2665 (2000). Copyright (2000) American Chemical Society.)

at high stirring. The hysteresis of the change has not been reported in detail but it is known from experience that the reverse inversion from E to D does not happen in practice, which is a confirmation of the existence of a memory effect, as illustrated in Figure 4.23, lower right graph. Consequently, such high internal phase content emulsions have to be pumped with a low shear device at a low Reynolds number.

Figure 4.23 allows a discussion of the apparently capricious effect of any third variable, such as an increase in stirring energy along an upward arrow. D and F are located in the hysteresis region at low stirring and may represent either a W/O or an O/W emulsion depending on the path used in the first place to reach this location. If the original normal O/W emulsion representative point is at F and the stirring energy is increased to G, there is no change in morphology. With a higher internal phase ratio of normal O/W emulsion at D, the same increase in stirring energy triggers the inversion to point E where an abnormal W/O emulsion is produced. If an abnormal W/O emulsion at D is submitted to increased stirring to reach E, it does not change morphology. In contrast, an abnormal W/O emulsion located at F would invert by increasing stirring. The moral of the tale is that an increase in stirring can produce any of the four possible situations depending on the circumstances. As a matter of fact, such variety of alternatives would be quite difficult to explain without the 3D representation of Figure 4.23 at hand.

An increase in surfactant concentration has been found to exhibit exactly the opposite effect in the 2D F-WOR map, i.e., it increases the extension of the A region and it extends the hysteresis zone [70,112]. However, it is not known if the addition of surfactant could trigger a dynamic inversion as an increase in stirring does.

#### 4.4.5.5 Emulsification and Inversion of Non-Equilibrated Systems

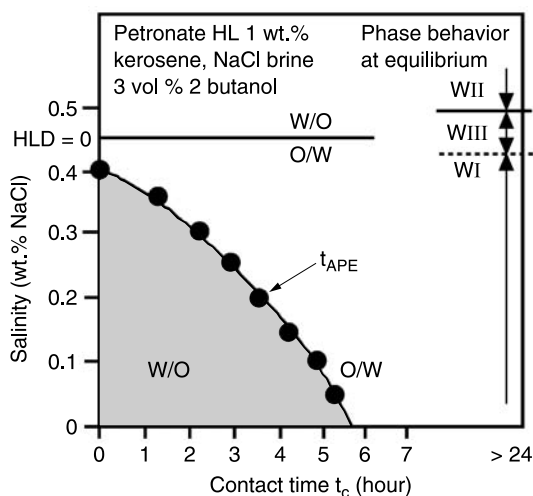
In most of the previous cases, at least those dealt with in the three types of 2D diagrams, the SOW system is at equilibrium prior to the onset of the emulsification process. In such cases and provided that the WOR is not very different from unity, Bancroft's rule indicates that the external phase of the emulsion is the one which contains most of the surfactant at equilibrium.

In industrial practice, the SOW system is not necessarily at equilibrium and a phase contact might be needed for the surfactant to migrate from one phase to the other if it is originally

placed in the phase in which it will not be located at equilibrium. The practical question is to know how the location of the surfactant influences the type of emulsion attained upon stirring a non-equilibrated system. There is no simple answer, and the best way to discuss it is to separate two extreme cases: the first is when the surfactant is totally in the phase in which it would be at equilibrium (say, the “good” location) and the second is when the surfactant is totally in the other phase, referred to as the “wrong” location. For instance, if the phase behavior at equilibrium is W I, and the surfactant is placed in the oil phase, it is in the wrong location, and vice versa.

Experience shows that Bancroft’s rule seems to apply in any case when emulsification is carried out immediately upon contact of the phases, whatever the good or wrong location of the surfactant. It means that an SOW system whose formulation is W I, but in which the surfactant is (wrongly) located in the oil phase, would result in an abnormal W/O emulsion. If the same system is equilibrated for several hours, the surfactant would have migrated in the water phase and the emulsification will result in a normal O/W emulsion. The question now is how long the SOW system has to be left to equilibrate so that the emulsification produces the same morphology as in a completely equilibrated system, i.e., the normal emulsion. The minimum time of contact for this normal emulsion to be produced has been called the apparent equilibration time ( $t_{APE}$ ). Initially, it was thought that  $t_{APE}$  was essentially linked to the time required for most of the surfactant to transfer to the other phase in the contacting conditions, e.g., several hours or days for a SOW at rest. The experimental evidence shows that it was not so and that in some cases only a very small amount of the surfactant had been transferred when the normal emulsion is produced from a quite non-equilibrated system [102].

