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# Visible light backscattering monitored in situ for transitional phase inversion of BrijL4-isopropyl myristate-water emulsions

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**ABSTRACT:** The transitional phase inversion of BrijL4/isopropyl myristate/water emulsions is detected by monitoring the visible Light BackScattering (LBS) using an optical fiber. For comparison, electrical conductivity is simultaneously followed during the heating-cooling cycle. The LBS signal exhibits always a minimum near the Phase Inversion Temperature value determined with conductivity. The LBS results are also analyzed in terms of Winsor type for equilibrated systems and particle size of O/W emulsions. LBS signal points out transparency area for inversion through Winsor IV type and allows thus to determine the X point of fish diagram for equilibrated systems more quickly. The LBS signal presents a maximum for average diameter of O/W emulsions around 1 micron, and depends on the particle size distribution. The use of a commercial visible light

backscattering optical fiber exhibits thus several advantages over the classical conductivity measurement for transitional inversion phase emulsification process monitoring.

## 1. INTRODUCTION

A temperature increase tends to trim down the interactions between water molecules and polyether chains of polyethoxylated nonionic surfactants; in the same way, these surfactants allow the emulsion to inverse during heating from O/W to W/O morphology, at the so-called Phase Inversion Temperature PIT<sup>1</sup>. Reverse direction phase inversion from W/O to O/W takes place upon cooling at a temperature more or less close to the PIT. Such phase inversions driven by a phase behavior transition often produce fine droplets emulsions with a low energy expense, even with high viscous phases. This has been used for decades for such purpose<sup>2</sup> and is called the PIT emulsification-method<sup>3</sup>.

Any *in situ* emulsion characterization method able to detect changes in drop size, electrical properties or viscosity is likely to be a candidate to monitor the phase inversion process, and to pinpoint the PIT with accuracy. The classical way to detect the emulsion inversion temperature consists in measuring the conductivity of the emulsion. Conductivity is typically high for the O/W morphology and low for the W/O one, particularly if the aqueous phase contains some electrolytes as often the case in practice. Conductivity of O/W emulsions can be calculated through mathematical models<sup>4</sup>; equations have also been established for three-phase systems considering volume fractions of each dispersed phase<sup>5</sup>. Electrical properties of emulsions under sinusoidal constraints have been studied and the phase inversion temperature was detected from impedance at low frequencies by use of parameters such as double layer capacitance and charge transfer resistance.<sup>6-9</sup> However, the conductimetric method has some drawbacks. First of all, it needs to add an electrolyte such as NaCl

in the aqueous phase to get a clear-cut detection of the phase inversion, and is not totally reliable with very high viscous systems for which creation of stagnant unmixed zones is favored <sup>10</sup>. Moreover, conductivity is inefficient to detect multiple emulsions of the o/W/O type. Finally, conductivity does not give any valuable information about the drop size, which is often an important issue in practical cases.

For *in situ* inversion phase process monitoring, optical fibers can be used to measure Light BackScattering signal (LBS). As conductivity, this is a non destructive and non invasive emulsion characterization technique. Fiber in Near-InfraRed area (NIR) has been used to study transitional phase inversion of water-heptane/toluene emulsions <sup>11</sup>. More recently, the same team followed NIR spectra during catastrophic inversion of emulsions <sup>12</sup>. The NIR backscattering at 850 nm has also been used to study on line transitional <sup>13,14</sup> (technical-C<sub>12</sub>E<sub>4</sub>/decane/water emulsion) and catastrophic (Tween 80 or Span 20/petroleum ether/water emulsion) inversions. However, evaluated emulsion was circulating outside the reactor through the cylindrical cell of the used apparatus (Turbiscan-on-line) <sup>14</sup>. The authors have noted a variation of the LBS near the catastrophic inversion point, neat when increasing the oil content in a O/W emulsion and more gradual when adding water into an W/O emulsion. Surprisingly no study considering emulsion phase inversion monitored with backscattered light in the visible range has been published.

In the present article, we analyze the visible part of the backscattering signal transmitted by an optical fiber during phase inversion of ethoxylated alcohol BrijL4/isopropyl myristate/water systems at different concentrations of surfactant. The purpose of this work is to study if on line LBS in visible range can be used as a method to detect the phase inversion temperature with accuracy. For each emulsion, both conductivity and visible light backscattering measurements were monitored during heating-cooling cycle. Moreover, obtained light backscattering signals are analyzed with respect to

the phase diagram (temperature vs. surfactant concentration) of equilibrated studied systems and also with respect to the diameter and polydispersity of the O/W emulsions at 20°C-

## 2. MATERIALS AND METHODS

### 2.1. Materials

Technical grade polyoxyethylene lauryl ether with an average of 4 ethylene oxide groups per molecule was supplied by Sigma–Aldrich as BrijL4. Isopropyl myristate (IPM) was purchased from Cooper. Sodium chloride NaCl (purity  $\geq 99.5\%$ ) was obtained from Acros Organics. Demineralized water (conductivity  $1.34 \mu\text{S}\cdot\text{cm}^{-1}$  at  $21^\circ\text{C}$ ) was used in the aqueous phase.

