

EMULSION MORPHOLOGY FOLLOW-UP BY SIMULTANEOUS IN SITU CONDUCTIVITY AND VISCOSITY MEASUREMENTS DURING A DYNAMIC TEMPERATURE-INDUCED TRANSITIONAL INVERSION

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1 INTRODUCTION

The effect of the physicochemical formulation variables can be brought together by using a generalized concept such as Winsor's R ratio or the Surfactant Affinity Difference (SAD) Concept or its Hydrophilic Lipophilic Difference (HLD) numerical equivalent [1,2], which defines the free energy of transfer of a surfactant molecule from oil to water phase. HLD may be expressed, for non ionic surfactant systems by Equation (1), that specifies the compensating effects of formulation variables (a similar, although not shown here, equation exists for ionic systems) :

$$\text{HLD} = \alpha - \text{EON} + bS - K \text{ACN} + t \Delta T + aA \quad (1)$$

Where

α is a parameter characteristic of the Surfactant Lipophilic group,

EON is the average number of ethylene oxide groups per surfactant molecule,

S is the salinity of the aqueous phase in wt% NaCl (or equivalent),

ACN is the number of carbon atoms in the alkane molecule (or equivalent),

ΔT is the temperature difference with respect to a reference temperature (for instance 25°C),

A is the concentration (% vol) of alcohol,

k,t are constants, characteristic of the surfactant type,

a,b are constants, characteristic of the alcohol and electrolyte.

HLD measures the relative affinity of the surfactant for the aqueous and oleic phase. At a value $\text{HLD} = 0$, the surfactant affinities are exactly matched, and a minimum interfacial tension is reached, sometimes in the ultra low range ($<0.001 \text{ mNm}^{-1}$) so that the capillary phenomena virtually vanish. If HLD is positive (respectively negative), the surfactant exhibits more affinity for the oil (respectively water) phase. Such a concept presents the advantage of handling the influence of formulation through a single variable. It is essentially nothing but a generalization of previously proposed concepts such as the Griffin's HLB or the Shinoda's PIT, with the main advantage of including the effects of all formulation variables in a quantitative way [3]. The result is a significant reduction in the number of degrees of freedom for describing the phase behavior of a surfactant-oil-water (SOW) system, with three independent variables: the generalized formulation HLD, the water-oil ratio (WDR) and the surfactant concentration. These 2 last variables are known as composition variables [4]. A now commonly accepted 2D phase behavior mapping is that corresponding to a constant surfactant concentration, as illustrated in Figure 1 :

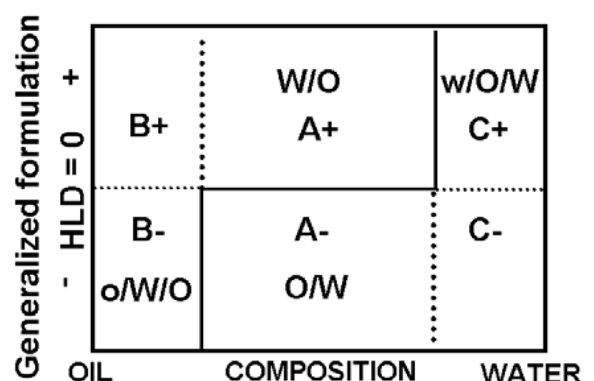


Figure 1: Generalized formulation – composition Bidimensional map

This map is divided into six zones. Those labelled as “+” (surfactant affinity greater for the oil) are separated from those labelled as “-” by the so-called optimum formulation for three-phase behavior or low interfacial tension. On the other hand, zones labelled as “A”, “B” or “C” differ in the water (or oil) content. The line that separates W/O emulsions from O/W emulsions is the inversion line, and generally exhibits a stair shape [5]. The horizontal branch (HLD=0) has been labelled as the transitional inversion line, whereas the vertical ones are known as catastrophic inversion lines.

In this paper, we will concentrate on the (dynamic) transitional inversion process, in other words in a process in which the generalized formulation is changed continuously, while the system is maintained under constant stirring conditions (rotational agitation speed for a given stirrer-vessel geometry). Among the different possibilities for changing the HLD, we will choose the temperature change method, also called the Phase Inversion Temperature (PIT) method. This method is facilitated provided the chosen surfactant system is very temperature sensitive, for example a non ionic surfactant which becomes less hydrophilic as temperature increases and conversely.

