Supplementary Material (ESI) for *Soft Matter*
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Supporting Information

Formation and structure of slightly anionically charged nanoemulsions obtained by the phase inversion concentration (PIC) method

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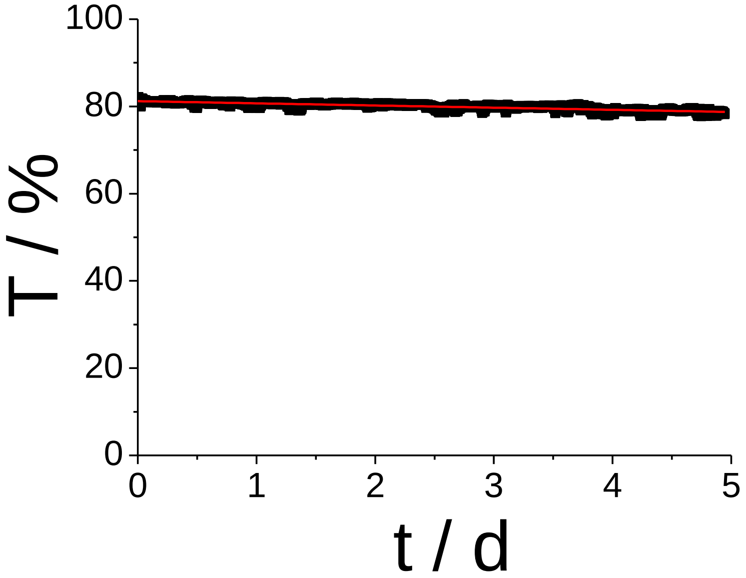
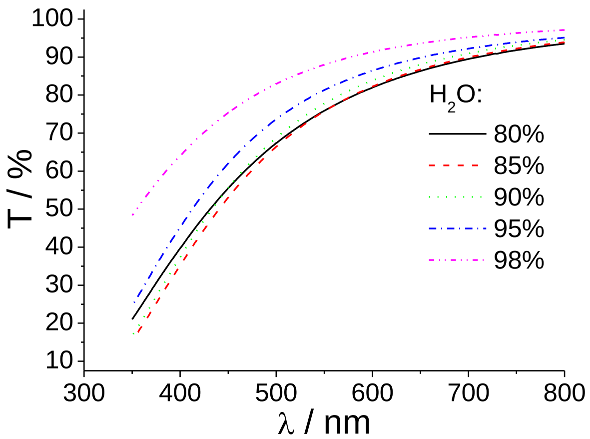
Long-time turbidity measurements:



S1: Transmittance (T) of an o/w-nanoemulsion (95% H_2O) was measured at 25.0 ± 0.1°C and 633 nm time-dependently for five days. Measurement was done using an in-house transmittance-setup; built-on a 4 mW He-Ne-Laser, a thermostated sample holder and a PH100-Si photodetector (Gentec-E0) connected to a Gentec-E0 SOLO PE Laser Power & Energy meter. No significant structural changes (decrease of transmittance T ~ 1.5% per day) could be observed during our typical experimental time window of 2-5 days.

UV/Vis-Transmittance measurements:



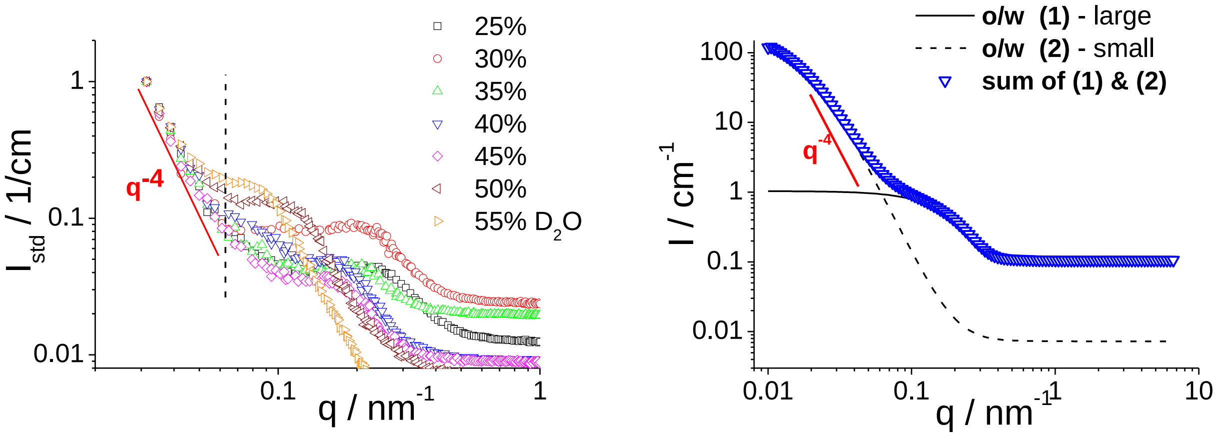
S2: UV/Vis-transmittance spectra for oil/water solutions in the nanoemulsion region (> 75% H_2O) using 0.5 mm cells at 25.0 ± 0.1°C

