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Light Backscattering as an Indirect Method for Detecting Emulsion Inversion

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Many phenomena take place during different types of emulsion inversions, particularly a change in interface curvature and drop size, which could be detected by backward light scattering. Monitoring the backscattering signal allows us to detect the emulsion inversion in three main cases, one transitional and two catastrophic types. The backscattering data could give some clue as to emulsion morphology, which is not available from conductivity measurements.

Introduction

Emulsion inversion is an important phenomenon because it is a way to produce emulsions with characteristics such as fine drops at a low energy level[1] or with an extremely viscous internal phase[2] when a very energetic method is not suitable.[3] There are several inversion mechanisms,[4] and most of them depend on many variables.[5] In practice, it is extremely important to monitor morphology changes, particularly those related to the intermediate stage (e.g., three phase or multiple emulsion occurrence), which are often impossible to follow by visual (microscopic) means, particularly because of the fast evolution taking place near inversion.

The classical method of monitoring inversion is to measure the emulsion conductivity, which is a way to estimate the external or continuous phase proportion when it is an aqueous phase. In most applications, the aqueous phase contains some electrolyte at a concentration large enough to provide a high enough conductivity. The monitoring of viscosity has recently been proposed as a substitute or complementary measurement, and it offers promising results.[6−8] However, the emulsion viscosity depends on many variables other than the emulsion type, and the interpretation is not always clear cut, particularly with viscous fluids and high internal phase content or with multimodal emulsions.[9,10] Drop size variations also correlate with inversion in some cases, such as transitional inversion, though not in a simple way.[6,11] But in any case, the drop size and distribution depend on many other variables, particularly formulation and composition.[12]

Because the structure of the emulsion and the interfacial curvature drastically change during inversion, it is believed that an optical signal related to curvature (e.g., some reflectivity measurement) should allow us to detect the inversion.[13] This is sustained by the fact that the curvature swaps at inversion, at least in some specific cases, and therefore goes through a near-zero value. This letter reports the detection of emulsion-phase inversion by means of light backscattering measurements.

Experimental Section

The two main kinds of emulsion dynamic inversion (i.e., transitional and catastrophic protocols[14]) are carried out in a conventional way,[15,16] with continuous monitoring of the backscattering through an available commercial apparatus (i.e., Turbiscan on-line model (TOL) from Formulaction, France). This equipment produces a backscattering signal that is a measurement of the near-infrared ($\lambda = 850$ nm) light diffused at an angle close of to 135°. The backscattering percentage is reported with respect to a reference suspension of 0.3 μm latex particles in silicone oil. The equipment has been routinely used to evaluate the variation of particle size in suspensions and emulsions.[17]

The emulsion sample to be evaluated is circulated with a peristaltic pump through the cylindrical cell of the apparatus in a closed circuit connected to the emulsion vessel.[18] The conductivity is measured with a Radiometer Analytical conductimeter with a platinized platinum cell located inside the emulsion vessel. The emulsion vessel is a jacketed glass cylindrical tank continuously stirred with a Rushton turbine rotating at approximately 1000 rpm. The changes in water

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or oil content are provided through peristaltic pumps that inject programmed volumes into the system; the change in temperature is produced by circulating hot and cold water through the jacket.

The surfactant used in the transitional inversion experiments is a commercial hexaethoxylated iso-tridecanol from Seppic France. The oil phase is *n*-heptane. The water phase contains 1 wt % sodium chloride to provide the required high conductivity. The water/oil ratio is unity on a volume basis, and the experiment is carried out in a thermostated 100 mL vessel. Alcohol (3 vol % 2-propanol) is added to avoid the formation of mesophases, which are known to complicate the interpretation. Transitional inversion is carried out according to the phase-inversion temperature (PIT) method,[19] whose protocol is described elsewhere.[6]

With nonionic surfactant systems, the temperature increase induces a formulation change from hydrophilic to lipophilic, passing through balanced hydrophilicity three-phase behavior that matches the PIT (here 55 °C). In the present experiment, the temperature increase is a linear gradient at 0.9 °C/min, which is known to be slow enough to preclude the occurrence of a significant delay,[20] whose existence in any case does not affect the conclusions.

