

## **Supplementary Material**

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### **Part I: Samples formulation**

We describe here the formulation for a 10mL sample as used for the Micro-CT and DLS measurements. The same formulation steps were used for the 3mL sample in NMR. We give the exact compositions of the 10mL and 3mL samples in the attached Table 1. Each mass was measured with an electronic mass balance (AE200, Mettler toledo) with a precision of  $\pm 0.1$  mg. Each volume was measured by automatic pipettes. All formulations steps were performed at ambient temperature (20°C).

The microemulsion was prepared in a glass tube by the following procedures. First, a mother solution of NaCl (Merck grade analysis) at 200 g/L was prepared separately in a flask.

In the sample tube, 0.2200g of SDS (Alfa Aesar CAS 151-21-3 Sodium dodecyl sulfate > 98.5 wt%, water <1.5% CAS N°151-21-3) was added as solid and dissolved in 3.4500 mL of distilled water. When total solubilization of SDS was obtained, 0.5500mL of n-butanol (Merck (grade analysis) was added. The tube was turned up and down three times to allow mixing.

After that, 1.2740 mL of NaCl mother solution were inserted in the glass tube with a pipette. Here, the volume of the NaCl solution was calculated to reach the final salinity of 54g/L in the aqueous phase. The solution was carefully mixed up and down three times.

Finally, 4.7300 mL of Toluene (VWR , AnalaR Normapur), was added in the glass tube at a speed of 126.8mL/h via a syringe driver. The volume of Toluene was the same as the aqueous phase (WOR =1).

*Table 1 Quantities added for the formulation of the SDS/n-butanol/NaCl brine/Toluene microemulsion at optimal formulation – 3mL and 10mL samples – 20°C +/- 2°C*

Sample/ Quantities	1) SDS	2) Distilled Water	3) N-butanol	4) Solution of brine (200g/L of NaCl)	5) Toluene
3mL	0.07 g	1.0300 mL	0.1650 mL	0.3827 mL	1.4200 mL
10mL	0.22 g	3.4500 mL	0.5500 mL	1.2740 mL	4.7300 mL

### **Part II: NMR methodology**

Low-Field NMR acquisitions were carried out on a 23MHz set up in a 3mL tube of 1.8cm-diameter at 30°C. The relaxation times  $T_{2i} = T_{1i}$  of each species  $i$  in the microemulsion were deduced from common CPMG sequences (Carr-Purcell-Meiboom-Gill) and are listed in Table 2. Given the contrasts, we developed a novel quantification method which is non-destructive and sensitive to T1-relaxation times. The principle is based on classical 1D-imaging using T1-relaxometry. After a perturbation of the magnetic field, each species of the system returns to its initial state after a lapse time estimated at  $5 T_{1i}$ .

To allow quantification in the quaternary system, we observed the relaxation process in two different modes: total and partial relaxation modes. A parameter RD is implemented to pass from one mode to another. The data collected are in the form of protons density profiles  $\rho$  in arbitrary unit (Equation 1). First, we account for the total relaxation process ( $RD \gg 5T_{1i}$ ), the collected density of protons  $\rho_{total}$  only depends on the intrinsic hydrogen densities of the components and is depicted on Table 3. A contrast in intrinsic H-density between Toluene and [n-butanol/water/SDS] permits the direct quantification of Toluene. Secondly, we focus on the partial relaxation process. In this mode, the relaxation process is subpolarized for components  $i$  that have  $T_{1i}$  higher than the time allocated to the relaxation (RD set up here at 1s). Consequently, the measured H-density corresponds to a unique composition of the system and follows sharp and detectable variations when local compositions change in the system.  $T_{1i}$ -Contrasts between each component allow to extract n-butanol and water volume fractions according to Equation . Because of a lack of precision in collected signals, SDS quantification is not possible. In agreement with previous studies [1], we thus made the hypothesis that SDS is homogeneously distributed in the middle phase. Profiles resolution along the height of the tube is 0.1 mm. More technical description on the NMR methodology could be found in our corresponding submitted publication [2].

$$\rho = \rho_{total} \left( 1 - \sum \varphi_i \exp \frac{-RD}{T_{1i}} \right) \quad \text{Equation 1}$$

$\varphi_i$ : Volume fraction of component  $i$  and  $\rho_{total}$ : density profile collected for total relaxation mode

Table 2 T2 relaxation times of microemulsion's species deduced from CPMG sequence

Toluene	Brine 54g/L	n-Butanol	SDS
2.7 s	2.9 s	1.1 s	2.5 s (in solution)

Table 3 Calculated protons densities of Toluene, Water, SDS, n-butanol

Species	H protons density ( $\times 10^{22}$ H/cm3)
Toluene	4.53
Water/Brine	6.70
SDS	5.23 (pure)
N-butanol	6.59

### Part III: Teubner-

### Strey model

For medium  $q$  range,  $I(q)$  curves were fitted using the Teubner-Strey model [3,4] widely used for microemulsions SAXS data interpretation. The associated correlation function is given by Equation as a function of the diffusion vector  $r$  in direct space. After Fourier transform, it gives an expression of the scattered intensity as a function of three parameters  $a_2$ ,  $c_1$ ,  $c_2$  in the form (Equation ) giving access to the periodicity of the structure  $d$ , the correlation length  $\xi$  (characteristic decay length of periodic order) and amphiphilicity factor  $fa$ . (Equation , Equation , Equation ).