### 2.2. Definitions

The percentage of BrijL4 and the water weight fraction  $f_w$  are calculated below where  $m_{\text{BrijL4}}$ ,  $m_o$  and  $m_w$  are the weights of BrijL4, IPM and water respectively.

$$\%BrijL4 = \frac{m_{BrijL4}}{m_w + m_o + m_{BrijL4}} \cdot 100$$
$$f_w = \frac{m_w}{m_w + m_o}$$

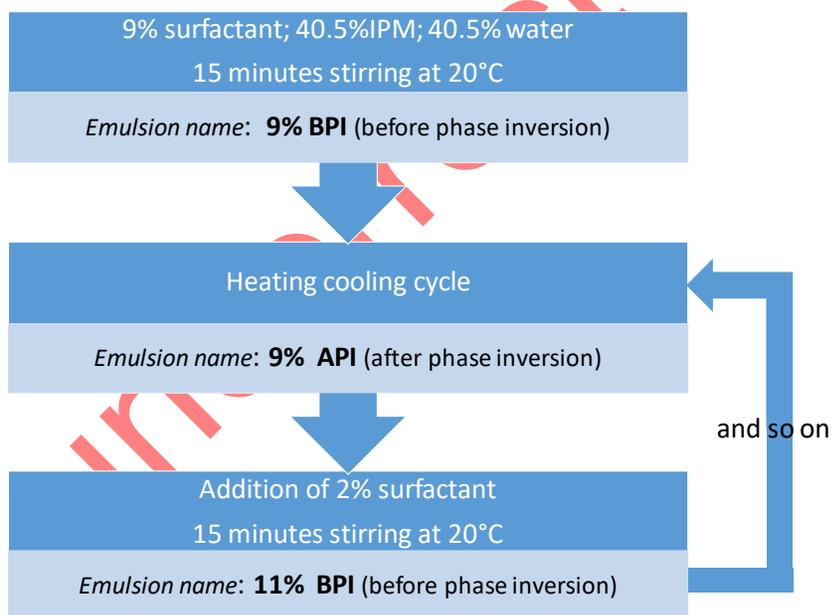
### 2.3. Preparation of emulsions by magnetic stirring at room temperature

9% BrijL4/IPM/water system ( $f_w = 0.5$ ) was prepared by pouring in a 25 ml glass bottle 22.75 g water, 22.75 g IPM, and then 4.5 g of BrijL4. The system is mixed at room temperature by continuous magnetic stirring at 800 rpm. 0.5 g samples are withdrawn at different stirring time for size analysis of formed emulsions.

#### 2.4. Preparation of emulsions by phase inversion temperature process

A 50 mL double jacketed reactor that permits introduction of both conductivity cell and optical fiber was used. To ensure homogeneity inside the reactor, mechanical stirring at 400 rpm is performed using a turbine. Heating-cooling cycles are achieved by circulation of water in the double jacket of the reactor. Temperature changes are achieved thanks to a cc3 Huber Ministat bath. This experimental setup is different from that already described for rheological studies<sup>15</sup>.

The first 9% BrijL4/IPM/water emulsion is prepared by pouring in the reactor 22.75 g of water, 22.75 g of IPM, and then 4.5 g of BrijL4 ( $f_w = 0.5$ ). This mixture is stirred for 15 min at 20°C. A heating-cooling cycle (20-65-20 °C) under stirring is then applied with a gradient of temperature of 1 °C.min<sup>-1</sup>. The next emulsions with 11, 13, 15 and 17% surfactant are formulated, by adding an aliquot of 2% BrijL4 between each heating-cooling cycle. **Schema 1** lists the successive steps of the process and specifies the names used for each of the obtained O/W emulsions.



**Schema 1.** Fluxogram of successive steps of the process managed at 400 rpm and specific names used for each of the obtained O/W emulsions.

In place of the protocol of **scheme 1**, we could have made 5 emulsions with 9, 11, 13, 15 and 17% of surfactant and apply for each emulsion a cooling heating cycle. However, for high concentrations of surfactants (15 and 17%) it is perfectly necessary to apply several cycles of heating cooling so that the system is stabilized (ie when there is practically no difference between PIT in heating ramp heat and PIT in cooling ramp. So we preferred to add fractions of 2% surfactant, to realize only one cycle of heating-cooling. In addition, this allows us to reduce the amount of oil and surfactants used.

It is to notice that the first 9% BPI emulsion is particular because not obtained like the others after two transitionnal phase inversions, but only by a simple stirring of the system at 20°C.

## **2.5. Conductivity measurements**

The conductivity and temperature are measured by a Radiometer Analytical CDM 210 conductimeter fitted with a CDC741T platinized platinum probe. The conductimeter and temperature signals are sent to a data acquisition system. The software used was custom written in the Labview 7.1 National Instruments platform software.

## **2.6. Light backscattering measurements**

The Light BackScattering (LBS) intensities are measured with an UV/VIS/NIR optical reflection and backscattering probe from *Ocean Optics*. The light source end of the probe is connected to a tungsten halogen light source (HL-2000-FHSA by *Mikropack*). The spectrometer end fiber is connected to a USB2000+ miniature spectrometer configured for visible and near-IR measurements (wavelength range: 327.0-1105.5 nm) from *Ocean Optics* controlled with the SpectraSuite software.

## **2.7. Droplet mean size and size distribution measurements**

The emulsion average droplet size and the size distribution were determined by the laser diffraction instrument MasterSizer3000 (Malvern Instrument). The emulsion sample (0.5 g) was

diluted (1/1000 or 1/100 depending of the obscuration level) with distilled water to until correct 10% obscuration was obtained. The size distribution is characterized with  $Dv(10)$ ,  $Dv(50)$ , and  $Dv(90)$  parameters which are particle sizes below which 10, 50 or 90 % respectively, of the sample falls; 100% being the total droplets volume. The width of the distribution is characterized by a polydispersity index called span that is a dimensionless number calculated as followed:

$$\text{span} = (Dv(90) - Dv(10)) / Dv(50)$$

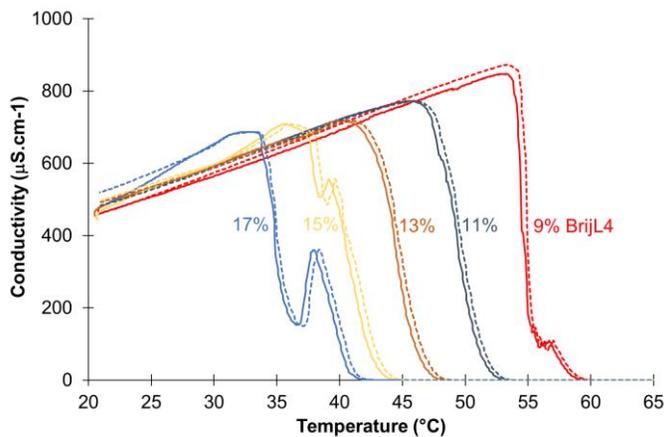
### 3. RESULTS AND DISCUSSION

Several emulsions were formulated with different surfactant percentages. For each emulsion, both conductivity and LBS measurements were monitored during heating-cooling cycle.