In Figure 4.24 the apparent equilibration time ( $t_{APE}$ ) is plotted as a function of the formulation (salinity) and it is found that the departure from optimum formulation (i.e.,  $HLD = 0$ ) is directly associated with the apparent equilibration. Figure 4.24 shows that  $t_{APE}$ , which represents the contact time for a change in morphology to take place, is zero for systems close to  $HLD = 0$ , which means that at near optimum formulation the emulsification takes place as if the SOW system



**FIGURE 4.24** Apparent equilibration time ( $t_{APE}$ ) as the minimum contact time to attain the normal O/W morphology, when the surfactant initial location is in the O phase, as a function of formulation (salinity). (Reprinted with permission from J.L. Salager, N. Moreno, R.E. Antón, and S. Marfisi. *Langmuir* 18: 607 (2002). Copyright (2002) American Chemical Society.)

were at equilibrium, even if only a very small amount of the surfactant has had the time to transfer to the other phase. On the contrary, in systems far from  $HLD = 0$ , e.g., at  $S = 0.1$  wt% NaCl, more than 5 h of phase pre-equilibration time is required to produce a normal emulsion. Recent research has shown that the presence of low MW co-surfactant such as sec-butanol considerably reduces the pre-equilibration time, although it is still a function of the HLD [103].

This apparent pre-equilibration time is the only concept which has been proposed to handle the out-of-equilibrium cases, and further research is needed on these phenomena because many practical cases of great interest, such as crude oil dehydration or resin emulsification with ionomers, are intrinsically out-of-equilibrium processes.

#### 4.4.6 EMULSION INVERSION IN PRACTICE

In spite of being an instability phenomenon that is intrinsically difficult to harness, emulsion inversion has been used as the basis of different processes, particularly to make fine emulsions [117,143]. Cosmetic nanoemulsions of the O/W type are usually made starting with an oil phase and adding a water phase containing an hydrophilic surfactant. The original emulsion is of the W/O type in B<sup>-</sup> region, and it slowly evolves into an o/W/O emulsion (path 1 in Figure 4.25) and finally an O/W normal nanoemulsion (path 1'). In most instances, a small amount of water (10 to 20%) is slowly added first (path 2) and then slow motion stirring is continued for several hours without adding water (location 3) and an o/W/O emulsion forms, so that the water content at inversion is often less than the value expected from the standard inversion (dashed line). The process is long but does not consume much energy.

A similar inversion process (2–3) is used for making waterborne epoxy resin [151,152], polydimethyl siloxane [153], or alkyd emulsions [122,154]. This time the oil phase is extremely viscous and practically impossible to disperse as a nanoemulsion by brute force. The  $HLD < 0$  formulation ensures that in the multiple o/W/O emulsion the stable one is the inner one, and the high viscosity external oil phase is particularly efficient in transferring the slow shear from the mobile device. The multiple emulsion becomes extremely viscous, actually viscoelastic, as more “o” droplets are included in drops, particularly if the W amount is low [57].

When inversion takes place, a very high internal phase content O/W fine emulsion is produced, which is still quite viscous in spite of being water external. Further slow mixing of such emulsion results in the formation of a monodispersed nanoemulsion according to a recently elucidated mechanism [89]. The experience shows that the surfactant concentration plays an important role in particular if a LC can be formed in the W phase [152]. Since the water phase might be in a very small amount, a 10% surfactant in water might represent only a 1% surfactant in the system, indeed a reasonable concentration.

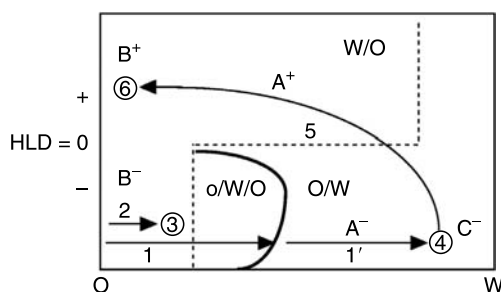


FIGURE 4.25 Paths in the F-WOR map illustrating complex inversion processes in industrial applications.

In some instances the oil phase is a polymer that contains ionomer or reactive molecules, which are able to activate as a surfactant in the presence of an alkaline water phase [154]. It is also the case of acidic crude oil in contact with alkaline brines. In most cases the *in situ* formation of the surfactant molecule at interface is accompanied by some spontaneous emulsification. Nevertheless, it can be considered that the process is essentially a  $B- \rightarrow A-$  inversion in which the hydrophilicity of the surfactant at interface depends on the alkalinity of the water phase, i.e., on the percentage of potentially hydrophilic groups which are activated.

