Supporting information for: Looking into *Limoncello*: the structure of the Italian liquor revealed by small-angle scattering

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1 Additional ^{1}H-NMR spectra

To clearly assign the signals in the ^{1}H-NMR spectrum of the ethanolic extract reported in the main text, the spectra of the pure d6-ethanol and an ethanol/water mixture were recorded and are reported in Figs. S1 and S2.

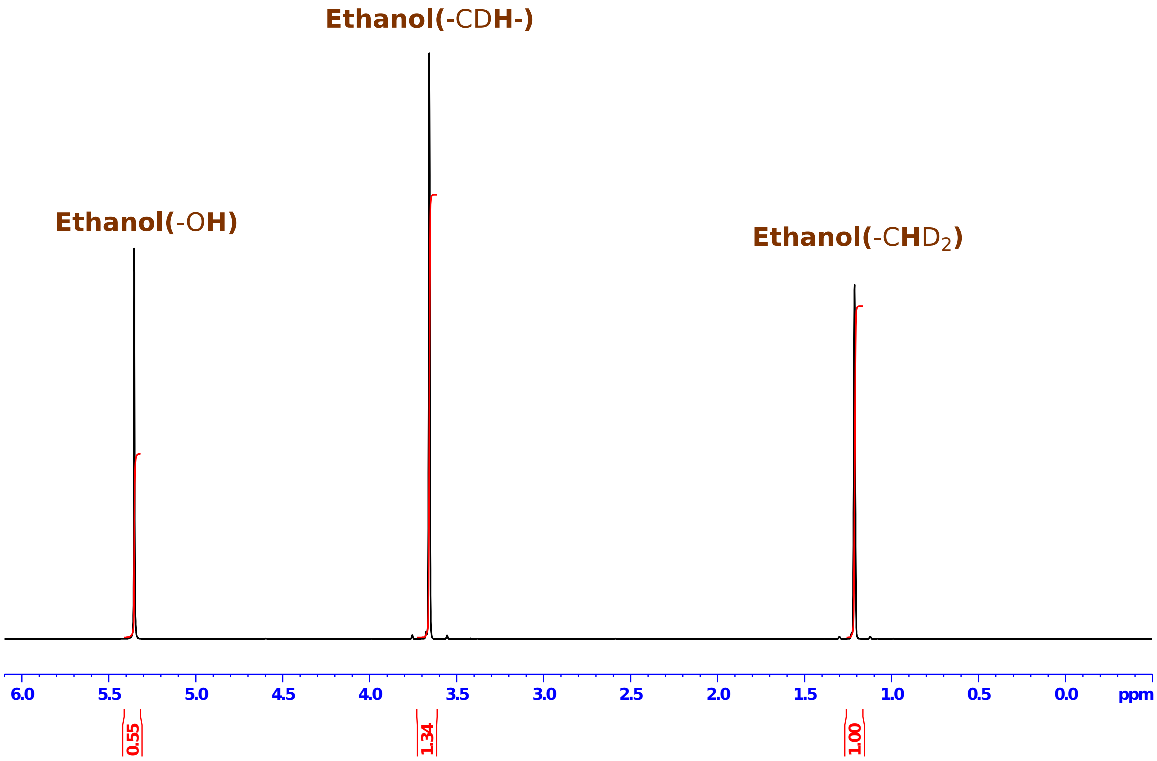

Figure S1: ^{1}H-NMR spectrum of the d6-ethanol used for the preparation of the lemon peel ethanolic extract.