In the previous paper <sup>15</sup> the authors have shown that because of the high solubility of the surfactant in the MIP, it was not possible to obtain a phase inversion for Brij30 concentrations lower than 7% surfactant. For excessive concentration of surfactant with concentrations greater than 16%, the viscosity of the medium becomes too high to ensure good homogenization of the emulsion. This is the reason why we worked with Brij30 concentrations between 9 and 17%.”

#### 3.1. Conductivity curves versus temperature and BrijL4 concentration

**Figure 1** presents the variation of conductivity with temperature for BrijL4/IPM/water (NaCl  $10^{-2}$  M) systems for surfactant concentrations ranging from 9 to 17%. The phase inversion occurs during heating and cooling for the five tested concentrations of BrijL4.



**Figure 1:** Conductivity of BrijL4/IPM/water ( $\text{NaCl } 10^{-2} \text{ M}$ ) systems at  $f_w = 0.5$  versus temperature during heating (—) and cooling (-----) ramps ( $1^\circ\text{C}\cdot\text{min}^{-1}$ ; 400 rpm) for 9 to 17% BrijL4.

The conductivity decreases sharply from a very high value to a low one within a small interval of temperature. The temperature at which the conductivity is half of the maximum conductivity value on an arithmetic scale is used to define the Phase Inversion Temperature named  $\text{PIT}_{\text{cond}}$ . **Figure 1** shows that phase inversion temperature determined from conductivity curves during heating ( $\text{PIT}_{\text{cond,heat}}$ ) and cooling ( $\text{PIT}_{\text{cond,cool}}$ ) ramp temperature are practically the same. Preliminary trials have shown that for a slow rate of temperature change only a small hysteresis phenomenon is exhibited between heating and cooling. Some authors<sup>14</sup> proposed to repeat the procedure on a same system: second and third temperature cycles lead to some PIT differences if the temperature variation is relatively rapid<sup>16</sup>.

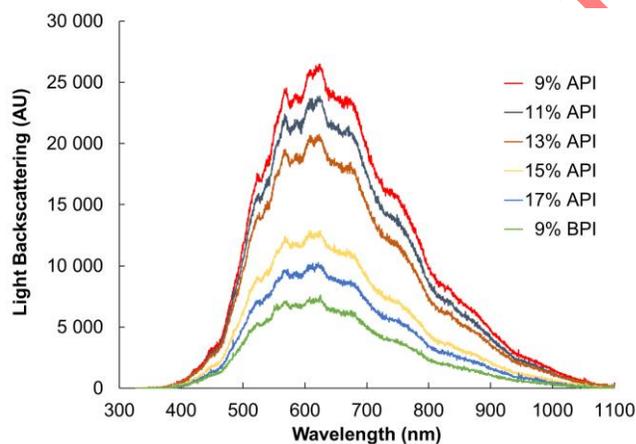
Transitional phase inversion temperature with oligomeric surfactant varies depending on the surfactant concentration<sup>17-19</sup>. **Figure 1** shows lower PIT for higher concentrations of BrijL4. An

increase of surfactant concentration tends to decrease the selective partitioning of less hydrophilic EON (low Ethylene Oxide Number oligomers) species to the oil phase, the remaining oligomer mixture at interface becoming thus more lipophilic. A lower temperature is then required for O/W to W/O phase inversion during heating.

The small peaks of conductivity at 57, 39.5°C and 38.5°C observed for 9, 15 and 17% BrijL4 respectively (**Figure 1**) could correspond to liquid crystals as suggested by Saulnier *et al.*<sup>20</sup> that gradually appear with surfactant concentration.

### 3.2. Light backscattering spectra (350-1100 nm) of O/W emulsions at 20°C

**Figure 2** presents the light backscattering (350-1100 nm) raw spectra at 20°C for O/W emulsions with 9, 11, 13, 15 and 17% BrijL4 after phase inversions. Starting 9% BrijL4 emulsion before phase inversions is also represented.

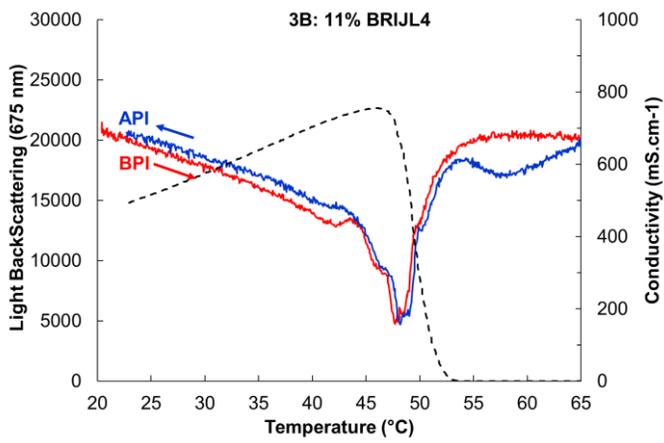
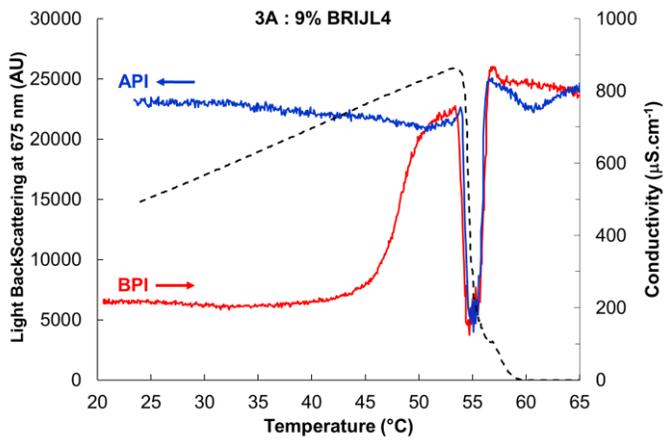