Emulsion inversion can take place as a part of the end use of an emulsion, as in so-called cutting or laminating oils. The commercial products are in most cases sold as oil phase concentrates which self-emulsify at the contact of water to produce a diluted fine O/W emulsion along path 1+1'. This whitish emulsion is sprayed, in order to cool and lubricate, where there is a metal-metal high speed or high pressure contact. Hence, the original O/W emulsion is generally at  $HLD < 0$  in the  $C-$  region (location 4). Because it contains an ethoxylated nonionic system which is temperature sensitive, the contact with the hot metal tends to increase HLD and to produce the evaporation of most of the water, so that the location of the representative point of the emulsion moves rapidly along path 5 to end up almost instantly at location 6 in the  $B+$  region with a W/O morphology. The now continuous oil phase is able to wet the solid surface and to provide lubrication at the friction point, whereas the high latent heat of the remaining water can still contribute to the heat-removal process.

## 4.5 APPENDIX: HOW TO RETRIEVE INFORMATION

The technical literature on emulsion phase inversion is not very extensive, but it is not easy for the non-specialist reader to extract from it a good grasp of the state of the art, and there are several reasons for this. Firstly, there is a logical but long and tortuous sequence, which must be followed as a guideline. It should begin with a good understanding of the phase behavior of SOW systems, and not only the simple cases close to Winsor diagrams. Secondly, it is necessary to understand how phase behavior is related to formulation in different maps, then how emulsion type is related to formulation, composition, and other variables. Finally, knowledge of how to handle more complex dynamic processes with memory features is required.

A second problem is that the few research groups which have dealt with these issues have developed their own methodology independently of each other. Consequently, the reader is confronted with different ways of approaching and presenting the same phenomena, with several notations and terminologies, dealing with completely different applications and often quite different systems, so that the integration and generalization of the available information is not a straightforward matter.

It is not actually known why this situation arose, but it may be related to very different applications and different sponsoring orientations that result in diverse systems, different goals and interests particularly with confidential issues, and the use of a large assortment of divulgation media from fundamental journals like *J. Physical Chemistry* or *Langmuir*, to applied ones like *Industrial and Engineering Chemistry Research*, or *J. Dispersion Science and Technology*, or other wide ranging periodicals like *Colloids and Surfaces*, *J. Colloid and Interface Science*, or *Advances in Colloid and Interface Science*. In addition, there is some kind of competition between research and development groups that has resulted in systematic self-citations and little cross-references, and in the introduction of new and sometimes incompatible terminology when a proper one already existed elsewhere. This isolation prevented a unified approach to develop spontaneously, and some very old and outdated concepts like HLB are still used when generalized new ones have been available for decades.

This section gives an overview of the development of the current knowledge and mentions the names of the main researchers who contributed to the field. Current computer search by author name is probably the best way to quickly get a fair listing of relevant publications, and is certainly much better than using a keyword search which is likely to confront different difficulties such as variations in terminology and excessive use of some terms in other fields of research. Another way is to start with the few review papers which were written with a pedagogical approach [60,69,106,117,155–157].

Phase behavior of surfactant–oil–water systems was pioneered by P. Winsor 50 years ago. In the 1970s the enhanced oil recovery (EOR) research drive financed a great deal of research and development (R&D) toward the attainment of ultra-low tension, as a condition to displace crude oil trapped in the pores of an oil reservoir. Optimum formulation for EOR was found to coincide with the attainment of three-phase behavior of SOW systems, in which case Winsor's R ratio of interactions of the surfactant for the oil and water phase is unity. Extensive research effort focused on anionic surfactant systems in university and industrial R&D groups mostly in the U.S.A. and Europe, and can be retrieved with the following names: R. S. Schechter, W. H. Wade, D. O. Shah, D. T. Wasan, L. E. Scriven, C. A. Miller, R. L. Reed, R. N. Healy, G. Hirasaki, J. E. Vinatieri, S. Friberg, H. T. Davis, D. Langevin, M. Bourrel, P. Doe, and A. M. Bellocq. Complementary studies on polyethoxylated nonionics indicated that the phase inversion temperature (PIT) concept introduced in the mid-1960s by K. Shinoda and collaborators (H. Arai, H. Saito, and H. Kunieda) was a particular case of the multivariate correlations for optimum formulation presented in the late 1970s by R. S. Schechter, W. H. Wade, and collaborators (J. L. Salager, M. Bourrel, and M. Hayes), and transformed into a generalized formulation concept in the next decade (surfactant affinity difference (SAD)) by J. L. Salager, or as a diagram correlation by J. C. Ravey, or other similar equations by H. Kunieda, T. Förster, and A. Wadle. A source of difficulty was, with the exceptions of Winsor SOW ternary which was used by most people, that different groups used dissimilar representations: formulation–surfactant concentration or “gamma” plot (M. Bourrel and C. Chambu), and its equivalent (with 90° rotation) “fish” diagram, mostly used by people working with ethoxylated commercial or pure nonionics and a variation of temperature (K. Shinoda, H. Kunieda, M. Kahlweit, and R. Strey), bidimensional optimum formulation plots (R. S. Schechter, W. H. Wade, J. L. Salager, and M. Bourrel), formulation–WOR map (J. L. Salager) or its equivalent temperature–WOR map (K. Shinoda).