		800 nm		700 nm		626 nm	
oil	**H_2O**	**T**	**R**	**T**	**R**	**T**	**R**
%	**%**	**%**	**nm**	**%**	**nm**	**%**	**nm**
20	**80**	97.1	14.5	95.1	14.6	92.5	14.5
15	**85**	91.7	23.7	86.7	23.4	80.2	23.3
10	**90**	91.0	28.4	85.2	28.4	77.6	28.5
5	**95**	93.5	32.3	89.3	32.1	83.8	32.1
2	**98**	96.0	39.3	93.5	38.9	90.1	38.7

600 nm		500 nm		400 nm		350 nm	
T	**R**	**T**	**R**	**T**	**R**	**T**	**R**
%	**nm**	**%**	**nm**	**%**	**nm**	**%**	**nm**
91.2	14.5	82.7	14.5	60.8	14.8	39.1	15.3
77.1	23.3	58.5	23.2	26.7	23.3	10.2	23.4
74.0	28.5	53.0	28.7	20.3	29.0	6.58	29.0
81.1	32.1	64.4	32.3	33.6	32.4	16.1	32.2
88.5	38.6	78.2	38.2	56.7	37.5	40.1	36.8

S3: Values of approximated particle size R for o/w-nanoemulsions (> 75wt-% H_2O), calculated from the transmittances obtained by UV/Vis measurements (fig. S2)

SANS measurements – Scattering curves (lower phases):



a) b)

S4: a) lower (eg. Fig. 8) scattering curves have been normalised to a maximum intensity of 1 cm^{-1} respectively; b) theoretical simulation (polydisperse Log-normal distributed spherical model) of a scattering curve consisting of two populations (large and small o/w droplets), observed q^{-4} dependence in Porod regime evidences assumptions of small o/w-droplets in the lower phase with bigger dispersed oddments of upper one

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SANS measurements – Teubner Strey analysis (upper phases):

H_2O %	Chi-Sqr	c0 [1/cm]	c2 [nm^4]	V [nm^3]	a2 [ ]	c1 [nm^2]	ξi [nm]	Ds [nm]	fa [ ]
5	0.9990	0.89	201	66979	11.2	0.778	2.90	18.4	0.008
10	0.9994	0.92	2.30E+06	104401	52959	-219444	4.38	19.9	-0.314
15	0.9995	0.95	1.86E+06	124125	24368	-185291	5.56	21.9	-0.435
20	0.9991	0.98	502	136081	4.05	-46.1	6.75	24.1	-0.511
25	0.9991	0.98	14036	137582	73.6	-1153	7.99	26.4	-0.567
30	0.9988	1.01	240886	139747	846	-17309	9.26	28.8	-0.606
35	0.9986	1.03	223197	136090	493	-13308	10.8	32.1	-0.634
40	0.9978	1.06	253	136936	0.356	-12.2	12.3	35.8	-0.645
50	0.9966	1.12	1.39E+07	148370	12285	-541774	14.0	40.1	-0.655
55	0.9913	1.04	3.01E+07	127838	7912	-581632	17.5	55.3	-0.595
60	0.9897	0.75	3.82E+08	112835	44164	-3.30E+06	17.6	72.4	-0.402
65	0.9884	0.58	4.22E+12	96696	2.86E+08	-1.91E+10	18.3	86.7	-0.275
70	0.9888	0.29	1.43E+12	15233	6.15E+07	-9.35E+09	24.7	89.6	-0.499
75	0.9894	0.38	2.22E+08	41363	11560	-2.17E+06	29.3	80.7	-0.678
80	0.9853	0.29	3.58E+07	23764	1641	-395349	40.0	80.2	-0.815
85	0.9984	0.20	4.67E+14	44763	2.22E+10	-2.95E+12	23.1	88.6	-0.458
90	0.9997	0.15	8.06E+18	41306	2.17E+14	1.32E+16	18.2	134	0.158
95	0.9994	0.08	1.04E+08	12109	344	80457	30.1	235	0.213
98	0.9996	0.05	3.88E+08	4057	654	123223	37.1	263	0.122