Catastrophic inversion experiments are also carried out according to the usual protocol from abnormal to normal morphology, as described in detail elsewhere.[15,16] It consists of the continuous addition of the internal phase of an emulsion in a formulation case that is not favorable to the initial emulsion type according to Bancroft's rule. The surfactants used are Span 20 and Tween 80 at 1 wt % concentration in the system. The water phase is a 1 wt % sodium chloride solution. No alcohol is added. The oil phase is a petroleum ether aliphatic cut with a boiling range of 60−80 °C (i.e., equivalent to a mixture of hexane and heptane). The two possible cases (i.e., increase and decrease of the water fraction) are reported: (1) an initial O/W emulsion with a lipophilic formulation (Span 20 HLB = 8.6) to which oil is added continuously under stirring until inversion to W/O takes place and (2) an initial W/O emulsion with a hydrophilic formulation (Tween 80 HLB = 15) to which water is added until inversion. The emulsification vessel has a 1 L capacity. The phase addition rate is set to 70 mL/min.

Both inversion types have been characterized from the phenomenological point of view, though the mechanisms and critical parameter values have been found to vary substantially according to the protocol.[15,16] Nonetheless, the purpose of this letter is not to consider the intricacies of the phenomenology but to evaluate the performance of an indirect detection method. Hence, the cases are selected as plainly typical of the two main kinds of inversion and are essentially insensitive to the surfactant type and concentration. Characteristics depending on the protocol will be discussed in forthcoming papers.

Results

In all cases shown in Figures 1−3, the double plotting represents the variations of the emulsion conductivity (in mS/cm) and backscattering (in %) as a function of the scanned variable (i.e., temperature or water fraction). The reported backscattering values are averaged over a short period of time (15 s) so that the instantaneous fluctuations that could deviate up to 20% are damped. In these experiments, the emulsion inversion is detected, unambiguously in all plots, from a very sudden variation of the conductivity.

Figure 1 represents the data of a transitional inversion due to a rising temperature scan, which results in an increase in lipophilicity. The corresponding decreasing temperature scan, which generates the reverse formulation change, is found to generate essentially the same data. It may be said that under the present experimental conditions, particularly because of a low temperature gradient and the presence of alcohol, there is no hysteresis in the transitional inversion, as expected from recent reports.

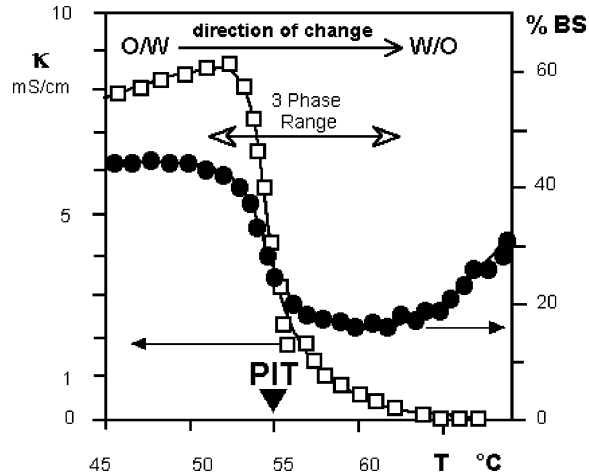

Figure 1. Variation of emulsion conductivity (κ) and backscattering (BS) in a transitional inversion produced by an increase in temperature. System: 5 wt % hexaethoxylated iso-tridecanol/*n*-heptane/1 wt % NaCl/3 vol % 2-propanol.

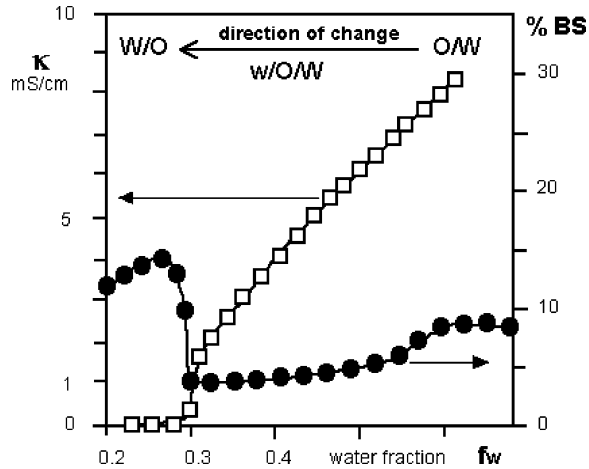

Figure 2. Variation of emulsion conductivity (κ) and backscattering (BS) in a catastrophic inversion produced by an increase in oil content. System: 1 wt % Span 20 (HLB 8.6)/1 wt % NaCl brine/petroleum ether.