**Figure 2.** Raw light backscattering spectra between 350 and 1100 nm at 20°C, 400 rpm, of BrijL4/IPM/water (NaCl 10<sup>-2</sup>M) O/W emulsions at  $f_w = 0.5$  after phase inversions for 9% to 17% BrijL4 and before phase inversions for 9% BrijL4.

For all the samples the raw light backscattering spectra have globally the same “shape” with changes in the overall intensity. The spectral shape is mainly due to the light source intensity, the fiber transmittance and the spectral sensitivities of the detector for the different wavelengths. Effectively the LBS maximum observed at 520, 570, 585, 610, 620, 675 and 750 nm, correspond to local maximum in the spectral sensitivities of the detector combined with the intensity of the source at these wavelengths. In term of overall intensity an important increase of LBS signal is observed between 9% BrijL4 emulsions before and after phase inversion. This confirms that LBS data are linked to the emulsification process. On the other hand, successive additions of 2% BrijL4 and heating-cooling cycles lead to a decrease of LBS intensity. The phase inversion process was followed at a wavelength of 675 nm for which the raw signal is relatively high and constant.

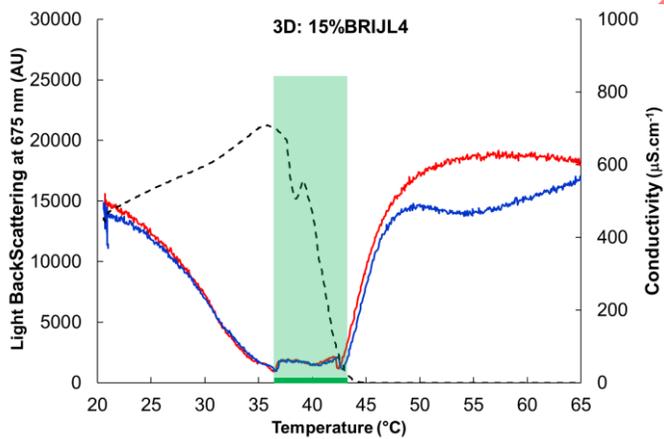
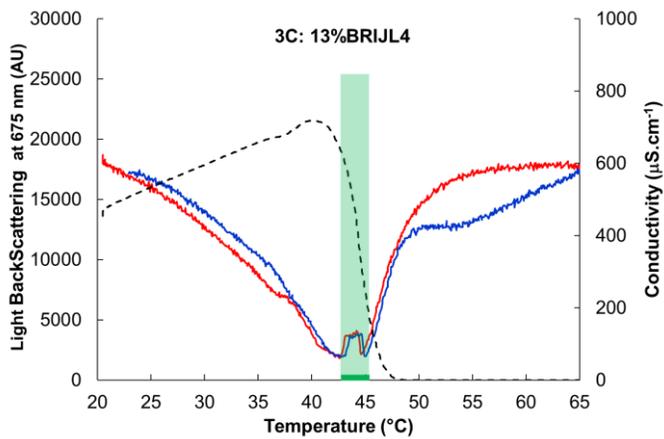
### **3.3 Comparison between light backscattering at 675 nm and conductivity signals during heating-cooling ramp**

LBS and conductivity signals during heating-cooling ramps are presented on **Figure 3**. Since conductivity curves during heating and cooling are relatively similar, only the cooling conductivity signal is represented for clarity reasons (dashed line).



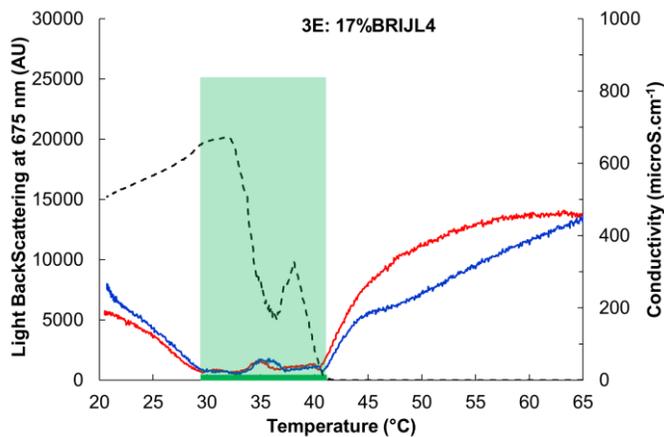
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pre version



**Figure 3.** Transitionnal phase inversion for BrijL4/IPM/water (NaCl  $10^{-2}$ M) systems at  $f_w = 0.5$  for 9% to 17% BRIJL4: conductivity during cooling (---) and LBS at 675 nm during heating (—) and cooling (—) ramps ( $1^{\circ}\text{C}\cdot\text{min}^{-1}$ ; 400 rpm) with indication of transparency observations (■).