S5: Obtained Teubner-Strey parameters for *upper phases* of SANS-data treatment using eq. 9-14; scattering length density difference between oil and water was calculated for oil dominated samples as $6.37\cdot10^{-4}$ nm^{-2} (5 < x < 40wt-% H_2O) and for water dominated samples as $6.06\cdot10^{-4}$ nm^{-2} (50 < x < 98wt-% H_2O); a_2, c_1 and c_2 are coefficients of various terms of order parameters in Landaus free energy. In the case of a microemulsion, c_1 indicates the tendency of forming interfaces between different domains and is usually negative, whereas a positive a_2 favours the microemulsion formation. For a stable morphology the criteria of $4a_2c_2 - c_1 > 0$ with a positive c_2 is required[1]; fa is the amphiphilicity factor and reaches from 1 for a completely disordered solution to -1 for a superlattice which assumes in case of microemulsions a lamellar structure.

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SANS measurements – Teubner Strey analysis (lower phases):

H_2O %	Chi-Sqr	c0 [1/cm]	c2 [nm^4]	V [nm^3]	a2 [ ]	c1 [nm^2]	ξi [nm]	Ds [nm]	fa [ ]
25	0.9956	0.18	8180	175	43.2	-633	7.67	26.6	-0.532
30	0.9904	0.15	1.02E+06	95.7	3485	-67869	8.91	29.3	-0.570
35	0.9665	0.13	360280	18.5	802	-23941	12.0	31.3	-0.704
40	0.9921	0.12	2.09E+06	26.9	2301	-100109	14.7	37.2	-0.722
50	0.9863	0.11	5.07E+06	14.7	5002	-230924	15.2	38.2	-0.725
55	0.9976	0.09	5.58E+15	22.3	1.16E+12	-9.37E+13	18.2	58.8	-0.583
60	0.9989	0.07	5.42E+07	76.6	3856	-498566	22.8	77.8	-0.545
65	0.9651	0.34	7.61E+07	9765	4379	-1.03E+06	50.4	74.1	-0.896
75	0.9863	0.33	1.02E+08	30108	3744	-883937	34.0	87.2	-0.715

S6: Obtained Teubner-Strey parameters for *lower phases* of SANS-data treatment using eq. 9-14; scattering length density difference between oil and water was calculated for water dominated samples as $6.06 \cdot 10^{-4}$ nm^{-2} ($5 < x < 98$wt-% H_2O); a_2, c_1 and c_2 are coefficients of various terms of order parameters in Landaus free energy. In the case of a microemulsion, c_1 indicates the tendency of forming interfaces between different domains and is usually negative, whereas a positive a_2 favours the microemulsion formation. For a stable morphology the criteria of $4a_2c_2 - c_1 > 0$ with a positive c_2 is required[1] ; fa is the amphiphilicity factor and reaches from 1 for a completely disordered solution to -1 for a superlattice which assumes in case of microemulsions a lamellar structure.