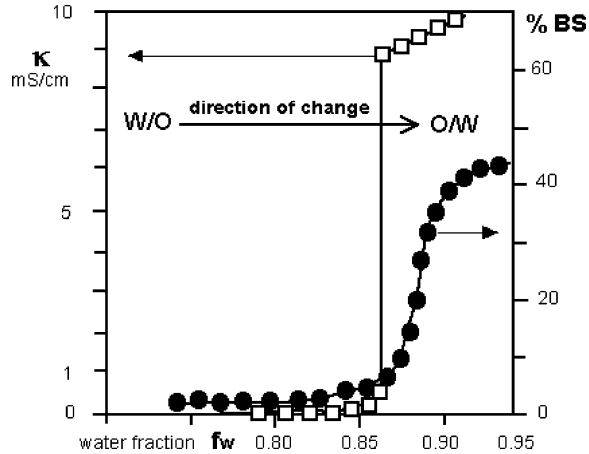

Figure 3. Variation of emulsion conductivity (κ) and backscattering (BS) in a catastrophic inversion produced by an increase in water content. System: 1 wt % Tween 80 (HLB 15)/1 wt % NaCl brine/petroleum ether.

In Figure 2 for the case of catastrophic inversion in which oil is added to an initial O/W emulsion, the lipophilic formulation

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induces the formation of the opposite W/O emulsion. This situation is likely to generate a multiple w/O/W morphology, in which (w) tiny water droplets are included in the (O) oil drops dispersed in the (W) water external phase. When this happens, the volume fraction of the external (W) water phase is reduced; consequently, the multiple emulsion conductivity decreases. This is just what is seen in Figure 2 in which the conductivity that continuously falls to about 1.5 mS/cm is systematically lower than the expected value from the total water content. In this experiment, the inversion actually takes place at fw = 0.3, where a sharp conductivity drop is exhibited. In the Figure 3 case (also catastrophic), the formation of a multiple emulsion before inversion (e.g., near fw = 0.8) is also very likely. However, this time it would be of the o/W/O type, which is essentially impossible to detect from the conductivity measurement.

In all three Figures, the inversion is clearly associated with a drastic change in backscattering. Nevertheless, it is worth remarking that there is no association of a high or low backscattering value with any type of emulsion, as is the case for the conductivity variation. O/W emulsions exhibit high backscattering in Figures 1 and 3, but the water external O/W and w/O/W emulsions show weak diffusion in Figure 2. On the contrary, the W/O emulsion exhibits strong scattering in Figure 2 but not in the others.

Actually, the change in backscattering seems to be related mainly to a change in drop size, which is likely to take place at or near the inversion point,[6,21−23] For instance, the steep increase and maximum in backscattering close to fw = 0.25 in Figure 2 is probably produced by the release of fine droplets that were the inner (w) droplets in the (O) drop in the multiple emulsion prior to inversion, according to what is known from other observations.[4,8] However, there is no straightforward explanation for the further decrease in backscattering below fw = 0.25, although this may be due to the normal increase in drop size as the formulation deviates from optimum.[24] However, the increase in backscattering at fw = 0.90 in Figure 3 is probably due to the same effect and suggests the presence of a o/W/O multiple emulsion prior to inversion, which is essentially impossible to determine from the conductivity measurement in the fw = 0.8−0.85 range.

In Figure 1, the strong backscattering around $T = 45-50$ °C might be associated with the small drop size that is generally found at some distance from the PIT or balanced formulation because of the best compromise between low tension and low stability.[6,22] Moreover, such an increase would be expected on the other side, around $T = 60$ °C, but it is found only beyond 70 °C and therefore seems to be shifted far away from the phase-inversion temperature (55 °C according to the conductivity data). This might not really be the case because the three-phase behavior region is found to extend up to 65 °C. Because the fine droplet structure is known to occur only out of this very low tension region where drops are elongated and where they coalesce very rapidly, the increase in the backscattering signal may again be conjectured to correspond to the fine structure on this side.[12,24] Nevertheless, the match in Figure 1 is not obvious with respect to interpretation and indicates that the method is to be considered to be indirect, at least for now.

In any case, there is no doubt that the backscattering signal exhibits a strong variation close to the inversion point and thus provides handy complementary information to use in following up on such events. As the learning curve progresses, this easy-to-use detection system is likely to bring more valuable information about the way the inversion is taking place, particularly a more quantitative hint of the drop size evolution, which will be discussed in a forthcoming paper.

Conclusions

The monitoring of reflectivity through the backscattering signal brings additional information on the events taking place during all kinds of emulsion inversion. A telltale abrupt variation points out the occurrence of inversion, and the actual value of the backscattering provides some clue as to other characteristics of the process.

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