The LBS curves in heating and cooling mode are always characterized by a minimum in the vicinity of the PIT, that can extend over a rather large temperature interval ( $TI_{\text{minLBSheat}}$  and  $TI_{\text{minLBScool}}$ ) reported in **table 1**. The PIT values obtained through conductivity (**figure 1**) are also reported. The conductivity defining the PIT ( $PIT_{\text{Cond}}$ ) is chosen as the temperature at which the specific conductivity of the emulsion is half of the maximum PIT value (on a arithmetic scale). In our experimental conditions, preliminary trials have shown that if the temperature ramp is lower than  $1^{\circ}\text{C}/\text{min}$  (heating and cooling) only a small hysteresis between  $PIT_{\text{Condheat}}$  and  $PIT_{\text{Condcool}}$  phenomenon is exhibited.

From Figure 1, at 17% BRIJL4 several temperatures correspond to half of maximum conductivity, due to a second extremum in conductivity linked with apparition of liquid crystals at high surfactant concentration. This secondary pic was not considered to determine  $PIT_{Cond}$ .

**Table 1.** Phase inversion temperatures determined for conductivity during heating ( $PIT_{cond,heat}$ ) and cooling ( $PIT_{cond,cool}$ ) ramps and Temperature Intervals for minimum value of light backscattering at 675 nm during heating ( $TI_{minLBS,heat}$ ) and cooling ( $TI_{minLBS,cool}$ ) ramps .

BrijL4 (%)	$PIT_{cond,heat}$ (°C)	$PIT_{cond,cool}$ (°C)	$TI_{minLBS,heat}$ (°C)	$TI_{minLBS,cool}$ (°C)
9	54.5	54.9	54.5 - 55.5	54.7 - 55.8
11	49.3	49.7	47.4 - 48.5	48.0 - 48.8
13	44.4	44.8	42.7 - 44.9	43.1 - 45.0
15	40.6	41.0	36.6 - 42.7	36.6 - 42.9
17	34.9	35.2	29.8 - 40.6	29.8 - 40.8

The temperature interval over which this minimum extends is more important as the BrijL4 concentration increases. For 9% BrijL4, the LBS signal whether in heating or cooling mode has a sharp minimum that spreads over one degree and includes the PIT values determined by conductivity<sup>11,13,14</sup>. For 13, 15 and 17% BrijL4, the minimum LBS temperature interval grows from 2 to 11 degrees and matches with observation of transparency emulsions. These temperature intervals also include the PIT values determined by conductivity.

For both O/W emulsions before and after phase inversions the LBS signal is the same, excepted for 9% surfactant emulsion (**figure 3A**: 6265 BPI and 23139 API). The 9% BPI emulsion is the only one obtained with mechanical agitation at 20 °C; for all others the emulsification process consists in two

transitional phase inversions. **Figure 3A to 3E** shows that for emulsions after phase inversions (API), the LBS signal decreases from 23139 AU to 7765 AU when surfactant % increases from 9 to 17%.

From the conductivity curves one often speaks of phase inversion temperature due to the mathematical method used to obtain a single temperature value (method of the tangents, or half-maximum method as in this study). But the decay of the conductivity curves also extends over several degrees, and a phase inversion temperature interval would be more suitable. If the graphical determination of the  $PIT_{cond}$  is somewhat arbitrary, a single value of PIT can easily be detected by LBS for 9% BrijL4.

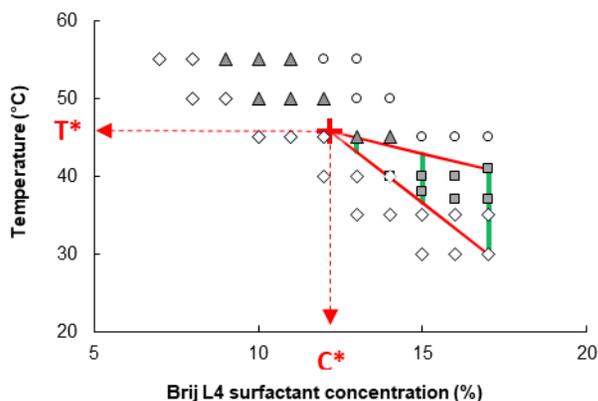
For temperatures higher than the phase inversion zone, the LBS signal in heating mode is always greater than those in cooling mode on the contrary to the conductivity profiles. In fact, since the continuous phase of the emulsion is oily, the conductivity signal is constant and equal to  $0 \mu S.cm^{-1}$ . For temperatures below the PIT the most striking difference is obtained for 9% BrijL4 (**figure 3A**). In the 20-45°C temperature range, the conductivity values in the heating and cooling ramps are identical, whereas the LBS curves are sometimes different, particularly for starting emulsion with 9% BrijL4 (**figure 3A** at 20°C: 6265 BPI much lower than 23139 API). In fact, additional cooling/heating cycles (data not shown) leads to LBS signals practically similar to those obtained during the first cooling ramp.

#### **3.4. In situ light backscattering with respect to equilibrated phase diagram**

The phase diagram based on visual observation of Winsor types (WI, WII, WIII and WIV) <sup>15</sup> of equilibrated BrijL4/isopropyl myristate/water (NaCl  $10^{-2}M$ ) systems with  $f_w = 0.5$  appears in **figure 4**. It is to notice that such observations required a very long time (several weeks) attributed to the slow kinetics of formation and destruction of liquid crystals <sup>21</sup>.

The usual fish contour plot of this diagram gives access to the characteristic  $X$  point of the system defined by the minimum surfactant concentration  $C^*$  and the temperature  $T^*$  at which aqueous and oily excess phases vanish and a single transparent WIV microemulsion phase is observed.

To analyze LBS signal with respect to equilibrated systems, Temperature Intervals corresponding to minimum LBS at 675 nm during cooling ( $TI_{\min LBS, cool}$ ) for transparent systems (13, 15 and 17% BrijL4) are superposed to the phase diagram in **figure 4**. These temperature intervals are represented in green. The transparency of emulsions formulated in the WIV area leads certainly to this minimum LBS temperature interval.