The emulsion drop size is the result of a dynamic equilibrium between the effects that tend to decrease the drop size and the ones that make the drop coalescing. As the HLD=0 formulation is approached from both sides, the interfacial tension decrease favors the breaking process and thus a smaller drop size. However, the emulsion stability decreases as well, and drops are likely to coalesce at once upon contact near HLD=0, which favors the opposite trend, i.e. a larger drop size. The first effect dominates far from HLD=0, whereas the second one prevails near it. This results in a complex variation in the drop size, which exhibits two minima, one on each side of HLD=0 line, and as a consequence a corresponding complex variation of the viscosity with two maxima, as shown schematically in Figure 2

The HLD change during a dynamic transitional inversion has been reported to induce complex morphologies as multiple emulsions [6,7]. This has been evidenced by indirect optical techniques through sampling procedures. Other authors [8] have identified, with the use of conductivity techniques and sampling procedures, the formation of multiple emulsions as the result of the inclusion of continuous phase into the dispersed one. Close the inversion line (HLD=0), due to the presence of a bicontinuous micro emulsion (M), this can be a M/O/M type multiple emulsion.

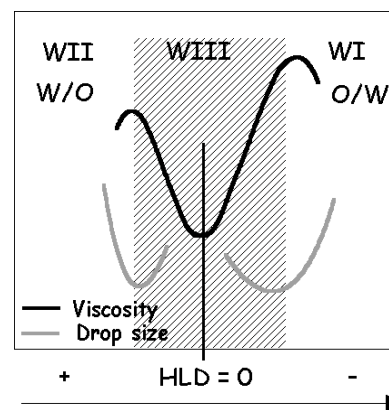


Figure 2: Viscosity and drop size variations during dynamic transitional inversion. The shaded area corresponds to a three-phase behavior, which corresponds to a bicontinuous microemulsion (also called WIII).

A more complete description of the mechanisms involved in the dynamic transitional inversion induced by a temperature change is still missing. This paper aims at the development of a new (original) technique allowing us to in situ follow-up the simultaneous evolution of both viscosity and conductivity during this dynamic transitional inversion without any sampling. This will contribute to shed a new light on the involved mechanisms.

2 MATERIALS AND METHODS

The oily phase is made of a mixture of kerosene and isopropanol (Fluka Chemika, France). The use of isopropanol (2 % vol in the total system) eliminates mesophases and liquid crystal formation, speeds up the drop breakup and thus eliminates any possibility of hysteresis or liquid crystal encapsulation near the PIT [9]. Moreover, its influence on the HLD is negligible ($aA \approx + 0.05$). The water is purified water (Milli-Q, Millipore) and the concentration of NaCl (purity > 99.5 %, Merck, France) is 1 g/100 ml of water phase. The surfactant used is a sorbitan trioleate (Tween 85, HLB=11) with an average of 20 moles of ethylene oxide per surfactant mole (Fluka Chemika, France). The concentration of surfactant is 4.5 g/100 ml of total volume.

The samples are prepared, placed in a closed vessel and are left to equilibrate for 24h at constant temperature (50°C).

The emulsification process is carried out in a “rheo-reactor”, which simply consists of a vessel and of an impeller adapted to a RFS II (Rheometric Scientific, USA) rheometer. The detailed geometrical arrangement is illustrated in Figure 3.

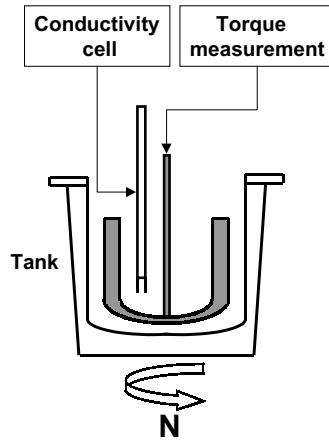


Figure 3: Rheo-reactor geometry

An analytical method based on a Couette analogy allows to quantitatively analyze torque-rotational speed data in order to extract “absolute” viscosity-shear rate data in such a non-conventional geometry [10].

The Couette analogy consists first in determining a radius R_i of an equivalent Couette inner cylinder, having the same height L than the impeller, which gives for the same rotational speed N , the same torque C , in a cylindrical vessel of radius R_e . Solving the equations of change in this virtual Couette geometry, assuming steady state, laminar regime and isothermal conditions for a power-law fluid (this last assumption is always valid for a limited shear rate range),

$$\eta = k\dot{\gamma}^{n-1} \quad (2)$$

where k and n are the consistency and the flow index respectively, the following expression for R_i is obtained:

$$R_i = \frac{R_e}{\left[1 + \frac{4\pi N}{n} \left(\frac{2\pi k L R_e^2}{C} \right)^{1/n} \right]^{n/2}} \quad (3)$$

For a given set of (N, C) values, R_i is a weak function of n , therefore the determination of R_i can be done in the particular case of $n=1$, that is with a Newtonian fluid of known viscosity. Once R_i has been determined in such a virtual Couette geometry, we can calculate the shear stress and the shear rate profiles, from which it is easy to deduce the viscosity at a given position in the virtual gap. The shear stress is given by:

$$\tau = \frac{C}{2\pi L r^2} \quad (4)$$

and the shear rate, for a power-law fluid, by:

$$\dot{\gamma} = \left[\frac{\frac{4\pi}{n} \left(\frac{R_i}{r} \right)^{2/n}}{1 - \left(\frac{R_i}{R_e} \right)^{2/n}} \right] N \quad (5)$$

