

Spontaneous Ouzo emulsions co-exist with pre-Ouzo ultra-flexible microemulsions

Supplementary Information

Sylvain Prévost¹, Sebastian Krickl², Stjepan Marčelja³, Werner
Kunz², Thomas Zemb⁴, and Isabelle Grillo¹

¹Institut Laue-Langevin, 71 avenue des Martyrs, CS 20156, 38042
Grenoble Cedex 9, France

²Institute of Physical and Theoretical Chemistry, University of
Regensburg, 93053 Regensburg, Germany

³Department of Applied Mathematics, Research School of Physics
& Engineering, Australian National University, Canberra, ACT
2601, Australia

⁴Institut de Chimie Séparative de Marcoule, CEA, CNRS,
ENSCM, Univ Montpellier, 30207 Marcoule, France

This document contains 9 pages.

List of Figures

S1	Ternary diagram: densitometry	S3
S2	Interfacial tension	S4
S3	Ternary diagram: SANS compositions	S5
S4	Ternary diagram: isotopic effect	S6
S5	Water volume fraction for SAXS dilution	S7

List of Tables

S1	Scattering Length Densities	S3
S2	Parameters from SAXS data Fig. 2A	S8
S3	Parameters from SANS data Fig. 3	S8
S4	Parameters from SANS data Fig. 4	S9

Ternary phase diagrams Initial phase diagrams were recorded at room temperature (20 °C to 25 °C) using a dynamic and static process according to M. Clausse, L. Nicolas-Morgantini, A. Zradba and D. Touraud, in *Microemulsion Systems*, Dekker, New York, H. L. Rosano and M. Clausse edn, 1987, vol. 24, pp. 387—425. To this purpose, binary mixtures (each 3 g) were prepared in screw-top tubes of borosilicate glass. The third component was added gradually until a visible change in the phase behaviour occurred. Phase transition was determined by the naked eye. Weight fractions were calculated from the mass of the individual components derived from precise weight measurements. There is a hysteresis for phase separation, which can be observed by temperature cycles or by determining the composition at which a biphasic sample becomes monophasic by addition of the hydrotrope.

Determination of the critical point The critical point is defined as the sample composition at the phase separation border, where both phases have equal volume. In order to determine the critical point, ternary mixtures near the phase separation border (each 6 g) were prepared in closable, volume-scaled tubes of borosilicate glass at room temperature (20 °C to 25 °C) and water was added dropwise until phase transition occurred. After complete phase separation the volume ratio between water- and oil-rich phases was determined by the naked eye. The position of the critical point is found at mass fractions of 0.16043 (octanol), 0.36477 (ethanol) and 0.47480 (water) in H₂O. In D₂O, the mass fractions are respectively 0.1527 (octanol), 0.3520 (ethanol) and 0.4953 (D₂O), and when correcting for the molar mass difference between H₂O and D₂O the “normalized” mass fractions are then 0.15235 (octanol), 0.34639 (ethanol) and 0.50126 (water).

Determination of tie-lines Biphasic samples (each 150 g) were prepared mixing first the essential amounts of ethanol and octanol resulting in a homogeneous solution. After addition of the residual amount of deuterium oxide, the solution was thoroughly mixed by hand. Subsequently, phase separation of the milky mixture was accelerated by gentle centrifugation (1500 g for 30 min) using a Sigma 3-18KS centrifuge. The obtained two phases were carefully separated (avoiding remixing) and collected in sealed vessels for further processing.

Interfacial tension The interfacial tension was determined for several compositions including those measured in the SANS experiment (compositions A, MHC and B). Values are presented in S2.