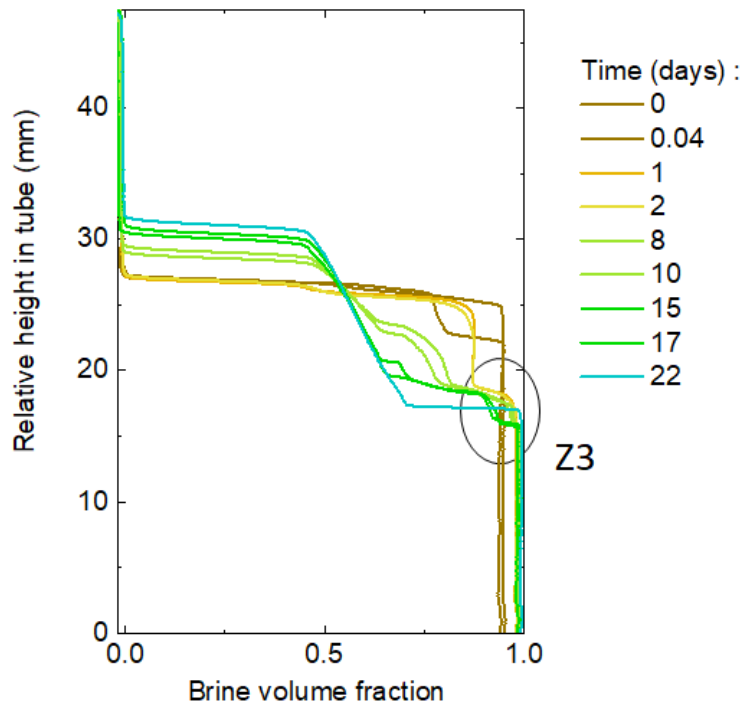
$$g(r) = \frac{d}{2\pi r} e^{-\frac{r}{\xi}} \sin \left( \frac{2\pi c}{d} \right) \quad \text{Equation 2}$$

$I(q) \frac{1}{a_2 + c_1 q^2 + c_2 q^4}$	<i>Equation 3</i>
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$\xi = \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} + \frac{1}{4} \frac{c_1}{c_2} \right]^{-1/2}$	<i>Equation 4</i>
$d = 2\pi \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} - \frac{1}{4} \frac{c_1}{c_2} \right]^{-1/2}$	<i>Equation 5</i>
$fa = \frac{c_1}{\sqrt{4a_2c_2}}$	<i>Equation 6</i>

#### Part IV: Micro-CT raw composition profiles

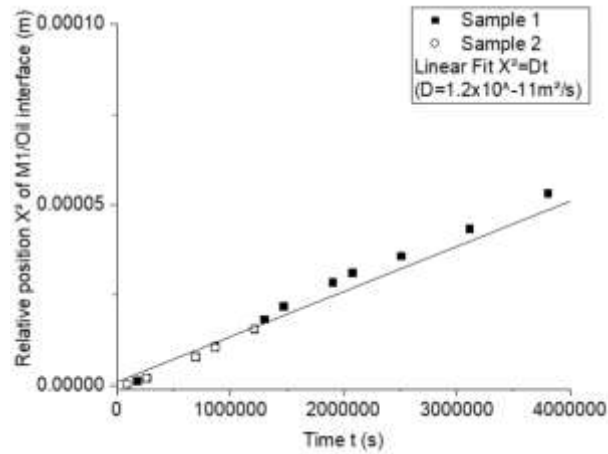
We plot the height in tube in function of the brine volume fraction, a vertical profile indicates an interface. Z3 is identified between aqueous excess phase and M2 from t=1 day to t=17 days. Also, from 0 to 1 day, we noted the brine volume fraction increases in the excess aqueous phase meaning n-butanol migrated into the supernatant phases.



#### Part V: Interfaces behaviors

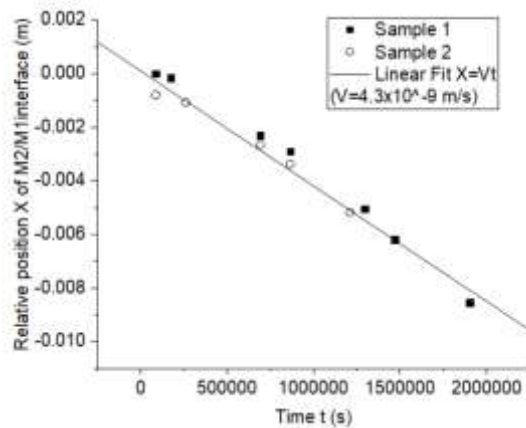
##### 1) M1/oil Penetration front

The square of the displacement of M1/oil interface is plotted versus time for two samples. We found a linear behavior where the slope corresponds to the diffusion coefficient of oil in M1 phase.

