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# Emulsion inversion from abnormal to normal morphology by continuous stirring without internal phase addition
## Effect of surfactant mixture fractionation at extreme water–oil ratio

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**Abstract**

When the emulsion inversion from abnormal to normal morphology is induced by continuous stirring only, it takes place through the formation of a multiple emulsion in which the external phase is continuously included as droplets in the dispersed phase drops. In the studied case the system exhibits an initial O/W morphology, then a w/O/W multiple one before inverting into a W/O emulsion. The general trend reported in the literature is that the higher the initial water content, the longer the incorporating process to swell the drops in order to attain the critical dispersed phase volume that triggers inversion. The present study reports, for nonionic systems with a given hydrophilic–lipophilic balance (HLB = 6) and 7 wt.% of surfactant concentration, that this trend is found to be unexpectedly reversed when the initial water content increases beyond 80%. This anomalous result is attributed to an indirect increase in the lipophilicity of the formulation due to the variation of the interfacial surfactant mixture with the water/oil ratio, and to the formation of liquid crystals at high water contents.

*Keywords:* Catastrophic inversion; Multiple emulsion; Phase behavior; Partitioning; Liquid crystal

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## 1. Introduction

An emulsion is a liquid–liquid dispersion stabilized by a surfactant. The classical emulsion preparation process consists in dissolving the surfactant in the suitable continuous phase (in which it has to be soluble), and to add the dispersed phase under appropriate agitation [1,2].

In the last decade, the interest in emulsion inversion, i.e. the change in the morphology from oil-in-water (O/W) to water-in-oil (W/O) or vice versa, has increased as it became a method to produce fine and concentrated emulsions at a low energy expense even with very viscous oils [3–5].

Depending on the changed variable, there are two types of emulsion inversion: the transitional inversion which is induced by the change of the surfactant affinity for the liquid phases, and the catastrophic inversion which is produced by a change in the composition or physical factors of the system, e.g. the water-to-oil ratio, the viscosity of the phases, or the stirring protocol [6].

The catastrophic inversion is usually triggered by the continuous addition of the internal phase of the emulsion [7,8], but it could be also generated by the continuous stirring of an abnormal emulsion [9–11], i.e. an emulsion type that does not correspond to the normal curvature requirement of the interface, according to the Brancoft's rule [12,13], Langmuir's wedge theory [14] or Winsor's interaction energy analysis [15,16].

Abnormal emulsions frequently exhibit a multiple morphology in which the dispersed phase drops contain some tiny droplets of the continuous phase; the presence of these droplets satisfies Bancroft's rule and as a consequence, this inner emulsion is quite stable. Fig. 1 illustrates such a situation for a w/O/W multiple emulsion in which the low case "w" refers to the droplet phase which is inserted in the "O" drops [1].

When an abnormal emulsion is submitted to a continuous stirring, the external phase is continuously included as droplets in the dispersed phase drops and the process goes on indefinitely

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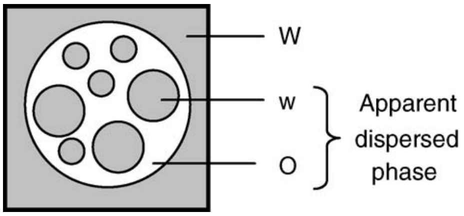

Fig. 1. Symbols for a w/O/W multiple emulsion.

since the inner droplets are stabilized against coalescence. As a consequence, the dispersed phase volume, i.e. w + O, increases until a critical dispersed phase content is reached at which the inversion is triggered [17,18], according to the so-called static inversion protocol. The validity of the critical dispersed phase concept was recently corroborated as the condition for an abnormal emulsion to invert into a normal one, no matter what protocol of inversion is used (dynamic, standstill dynamic, or static) [19].

The surfactant affinity and the water-to-oil ratio required to prepare an abnormal emulsion and to apply an inversion protocol are easily identified in a formulation–composition bidimensional map [6] (see Fig. 2).

The map is divided in three vertical regions. Region A corresponds to a mid-range water-to-oil ratio, while the B and C regions are associated with low and high water content, respectively. Multiple emulsions of the o/W/O and w/O/W type, are spontaneously formed upon stirring in the $B^-$ and $C^+$ regions, respectively. Simple W/O (respectively O/W) emulsions are produced in $A^+$ and $B^+$ (respectively $A^-$ and $C^-$) zones [20].