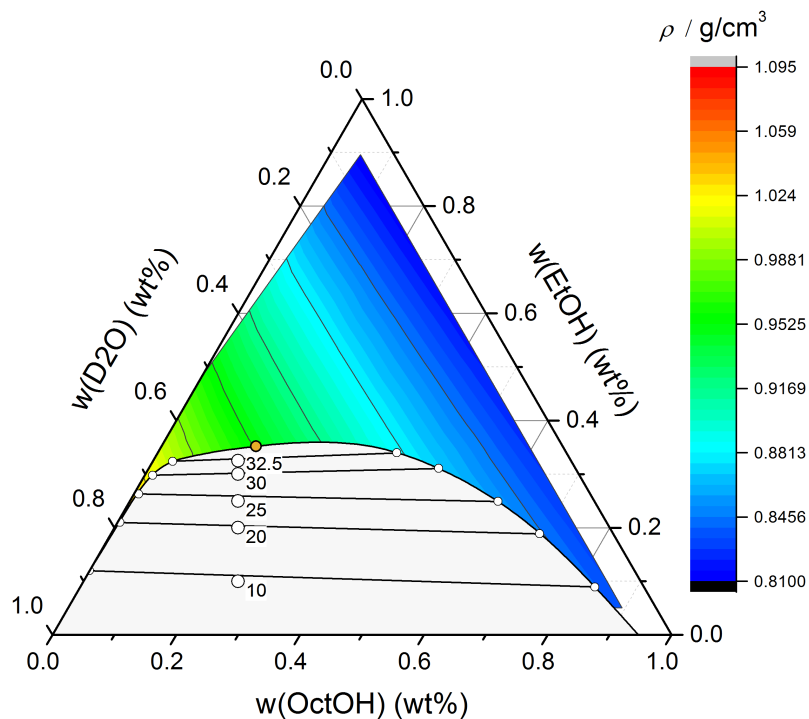


Figure S1: Ternary diagram at 25 °C in mass fractions with D₂O, with isolines from densitometry measurements, and tie-lines experimentally obtained.

Table S1: Scattering Length Densities for Neutrons (SLD_N) and X-rays (SLD_X) used in this work.

compound	formula	Mw / g·mol ⁻¹	d / g·cm ⁻³	v / nm ³	SLD_N ×10 ⁻⁴ / nm ⁻²	SLD_X
H-water	H ₂ O	18.01	0.99704	0.0300	-0.56	9.39
D-water	D ₂ O	20.03	1.10841		+6.38	
H-ethanol	C ₂ H ₆ O	46.07	0.78504	0.0974	-0.34	7.52
D-ethanol	C ₂ D ₆ O	52.11	0.88792		+6.07	
H-n-octanol	C ₈ H ₁₈ O	130.23	0.82209	0.2630	-0.32	7.93
D-n-octanol	C ₈ D ₁₇ HO	147.33	0.93007		+6.41	

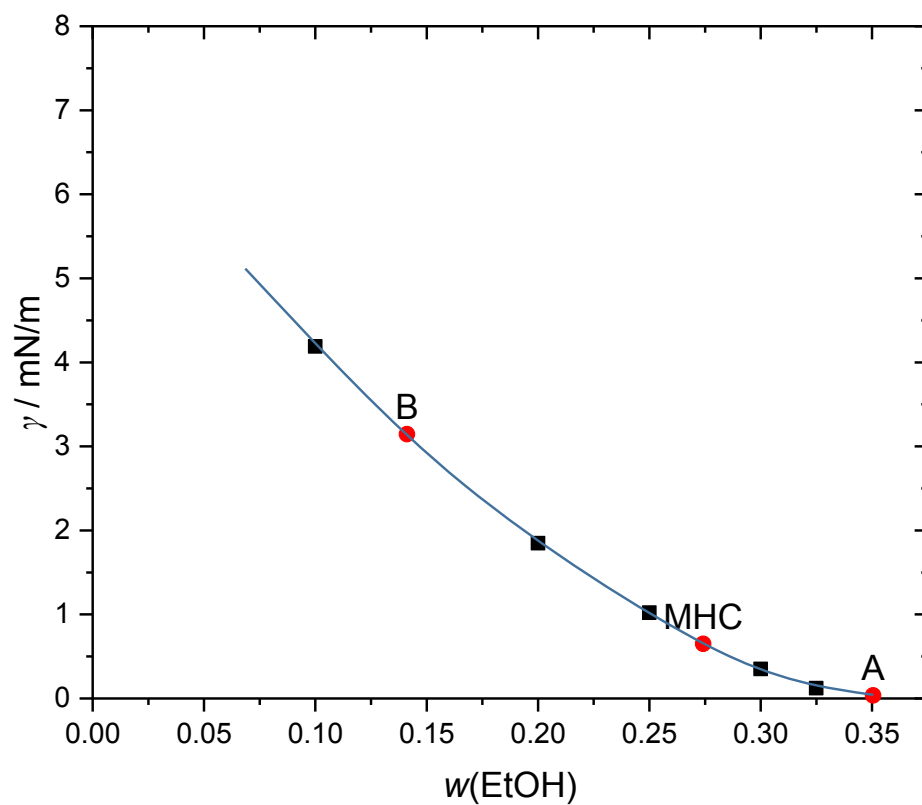


Figure S2: Interfacial tension determined at room temperature on phase separated samples at different ethanol fractions (see tie-lines in Fig. S1) including samples A, MHC and B from the main article. The continuous line is a visual guide.