Even for a large virtual gap, it has been found [10] that a specific position $r=r^*$ exists in the gap at which the term in brackets in this last equation is essentially independent of the power-law index n , in other words of the rheology of the fluid. This r^* value can be calculated in the particular case of $n=1$, and then both shear stress and shear rate are evaluated at this specific r^* value:

$$\tau_{r^*} = \frac{C}{2\pi L (r^*)^2} \quad (6)$$

and

$$\dot{\gamma}_{r^*} = \frac{4\pi N \left(\frac{R_i}{r^*} \right)^2}{1 - \left(\frac{R_i}{R_e} \right)^2} \quad (7)$$

The viscosity is then obtained by the ratio between τ_{r^*} and $\dot{\gamma}_{r^*}$, and corresponds to a shear rate equal to $\dot{\gamma}_{r^*}$.

This method has been tested for several vessel-impeller combinations and for a great number of rheologically complex systems, such as food emulsions like mayonnaise, salad dressing. The experimental results were found to fit fairly well with those obtained using conventional geometries over a wide range of shear rates, within the experimental error estimated to be no more than 5%.

The emulsification is carried out directly in the rheo-reactor at a constant rotational speed of the impeller that corresponds, for the specific geometrical arrangement, to an effective shear rate of 100s^{-1} , and at 50°C . The temperature is controlled with a thermostatic bath (Huber, Germany), and once an equilibrium in viscosity is reached, the temperature is started to decrease monotonically down to 10°C at a 0.05°C/s cooling rate. Because of the small effective volume of emulsion in the rheo-reactor, and because of the continuous homogenization and macromixing imparted by the action of the impeller, the measured temperature corresponds to that of the whole volume ($\pm 0.05^\circ\text{C}$). Parallel experiments with a specific device essentially equivalent to the rheo-reactor but without the torque transducer, allowing the possibility to carry out microscopic observations during the transitional inversion, have been performed.

Simultaneously to the viscosity and temperature measurements, we will in-situ follow-up the conductivity with a LF340 conductimeter and a Tetracon cell 325 (WTW, Germany), as illustrated in Figure 3. Provided a relation between the water volume fraction and the theoretical value of the conductivity of a simple O/W emulsion exists, the presence of encapsulated water due to a multiple emulsion morphology will be easily detected because of a lower than expected conductivity value.

Finally, drop size measurements will be carried out off-line from drawn small aliquots with the use of a Mastersizer Hydro 2000 MU analyser (Malvern Instruments, UK).

3 RESULTS AND DISCUSSION

We will only present the results concerning a system containing an equal amount of oil and water. Figure 4 reports the evolution of both conductivity and viscosity while the temperature is monotonically decreased and the system is maintained under constant agitation speed conditions ($\dot{\gamma} = 100\text{s}^{-1}$). The corresponding followed path on the bidimensional formulation-composition map during the transitional inversion is represented in a form of an insert in Figure 4.

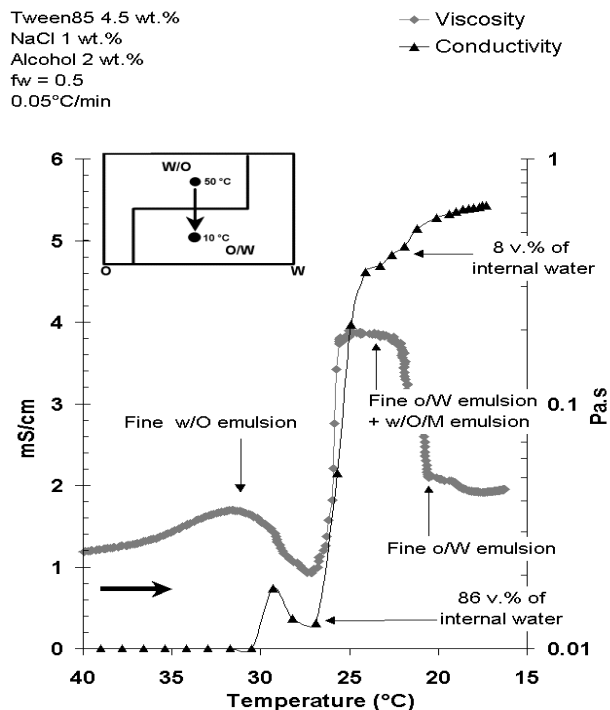


Figure 4: Evolutions of viscosity and conductivity during temperature-induced transitional inversion

The initial W/O emulsion exhibits as expected a zero conductivity from 50°C up to a temperature value around 31°C, that corresponds to a first maximum in

viscosity. This temperature also corresponds to a minimum in drop size, and is an indication of the frontier between the W/O – A⁺ zone and the bicontinuous microemulsion (WIII or three-phase) zone.