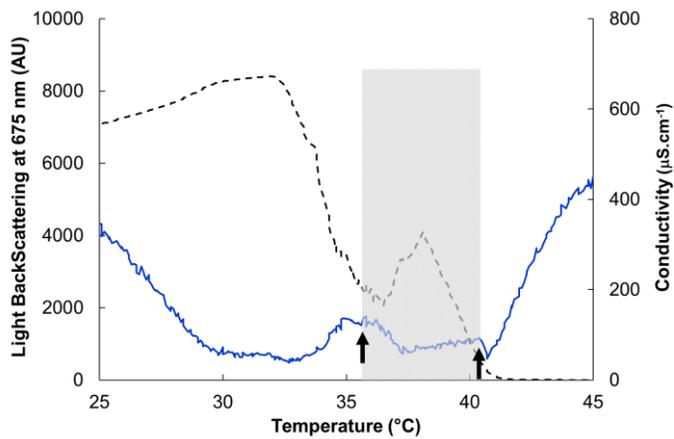
**Figure 4:** Determination of  $X$  point ( $C^*, T^*$ ) based on minimum LBS at 675 nm during cooling for transparent emulsions ( $TI_{\min LBS, cool}$  — green —) and comparison with previously determined equilibrated Winsor type (WI:  $\diamond$ ; WII:  $\circ$ ; WIII:  $\triangle$ ; WIV:  $\square$ )<sup>15</sup>.

These three Temperature Intervals (green vertical lines) are used to determine by simple linear regression of intervals end points (red lines) the  $X$  point ( $C^*, T^*$ ) of the studied system: the intersection of these both lines is assumed to correspond to the minimum surfactant concentration leading to transparent system. The comparison of this extrapolated  $X$  point with experimental

observations is rather good. More experiments with other S/O/W systems must be done in order to confirm this premise. Finally, for the studied BrijL4/IPM/water (NaCl  $10^{-2}$ M) system, there is a fairly good correspondence between visual observations of equilibrated mixtures after several weeks and LBS signals in dynamic mode on a time scale of one hour; this should allow to determine X points more quickly.

However we did not want to indicate the calculated value of (X, T) in dynamic mode with the optical fiber, because even if it is close to the one published in literature <sup>15</sup> with the fish diagram, we could not work with the same lot of surfactant (it was Brij30 in 2016, and BrijL4 in 2019).

**Figure 5** presents a zoom on the LBS minimum versus temperature obtained for cooling ramp with 17% BrijL4. Slight rises of the LBS signal can be observed (black arrows) which match exactly with the liquid crystals peak <sup>20</sup> visible on conductivity curve. These small increases of LBS signal in the  $T_{\text{minLBS,cool}}$  temperature interval could be due to particulate sprouts that appear in the beginning and at the end of liquid crystal formation. This indicates also that liquid crystals formation occurs as the LBS signal is very low, what is compatible with the transparent appearance of WIV observed emulsions. These slight variations of LBS are so small that they do not correspond to a detectable phenomenon by visual observation or by optical microscopy.

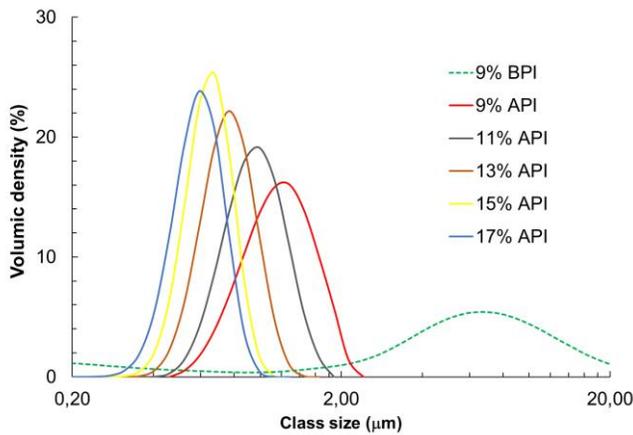


**Figure 5.** Conductivity and LBS at 675 nm versus temperature during cooling ramp at  $1^{\circ}\text{C}\cdot\text{min}^{-1}$  with 400 rpm stirring rate for 17% BrijL4/IPM/water ( $\text{NaCl } 10^{-2}\text{M}$ ) systems at  $f_w=0.5$ . Black arrows indicate rises in the LBS signal in the  $\text{TI}_{\text{minLBS,cool}}$  temperature interval.

### 3.5. In situ LBS and O/W emulsions droplets size

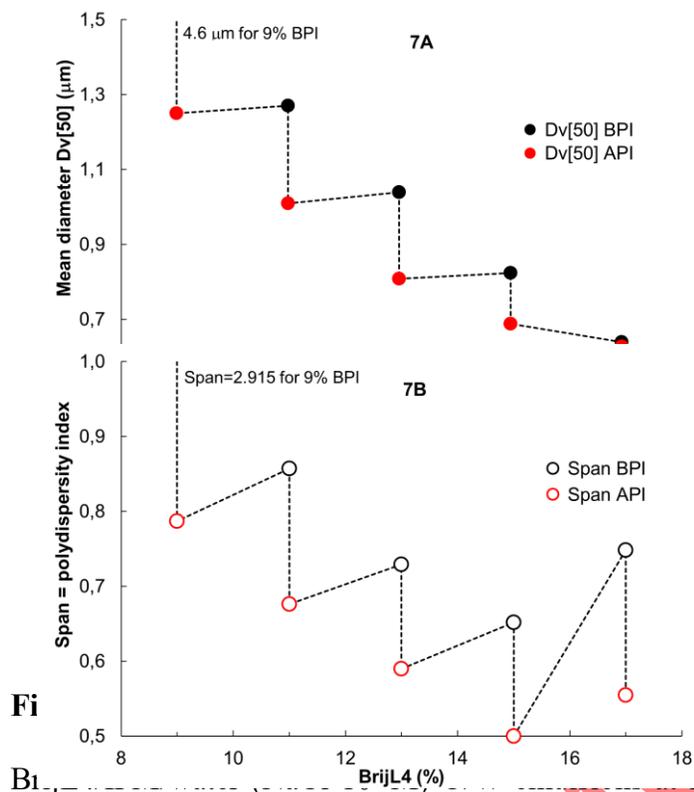
#### 3.5.1 BrijL4/IPM/water O/W emulsion droplets size evolution during process