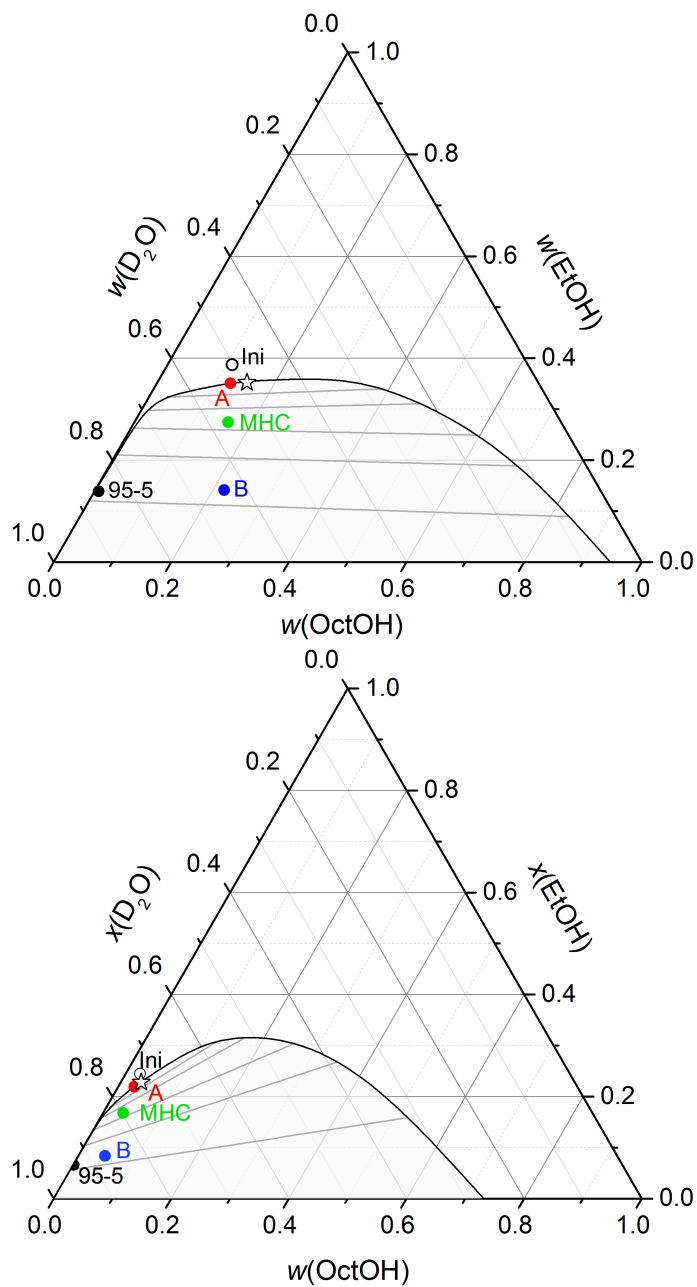


Figure S3: Ternary diagram at 25 °C with D₂O in mass fractions (top) and mole fractions (bottom) showing the position of the points investigated by SANS.