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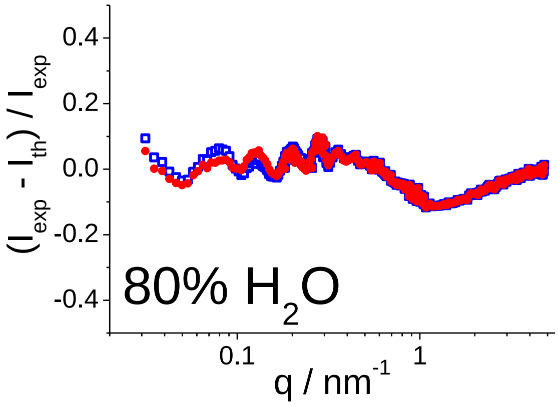
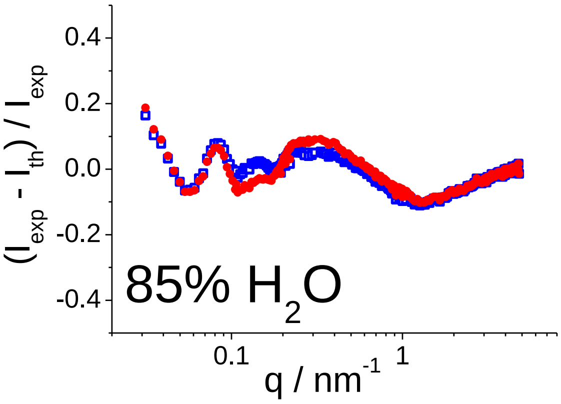
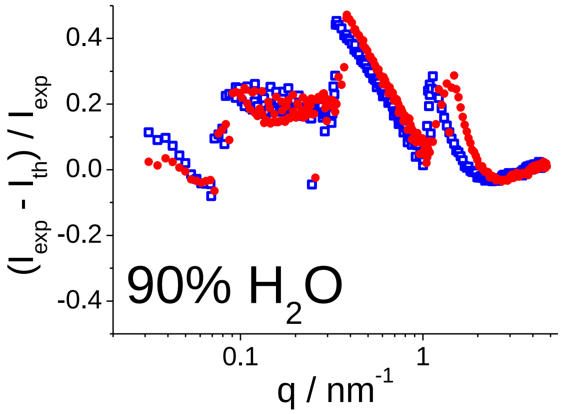
SANS measurements–Residuals for mono- and bimodal data analyses



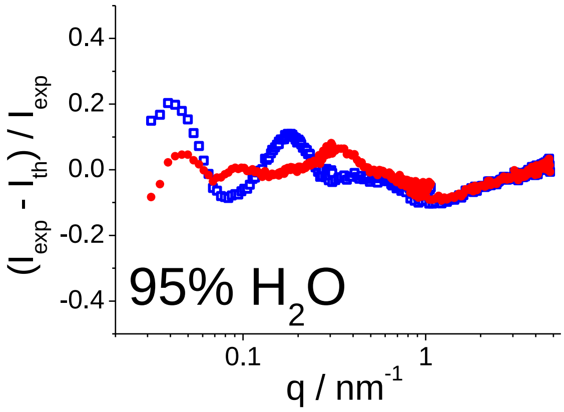
a)



b)



c)



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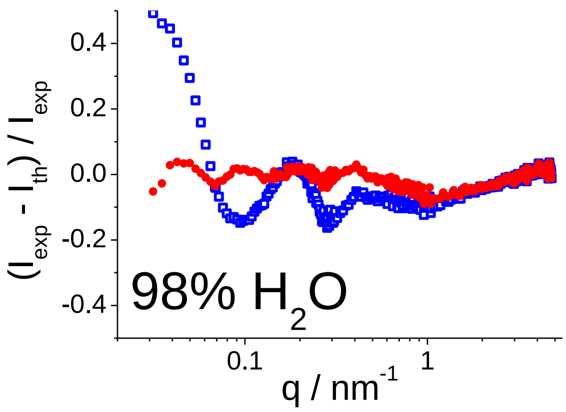

e)

S7: Residue of SANS-data fits with □ monomodal and ● bimodal size distributions for spherical o/w-nanoemulsion droplets (water conc. > 75% **a-e**)

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SANS measurements – number weighted radii:

wt(D_2O)	$R_{1,N}$	$R_{2,N}$	$R_{1,Mw}$	$R_{2,Mw}$
%	nm	nm	nm	nm
80	9.71	25.3	12.7	31.6
85	11.1	25.6	14.3	32.0
90	11.6	26.0	14.8	32.8
95	12.2	27.0	15.4	35.6
98	12.7	29.1	16.0	39.4

S8: Number-weighted (N) and mass weighted (Mw) radii R of population R_1 and population R_2 using Log normal distributed spherical model for two populations

Mass weighted radii $\langle R\rangle_{Mw}$ are accessible via the first four moments of distribution function f(R). Detailed information about its calculation and the four moments of most widely used distributions can be found elsewhere[2].

$$\langle R\rangle_{Mw} = \frac{\int R\cdot R^3 \cdot f(R)dR}{\int R^3 \cdot f(R)dR} \qquad \text{(i)}$$

[1] M. Teubner, R. Strey, *J. Chem. Phys.* **1987,** *87,* 3195-3200

[2] Y.D. Yan, J.H.R. Clarke, *Adv. Colloid Interface Sci.* **1989**, *29*, 277-318