Some groups worked with commercial surfactants of assorted types with typical applications in mind (A. M. Bellocq), often with alcohol to avoid the formation of mesophases; others voluntarily studied the behavior of surfactant mixtures (A. Graciaa, J. Lachaise, J. L. Salager, and R. E. Anton), while others focused on isomerically pure surfactant series such as the CiEj alcohol ethoxylate series to work on well defined as-simple-as-possible systems (P. Ekwall, M. Kahlweit, R. Strey, and H. Kunieda); others focused their studies on a single amphiphile like dihexyl sulfosuccinate (D. A. Sabbatini and E. Acosta) or butyl monoglycol ether (D. H. Smith and K. H. Lim). Oil phases were mostly alkanes and alkylbenzenes, and sometimes polar oil like triglycerides (M. Miñana), fatty esters (T. Förster), or chlorinated hydrocarbons (D. A. Sabatini and E. Acosta).

As far as emulsion inversion is concerned, its treatment is somehow influenced by the phase behavior approach, and the type of system and variables. A variety of ionic and nonionic systems with oils ranging from pure alkanes, to petroleum cuts, edible, and other polar oils (more or less viscous), were studied in formulation–WOR maps by J. L. Salager, R. E. Anton, and M. Miñana, with a variety of formulation variables: surfactant HLB in series or mixture, salinity of aqueous phase for ionic systems, ethoxylation degree for nonionic, alcohol effect, temperature, even pH for fatty acid or amine, and referred to generalized formulation SAD and generalized property maps.

A system containing a short amphiphile (butyl monoglycol ether C4E1), i.e., a solvent with a surfactant-like behavior, was extensively studied by D. H. Smith and K. H. Lim, mostly with ternary and fish diagram representations in which the effect of WOR is not easy to see. Another group (B. W. Brooks, H. N. Richmond, and S. Sajjadi) dealt with polymer applications (polyisobutene, polyurethane ionomer) with a variety of surfactants, also in a formulation/temperature-WOR map.

Transitional inversion has most often been studied by scanning temperature, according to the PIT method proposed by K. Shinoda, and refined by people (T. Förster, W. von Rybinski, C. Solans, P. Izquierdo, J. Esquena) who were involved in the preparation of nanoemulsions.

A special type of transitional process that is often associated with inversion is a half-transition from WIV to WI or WII, consisting essentially in the dilution of a single phase microemulsion or  $\alpha$  LC into a nanoemulsion. This is particularly used to make nanoemulsions without stirring energy, and the original PIT method can be extended to the case in which the formulation transition is produced by dilution and associated change in formulation, e.g., dilution by water that decreases the salinity or the alcohol or surfactant concentration (C. Solans, J. Esquena, and A. Forgiarini).

Catastrophic inversion data has been reported mostly by three groups for many different systems and conditions (J. L. Salager, B. W. Brooks, and D. H. Smith). The modeling of catastrophic inversion first proposed by E. Dickinson (1981–82) was then presented in detail but still as a qualitative interpretation by J. L. Salager (1986–88), and fitted with actual data by D. H. Smith (1990). Then, G. E. J. Vaessen and H. N. Stein showed that the catastrophe theory model was not completely satisfactory and proposed a competitive coalescence kinetic model along J. T. Davies' (1957) classical approach, but failed to provide a better approach from the practical point of view. Hence, the catastrophe theory model, which applies both to describe the phase behavior with the Maxwell convention and to interpret the dynamic emulsion inversion with the perfect delay convention, is probably the description that makes more sense to account for the thermodynamics underlayer behind emulsion inversion. Some purely physical model based on mixing considerations (A. W. Pacek and A. W. Nienow) allowed an explanation for some features but failed to explain and predict the effect of the surfactant and physicochemical formulation, which cannot be neglected in any realistic approach.

As far as experimental measurements are concerned, D. H. Smith and K. H. Lim have provided the only detailed analysis related to the value of conductivity of an emulsion according to Maxwell relationships in different cases of two- and three-phase emulsions. Unfortunately, they use a different terminology from other main groups which does not help the reader in following their complex discussion. On the other hand, most other groups use a high/low value of the conductivity to define the type of emulsion, and take for granted a cut-off at a fraction of mS/cm, although this is still a controversial issue in some cases. Rheological measurements have been carried out by L. Choplin, J. Allouche, and E. Tyrode. Drop sizes have been studied by B. W. Brooks and S. Sajjadi, by conventional sampling techniques and recently by an in-situ method (F. B. Alban and S. Sajjadi).

Reported applications of emulsification by phase inversion concern waterborne epoxy (Z. Z. Yang), poly-dimethyl siloxanes (J. Rouviere and G. Guérin), and polyisobutene and ionomer systems (B. W. Brooks).

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