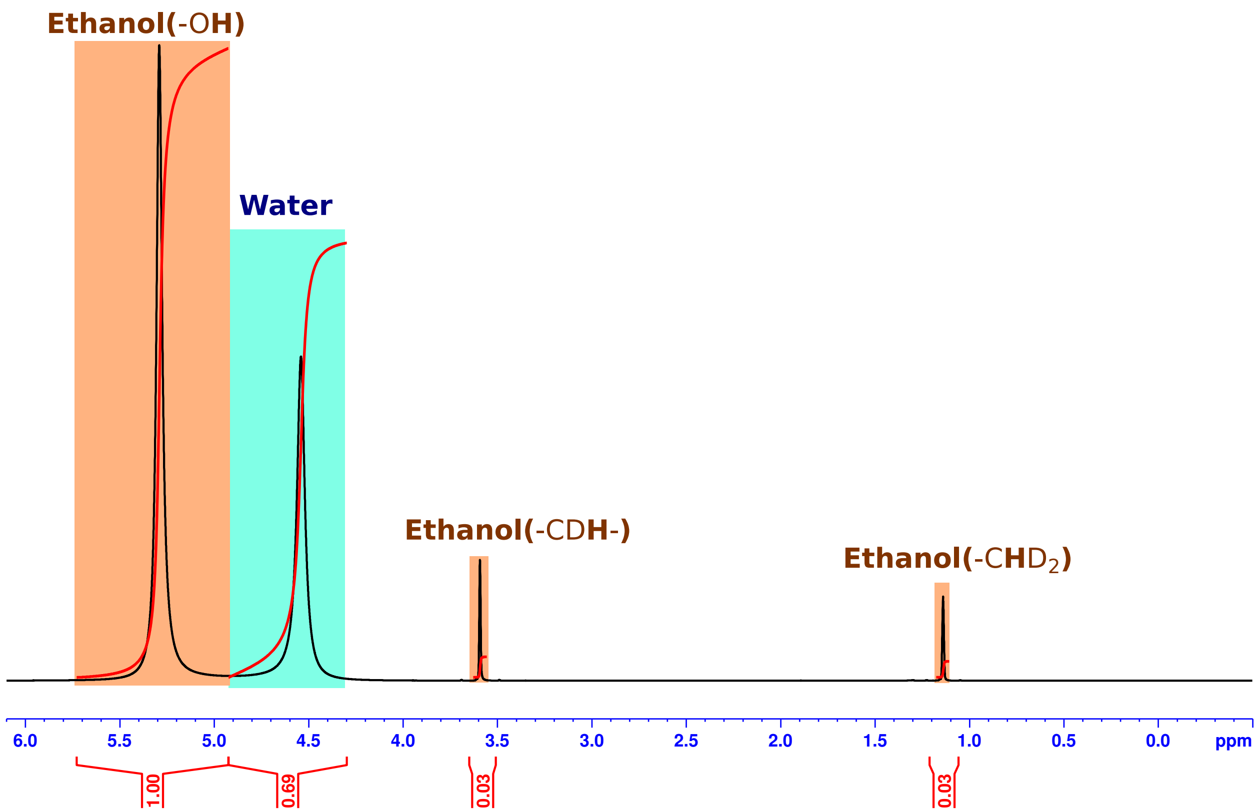

Figure S2: ^{1}H-NMR spectrum of a water/d6-ethanol mixture with 9 wt% water content.

2 Density and scattering length density measurements

The density of different water/ethanol/sucrose mixtures was measured as a function of temperature to evaluate the scattering length densities of the continuous phase used to obtain the scattering contrast. The composition of the investigated mixtures is given in table S1, and the temperature-dependent densities are plotted in Fig. S3. The density of limonene is also reported as a function of temperature in Fig. S4 with the data taken from Ref. S1. The experimentally obtained density values of the solutions are compared with the values calculated assuming additivity of the volumes of the single components:

$$d_{calc} = \left(\sum_i \frac{m_i}{m_{tot}} v_i \right) \tag{S1}$$

with v_i being the specific volume of the i^{th} components, whose weight fraction in the solution is given by m_i/m_{tot}. For the calculations, specific volumes of 1.274, 0.997, and 0.588 $\mathrm{cm^3\ g^{-1}}$, for ethanol, water, and sugar, were used, respectively. The deviation between calculated and experimentally obtained values is maximal 6%, and both values are given in table S1 and shown in Fig. S5. The small but systematic deviation is a consequence of the negative excess mixing volume of ethanol and water. The temperature dependence of the densities was used to calculate the scattering length densities of the ethanol, water, and sucrose mixtures of the "Limoncello" samples discussed in the main text.

Table S1: Composition and densities values obtained experimentally and calculated using eq. S1 of mixtures used in this work.