**Figure 6** shows the size distributions of the obtained O/W emulsions. For clarity reasons, excepted for the particular starting 9% BPI emulsion, only emulsions After Phase Inversions have been presented.



**Figure 6.** Volumic density versus class size for BrijL4/IPM/water ( $\text{NaCl } 10^{-2}\text{M}$ ) O/W emulsions at  $\text{fw}=0.5$  for 9 to 17%BrijL4. API : after phase inversion, BPI: before phase inversion.

Values of mean size  $D_v[50]$  and Span polydispersity index for all emulsions have been reported in **figure 7**. Starting 9% BPI emulsion just stirred at  $20^\circ\text{C}$  presents the higher mean size ( $D_v[50]=4.6 \mu\text{m}$ ) with the largest distribution (span=2.9). As expected, first heating-cooling cycle permits to reduce both size ( $1.25 \mu\text{m}$ ) and span (0.787). **Figure 7** shows that supplementary 2% BrijL4 addition and heating-cooling cycle leads to regular decrease of mean diameter (1.27 to  $0.565 \mu\text{m}$ ) and to more monodisperse size distribution (span = 0.787 to 0.555).



**Fi** **7A** Mean diameter Dv[50] (μm) and **7B** Span = polydispersity index (7B) at 20°C of phase inversions versus %BrijL4.  $\phi = 0.5$  before (black dots) and after (red dots) phase inversions.

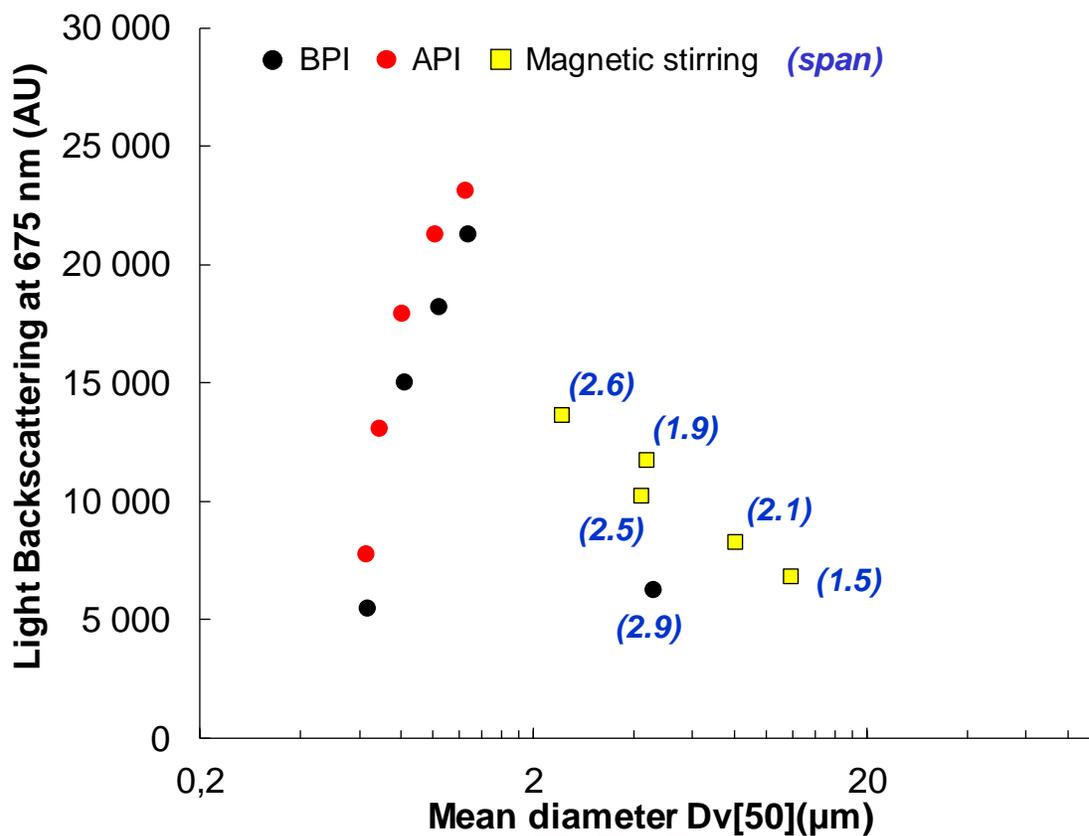
The addition of 2% BrijL4 by simple stirring at 20°C (change from red dots to black dots through horizontal dashed lines) does not significantly change the size of the droplets (**figure 7A**), but expands the size distribution (**figure 7B**). For a given BrijL4%, the transitional inversion by changing the temperature (change from black dots to red dots through vertical dashed lines) leads to a reduction of both size and span. The minimum size is thus obtained for 17% BrijL4 (0.628 μm). But even with several phase inversions cycles, this minimum droplet size is not the only condition needed to get a stable emulsion and after several hours most samples show a creaming separation at room temperature. This confirms that the PIT process certainly reduces the size of the droplets, but is

in no way sufficient to ensure the preservation of the emulsion if droplet size are still too important (superior to  $0.628\ \mu\text{m}$  in our case)<sup>22</sup>.