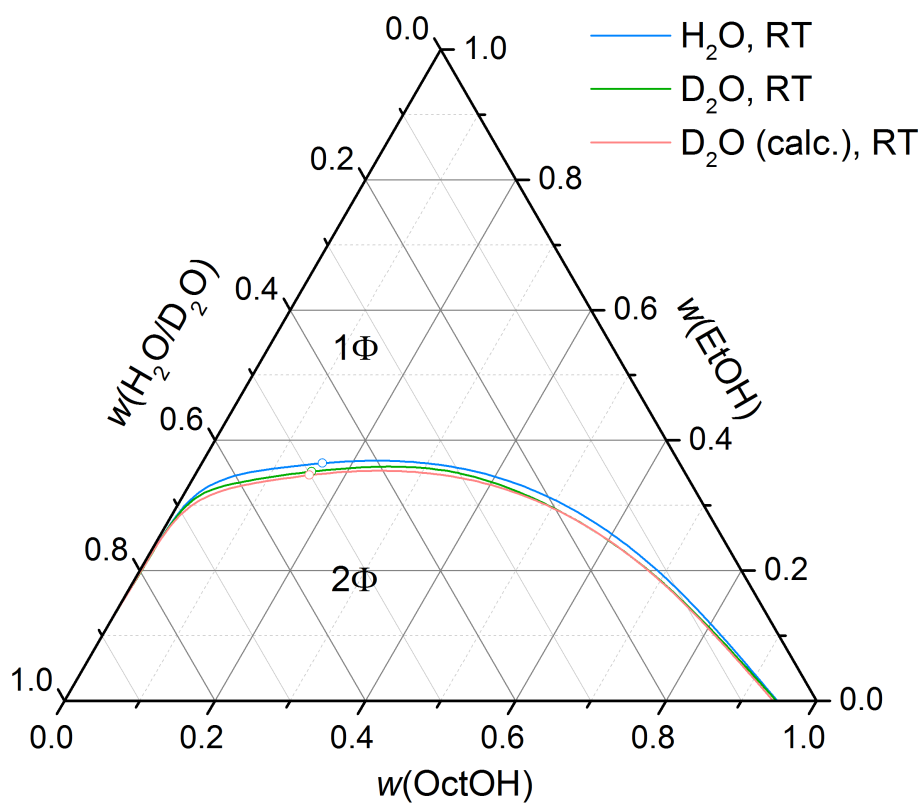


Figure S4: Ternary diagram at 25 °C in mass fractions with H₂O, D₂O, and D₂O after rescaling to account for the change in molar mass. The shift of the biphasic region is just noticeable, the isotopic effect is very weak.

