Supporting Information

Range of Winsor I, II, III microemulsions

A salinity scan together with measurements of interfacial tensions of all samples were performed to define the range of Winsor I, Winsor III and Winsor II systems. The interfacial tensions were measured on Kruss spinning drop tensiometer on equilibrated samples (Figure S1). We measured interfacial tensions corresponding at the oil/microemulsion interface for Winsor I systems, at both interfaces with the bicontinuous phases for Winsor III systems, and at the microemulsion/water interface for Winsor II systems. Error bars on the measurements were estimated from measurements on duplicates. We found the range of :

-Winsor I for salinities < 48g/L

-Winsor III for 48g/L < Salinity < 54g/L



Figure S1 Interfacial tensions measurements by spinning drop tensiometer: Laplace and Vonnegut method.

NMR method assessment

Essays on accuracy, reproducibility and repeatability of the method were performed before sample acquisition. For input parameters of RD=1 s and RD=15 s, satisfying reproducibility and repeatability were found. Accuracy on the acquired H-densities is found at +/- 4% a.u. After calculation, we estimate a global error on calculated volumes fractions of around +/- 4%vol for n-butanol and brine, and +/- 3%vol for Toluene.

1. Method accuracy

Before experiments, we assessed the method accuracy by comparing the theoretical densities to the experimental ones on four references samples (Table S1). Good agreement between experimental and theoretical responses is found on pure systems (Toluene, n-Butanol, Brine) but also on mixtures (Aqueous phase, SDS solution). With our input RD parameters, random errors on the measured signal are estimated at +/- 4%.

| Samples | T2(s) at 30°C | Mean Total density u.a | Mean Experimental apparent density a.u | Calculated apparent density a.u |
|----------------------------|---|---------------------------|---|--|
| Toluene | 2.70 | 10.5 | 3.1 | 3.2 |
| n-Butanol | 1.13 | 15.3 | 9.3 | 9.0 |
| Brine NaCl 54g/L | 2.93 | 15.0 | 4.2 | 4.3 |
| SDS solution 46.8g/L | SDS 0.32 ; Water 2.93 | 15.2 | 4.7 | 4.8 |
| Aqueous phase | SDS 0.32 ; Brine 2.93 ; n-butanol 1.13 | 15.3 | 5.3 | 5.4 |

Table S1 Experimental densities versus calculated densities on reference samples at30°C for method accuracy assessment

2. <u>Reproducibility</u>

We analyzed three samples of aqueous phase that compose microemulsions to assess reproducibility of the measurement. Samples were formulated and analyzed at different times independently in the same measuring conditions. According to Table S2, we found respective deviations of +/- 0.6% for total and +/- 4% for apparent

densities which are actually included in method accuracy deviations. Thus we assume a good reproducibility of measurements with no additional deviations on the measured signals.

| Samples | Mean Total density a.u | Mean Apparent density a.u | | |
|--------------------|------------------------|---------------------------|--|--|
| Aqueous phase 1 | 14.9 | 5.2 | | |
| Aqueous phase 2 | 15.1 | 5.2 | | |
| Aqueous phase 3 | 15.0 | 5.4 | | |
| Mean | 15.0 | 5.3 | | |
| Standard deviation | 0.1 | 0.1 | | |

Table S2 Experimental intensities for duplicates samples for reproducitibility assessment

3. <u>Repeatability</u>

Three microemulsions were formulated the same day and analyzed at the same time in the same experimental conditions. Samples 1 and 2 are formulated with a different mother solution of Brine to assess the impact of formulation deviation on the signals. Samples 2 and 3 are duplicates. From densities profiles (Table S3), we deduce total densities and apparent densities in each phase of the WIII-microemulsion. We respect the +/- 4% accuracy on the measurement in each phase for RD=15s and RD=1s, meaning that the method shows a good repeatability and that there is no significant impact of the experimental variability of the formulation.

| Table S3 Experimental densities for t | hree formulated microemulsions for repeatability |
|---------------------------------------|--|
| ć | assessment |

| | Mean Apparent density a.u | | | Mean Total density a.u | | |
|--|------------------------------|-----------------|----------------------------|------------------------|-----------------|----------------------------|
| Samples | Excess Oil | Middle Phase | Excess aqueous phase | Excess Oil | Middle Phase | Excess aqueous phase |
| WIII µEmulsion 1 Formulated with brine 1 | 2.8 | 4.2 | 4.0 | 10.3 | 12.6 | 14.1 |
| WIII µEmulsion 2 : Formulated with brine 2 | 2.9 | 4.4 | 4.2 | 10.4 | 12.7 | 14.6 |

| WIII µEmulsion 3 : Duplicate of µEmulsion 2 | 3.0 | 4.5 | 4.3 | 10.6 | 12.9 | 14.7 |
|---|-----|-----|-----|------|------|------|
| Mean | 3.0 | 4.4 | 4.2 | 10.4 | 12.7 | 14.5 |
| Standard deviation | 0.1 | 0.2 | 0.2 | 0.2 | 0.2 | 0.3 |