Below 31°C, the conductivity increases up to a value of 0.8 mS/cm. This indicates a morphological change in the system. Dispersibility experiments were carried out by with drawing a small aliquot and pouring it immediately into oil or water. The instantaneous dispersion occurs in oil, therefore the outer phase remains the oil. Because the conductivity value is too high for an ordinary W/O system, this indicates the presence of some bicontinuous conductive microemulsion. The concomitant decrease in viscosity supports this explanation.

From 27°C down to 23°C, the conductivity undergoes a sudden and significant increase up to 4.5 mS/cm. Dispersibility experiments carried out in between this temperature range indicate that the system is neither instantaneously dispersible in water nor in oil, which means that the “external phase” is very probably a microemulsion (M). Microscopic observations (Figure 5) clearly show large black oil drops at around 27°C, supporting the existence of a W/O/M morphology.

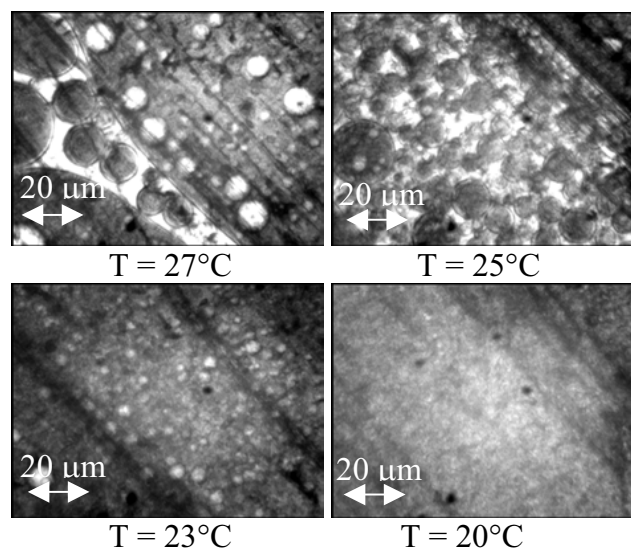


Figure 5: microscopic observations

The inner water phase which is quite high at 27°C starts to move towards the external phase and the conductivity increases accordingly. Concomitantly, the system viscosity increases significantly and reaches a maximum around 25°C – 23°C. This should correspond to a complex “mixture” of fine O/W emulsions with a multiple W/O/M emulsion.

From 23°C up to 20°C, the conductivity continues to increase slightly up to a plateau value around 5.5 mS/cm, meanwhile the viscosity decreases sharply.

Dispersibility experiments indicate that the system instantaneously disperses into water. This means that the system progressively becomes a simple fine O/W emulsion.

A further decrease in temperature shows no evolution of the conductivity, while the slight decrease in viscosity with decreasing temperature is the consequence of an increase in the drop size of the O/W emulsion as expected when we move away from the PIT.

The final drop size distribution is illustrated in Figure 6, showing a sub-micron average size, which is typical of the sizes obtained with PIT emulsification processes [11].

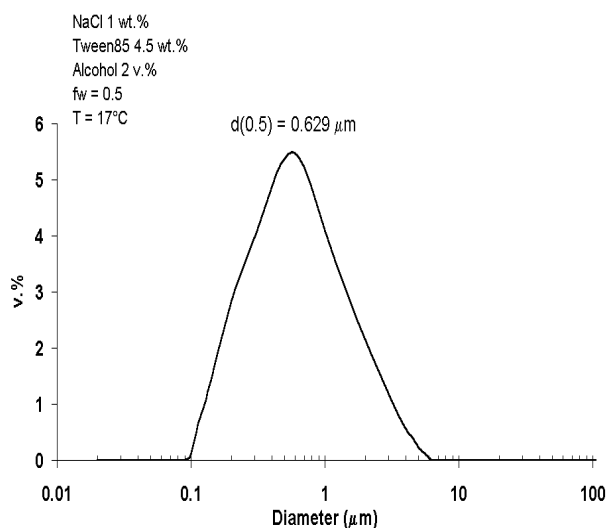


Figure 6: Final drop size distribution

4 CONCLUSION

Simultaneous in-situ follow-up of both conductivity and viscosity during a dynamic temperature-induced transitional inversion process has been realized in a simple SOW system. It has been shown that around the inversion line, complex morphologies are exhibited, in other words mixtures of fine simple emulsions and multiple emulsions having as the external phase a bicontinuous microemulsion. The existence of these complex morphologies should be the result of the dynamic character of the transitional inversion process.

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