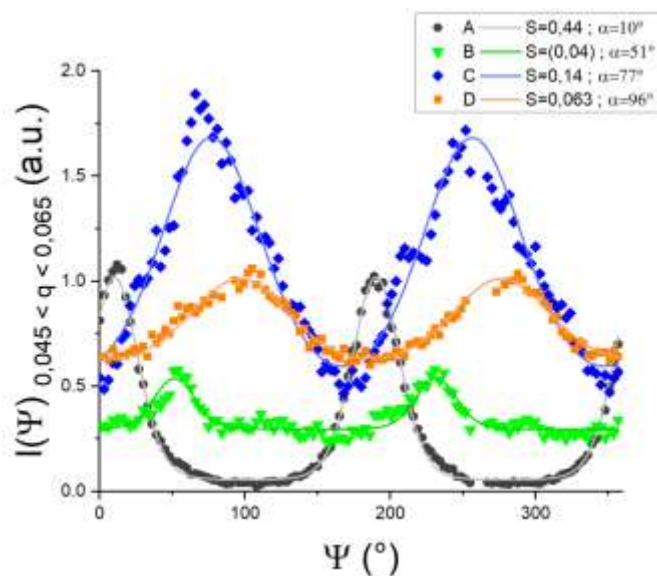


## 2) M1/M2 Penetration front

The displacement of M1/M2 interface is plotted versus time for two samples. We found a linear behavior where the slope corresponds to the rate of matter flow from M2 to M1.



**Part VI: Maier-Saupe fits - Azimuthal intensities and the corresponding Maier-Saupe fitting curves for position A,B,C,D in M2/M1 phase introduced in Figure 7.**



## Part VII: Interpretation of Z3 scattering pattern.

The Z3 phase is mainly made of brine and SDS. It could potentially contain some butanol. It is worth to mention that in this case, the SAXS scattering contrast is sensitive to the contribution of the polar head of SDS surfactant.

In the case of a polydisperse and diluted sample of  $l$  objects, the scattered intensity can be written in the form :

$$I(q) = V_{irr} \times \sum_l \mu_l^2 N_l \times P_l(q)$$

With  $V_{irr}$  the irradiated volume of the sample ;  $\mu_l$  the scattering length density contrast of objects  $l$  ;  $N_l$  a normalization constant proportional to the volume fraction of  $l$  in the sample ;  $P_l(q)$  the form factor linked to  $l$  scattering pattern.

For a core-shell structure of external radius  $R_e$  and internal radius  $R_i$ , the corresponding form factor can be written :

$$\frac{\sin(qR_e) - \sin(qR_i)}{qR_e} - \cos(qR_e) + qR_i \cos^2(qR_e)$$

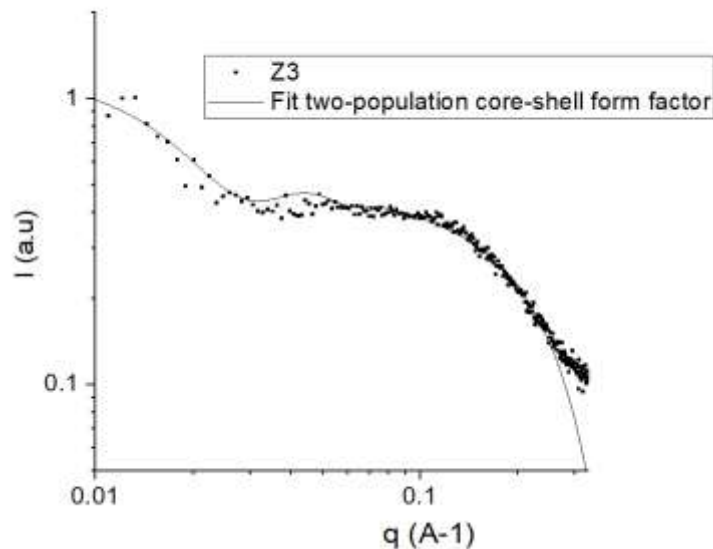
$$P(q) = 9$$

If the core-shell structures have a thin shell (ie for vesicles), the expression above can be reduced as long as  $R_e - R_i \ll R_{ext} = R$  , we obtain :

$$P(q) \approx \frac{\sin^2(qR)}{(qR)^2}$$

In our case, the fits of the scattered intensity for a two-populations vesicles of radius  $R_1$  and  $R_2$  thus takes the form below and leads to  $R_1 = 10nm$  and  $R_2 = 0.7nm$ .

$$I(q) = V_{irr} \mu^2 \times \left( N_1 \times \frac{\sin^2(qR_1)}{(qR_1)^2} + N_2 \times \frac{\sin^2(qR_2)}{(qR_2)^2} \right)$$



### Part VIII: Self-diffusion coefficients at 25°C

Species	Self-diffusion coefficients ( $\times 10^{-10}$ m <sup>2</sup> /s)	Literature
Water	25.7	[5]
Butan-1-ol	4.9	[6]
Toluene	26.6	[7]
SDS at 46,8 g/L	0.65	[8]

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