The sign after the letter indicating the regions corresponds to the affinity of the generalized formulation expressed through the hydrophilic–lipophilic deviation (HLD). It is positive if the surfactant affinity for the oil phase dominates and negative for the opposite case. HLD = 0 corresponds to the so-called optimal formulation at which the surfactant exhibits the same affinity for the oil and water phases. At this formulation many systems exhibit three-phase behavior with a microemulsion middle phase in equilibrium with excess oil and water. More information may be found in the recent literature [21–23].

This concept is based on the correlations for optimum formulation of enhanced oil recovery, which have been introduced 30 years ago [24]. The dimensionless generalized formulation expression for nonionic surfactant systems may be written as follows:

$$\mathrm{HLD} = \alpha - \mathrm{EON} + b \times S - k \times \mathrm{ACN} + t(T - 25) + a \times A \quad (1)$$

where $\alpha$, $k$ and $t$ are surfactant parameters, EON the average degree of ethoxylation of the surfactant, ACN the alkane carbon number (or eventually EACN, the equivalent alkane carbon number if the oil is not an alkane), $S$ and $A$ the salt and alcohol concentrations, $b$ and $a$ the constants characteristic of each type of salt and alcohol and $T$ the temperature.

Eq. (1) could be written as follows by defining the surfactant parameter $\beta = (\alpha - \mathrm{EON})/k$, which is available for many diferent surfactants in the literature [23].

$$\mathrm{HLD} = k \times \beta + b \times S - k \times \mathrm{ACN} + t(T - 25) + a \times A \quad (2)$$

Optimal formulation (HLD = 0) coincides with the horizontal branch of the standard inversion line (stair like bold line in Fig. 2), which is determined by stirring an equilibrated surfactant-oil-water system and measuring its electrolytic conductivity. The trespassing of the horizontal branch produces a transitional inversion, while the crossing over the lateral branches corresponds to a catastrophic inversion [25].

The central (horizontal) branch of the inversion line is always at the same location (i.e. at optimal formulation), whereas the lateral (vertical) inversion branches can move toward the center or the sides of the map, depending on the protocol and other variables such as phase viscosity or surfactant concentration [26,27]. As a consequence essentially all effects can be rendered in a three-dimensional diagram as introduced by Salager et al. [28].

In this paper, the influence of the water-to-oil ratio and the phase behavior in the emulsion inversion produced by continuous stirring only is interpreted on the two-dimensional generalized formulation–composition map. Since the formulation and composition remain constant, the point that represents the system in Fig. 2 map does not change position.

Hence the emulsion inversion is due to a change in condition, which shifts the $A^+/C^+$ branch of the inversion line from left to right as stirring goes on.

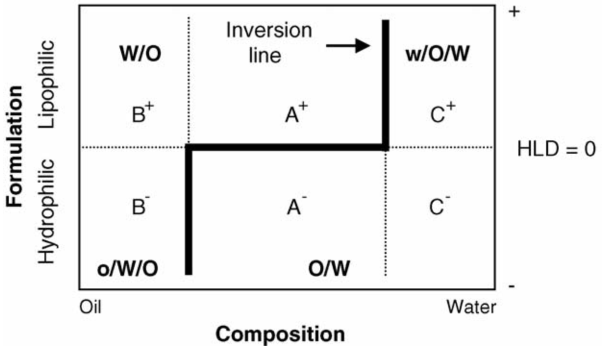

Fig. 2. Bidimensional formulation–composition map illustrating emulsion types and standard inversion frontier.

## 2. Experimental section

### 2.1. Surfactants and other reagents

In all experiments, the oil phase used is a kerosene cut equivalent to a mixture of nonane and decane (EACN = 9.6) supplied by Fluka. The aqueous phase consists of purified water (Milli-Q Millipore, France) in which 1 wt.% of NaCl (purity >98%, Aldrich) is incorporated to increase the conductivity of the water phase and allow the detection of the inversion point. Two nonionic surfactants supplied by Aldrich are used: Span80, a sorbitan monooleate (HLB = 4.3), is dissolved in the kerosene phase; Igepal CO-630, a polyethoxylated (9 EO) nonylphenol (HLB = 13) noted NP9EO is added to the water phase. The total surfactant concentration is 7 wt.%, and the Span/Igepal wt.% proportion is 80/20, and results in HLB = 6 when a linear mixing rule is used. A concentration of 7 wt.% of 2-butanol, supplied