### 3.5.2 Correlation between LBS and O/W emulsions droplets size

It is well known<sup>23,24</sup> that LBS of heterogeneous dispersions presents a maximum intensity for a mean particle size around  $1\ \mu\text{m}$  and is also affected by the particles size distribution<sup>25-27</sup>. **Figure 8** presents  $675\ \text{nm}$  light backscattering versus mean diameter  $D_v[50]$  for BrijL4/IPM/water O/W emulsions at  $20^\circ\text{C}$  before (black dots) and after (red dots) phase inversions. For these diameters less than  $1\ \mu\text{m}$ , LBS is an increasing function of  $D_v[50]$  which appears clearly sensitive to the Span index. For example, emulsions 9% API and 11% BPI have the same mean particle size ( $1.25$  and  $1.27\ \mu\text{m}$ ) but rather different span index ( $0.787$  and  $0.857$ ) leading to different LBS values ( $23\ 139$  and  $21\ 282$ ). For a same mean size, a smaller Span index corresponds to a higher LBS signal.

To complete **Figure 8** for particle sizes between  $1$  and  $10\ \mu\text{m}$ , 9% BrijL4 emulsions were simply formulated at room temperature with magnetic stirring for different times. For these emulsions (yellow squares) the span index is added in italics next to the points. The  $D_v[50]$  and span values are of course not sufficient to characterize a particle size profile. Nevertheless, the same trend seems to emerge regards to the three points with same  $D_v[50]$  ( $4.42$ ,  $4.22$ ,  $4.6\ \mu\text{m}$ ) but different span index values ( $1.9$ ;  $2.5$ ;  $2.9$  respectively). For a same mean size, the smaller the Span index, the higher the LBS signal.



**Figure 8.** Light backscattering at 675 nm versus mean diameter Dv[50] for 9 to 17% BrijL4/IPM/water (NaCl  $10^{-2}$ M) O/W emulsions at 20°C, obtained before (●) and after (●) phase inversions; and for 9% BrijL4 emulsions magnetically stirred at 800 rpm and room temperature for different times (□) with span values in parenthesis.

The size (Dv(50)) was calculated using the laser granulometer software, indicating the refractive index of the continuous (Water) and the dispersed (MIP) phase and the absorption coefficient of the dispersed phase. However, we also made simulations with BrijL4 (through its refractive index), and considering that the surfactant could modify the refractive index of the aqueous and dispersed phase,

depending on whether it is totally or partially dissolved in each of both phase. These different scenarii have not shown a significant change in size, as far as the  $Dv(50)$  is concerned.

#### 4. CONCLUSION

The contribution of light backscattering (LBS) measurement with an optical fiber to follow in situ the transitionnal phase inversion was studied on BrijL4/Isopropyl Myristate/Water emulsions with  $f_w = 0.5$  and 9 to 17% BrijL4. Obtained results were compared to the usual conductimetric method and analysed in regards to the phase diagram of equilibrated systems and O/W emulsions particle size. The 675 nm lengthwave was chosen corresponding in the spectra at a maximum for which the LBS signal is relatively constant. During transitional phase inversion, a minimum of LBS appears always near the phase inversion temperature detected by conductivity. This minimum is relatively sharp for low surfactant concentrations (9% and 11%) corresponding to inversion through WIII type, but becomes larger with higher surfactant concentrations corresponding to inversion trough WIV type. For these higher surfactant concentrations, minimum LBS signals corresponding to transparent emulsions allow to determine the X point ( $C^*, T^*$ ) of the system. In situ visible LBS can thus be envisaged for transitional phase inversion detection as well as a rapid way for X point determination.

The measurement of the light backscattered by the optical fiber is finally a complementary technique to the conductivity to follow the evolution of emulsification processes. The conductivity makes it possible to determine the nature of the continuous phase of the emulsion (unlike the optical fiber). For W / O emulsions the conductivity is zero so it is difficult to extract other information than the oily nature of the dispersed phase. On the other hand, the optical fiber indicates a backscattered light signal caused by the presence of the drops of the dispersed aqueous phase, this signal itself

being correlated with the size of these droplets. The evolution of LBS versus O/W emulsions average diameter  $D_v(50)$  is a curve (Figure 8) with a maximum of about 1 micron, which moreover depends on the particle size distribution (span index).

Thus it is necessary to distinguish 2 size classes. For droplets greater than one micron, the backscatter signal is dependent on the average size as well as the distribution profile (span), so it is not possible to obtain an accurate measurement of the size with only the signal at a minimum wavelength (675 nm). We have not studied the possible contribution of light retrodiffusion signals to other wavelength, because we did not find qualitatively spectrum profile variation (Figure 2) according to the emulsions.

For droplets smaller than one micron, the particle size profiles are narrower, and the span that remains constant is no longer an influencing factor in the size correlation, that varies almost linearly (rather affine) with the intensity of backscattered light.

Although it remains difficult to accurately determine the emulsion size from LBS measurements, this signal is a considerable contribution to size control throughout the emulsification process.

Finally, the use of a commercial visible light backscattering optical fiber exhibits several advantages over the classical conductivity measurement for transitional inversion studies: it does not imply any electrolyte addition in the aqueous phase; is adapted for highly viscous media; and brings informations during the process particularly for W/O emulsion.

concerning the emulsion size (mean diameter).

Finally, an optical fiber user can use it by controlling the evolution of the signal to control the reproducibility of an emulsification process. The user could also have information on the size of the

emulsion (provided if he knows that the size is smaller than 1 micron). The user could also realize a standard range of emulsions between 50 and 500 nm which are generally stable for calibrating the optical fiber.

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## Notes

The authors declare no competing financial interest.

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