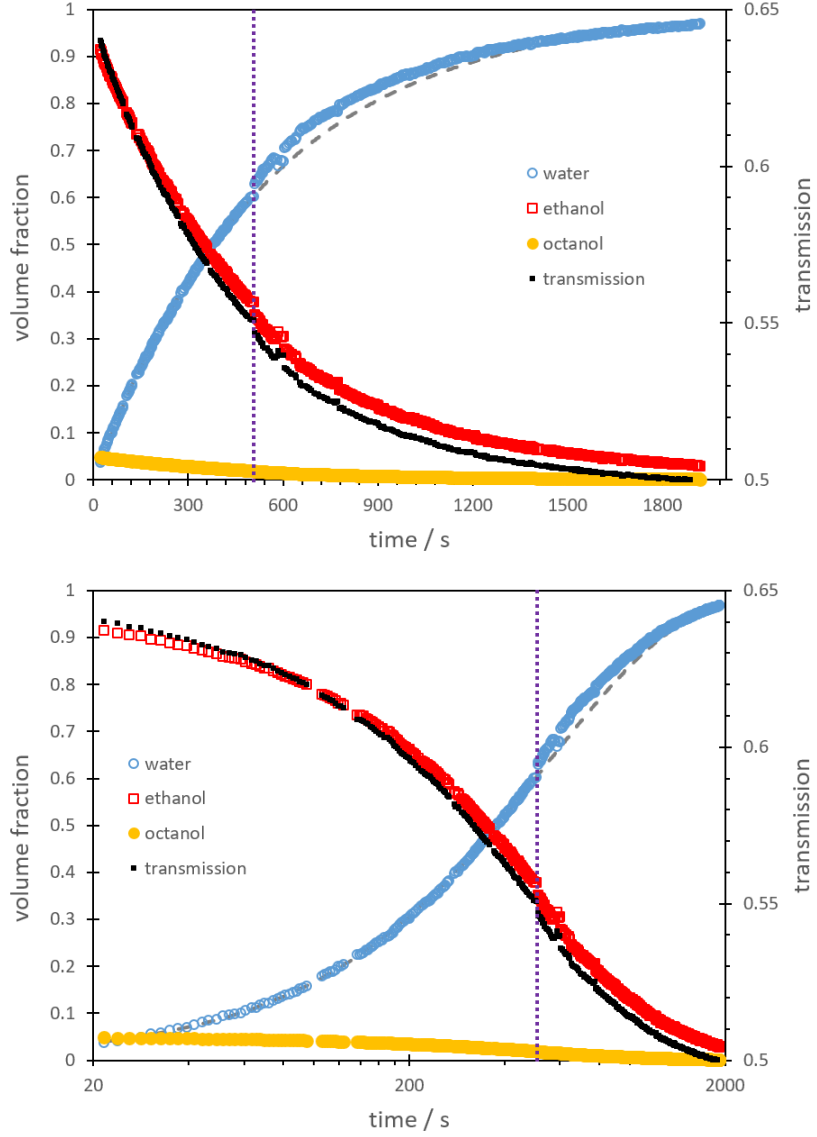


Figure S5: Volume fractions of water, ethanol and octanol versus time as obtained from SAXS (ID02@ESRF) from transmissions recorded simultaneously with scattering patterns at a sample-to-detector distance of 5.5 m. The occurrence of turbidity appears clearly from the small deviation from the expected exponential trend of the octanol/ethanol concentration (marked as a vertical dashed line).

Table S2: Parameters of the Ornstein-Zernike + Broad Peak + Porod model used for SAXS data of Fig. 2A (dilution with H₂O of a binary mixture octanol - ethanol with $\beta = 0.05$, sample-to-detector distance of 5.5 m). 291 frames were measured and fit; only 1 fit result every 20 files is shown here. The transmissions values (“trans”) and the deduced water volume fractions (“water”) are given.

frame	trans	water	$a_P / 10^{10} \mu\text{m}^5$	$\xi_{\text{OZ}} / \text{\AA}$	$I(0)_{\text{OZ}} / \text{cm}^{-1}$
1	0.6709	0.142			
21	0.6599	0.205			
41	0.6478	0.275			
61	0.6413	0.316			
81	0.6296	0.383		2.3	0.0015
101	0.6218	0.430		3.8	0.0020
121	0.6137	0.480		5.4	0.0026
141	0.6066	0.524		7.5	0.0037
161	0.5997	0.568		11.2	0.0061
181	0.5933	0.608	1.81	17.9	0.0095
201	0.5843	0.666	1.63	8.9	0.0011
221	0.5837	0.669	1.62	6.4	0.0003
241	0.5751	0.726	1.58		
262	0.5705	0.749	1.55		
281	0.5685	0.770	1.28		

Table S3: Parameters of the Ornstein-Zernike + Broad Peak model used for SANS data of Fig. 3 (vertical dilution with D₂O and octanol of an initial point near the plait point). “up” and “low” indicate upper and lower phases. For ξ_{OZ} , the value was found identical in upper and lower phases at composition A, so the parameter was then fixed to the value obtained from the upper phase for the two other samples MHC and B (where the signal is dominated by the Broad Peak, lowering the reliability of the fit for the Ornstein-Zernike contribution).

sample	$D^* / \text{\AA}$	$\xi_{\text{BP}} / \text{\AA}$	$I(0)_{\text{BP}} / \text{cm}^{-1}$	$\xi_{\text{OZ}} / \text{\AA}$	$I(0)_{\text{OZ}} / \text{cm}^{-1}$
Ini	-	-	-	14.8	3.016
A - up	61.6	6.5	0.163	30.1	10.079
A - low	-	-	-	30.1	6.442
MHC - up	24.9	10.1	0.073	3.8	0.328
MHC - low	-	-	-	3.8	0.072
B - up	19.9	10.0	0.100	0.8	0.077
B - low	-	-	-	0.8	0.062

Table S4: Parameters of the Ornstein-Zernike + Porod model used for SANS data of Fig. 4 (binary solutions of octanol and ethanol diluted with D₂O until turbidity is observed).

composition	$\xi_{\text{OZ}} / \text{\AA}$	$I(0)_{\text{OZ}} / \text{cm}^{-1}$	$a_P / 10^{10} \mu\text{m}^5$
$\beta = 0.0102$	1.5	0.051	2.17
$\beta = 0.0183$	2.6	0.059	2.98
$\beta = 0.0334$	4.0	0.090	4.01
$\beta = 0.0492$	6.6	0.190	5.64
$\beta = 0.0566$	7.8	0.239	5.45