Name	weight fraction EtOH	weight fraction Sucrose	weight fraction Water	Exp. Density kg m^{-3}	Calc. Density kg m^{-3}
L1	0.81	0.00	0.19	840	821
L2	0.63	0.09	0.28	903	881
L3	0.43	0.18	0.40	980	954
L4	0.30	0.23	0.47	1031	1006
L5	0.22	0.27	0.52	1064	1044
L6	0.30	0.17	0.59	990	933
L7	0.31	0.11	0.63	972	915
L8	0.31	0.06	0.66	959	914
L9	0.31	0.00	0.69	949	924

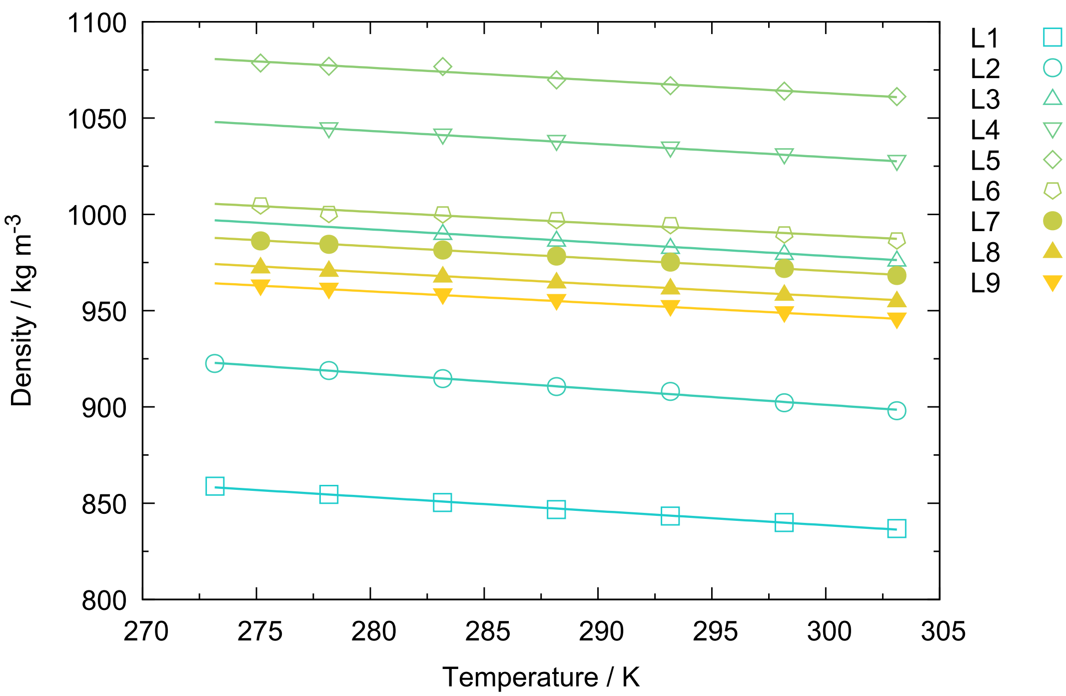

Figure S3: Densities of different mixtures of water/ethanol/sucrose recorded at different temperatures. For the exact composition of the samples, the reader is referred to table S1. Full lines show linear regression to experimental points.

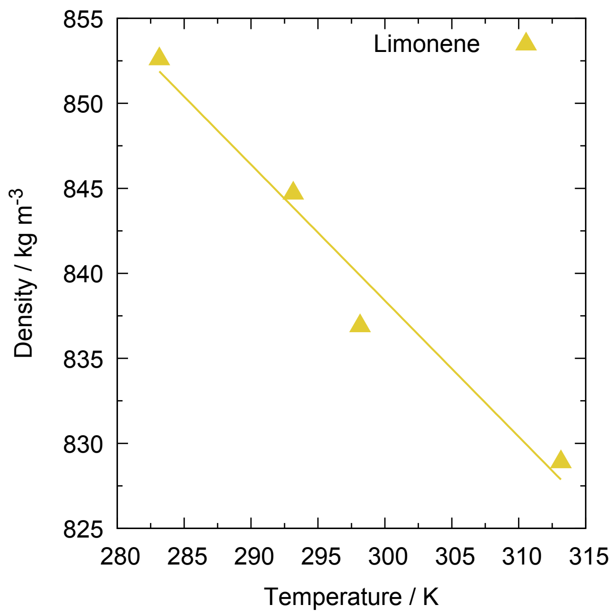

Figure S4: Densities of Limonene as a function of temperature taken from Ref. S1. Full lines show linear regression to experimental points.

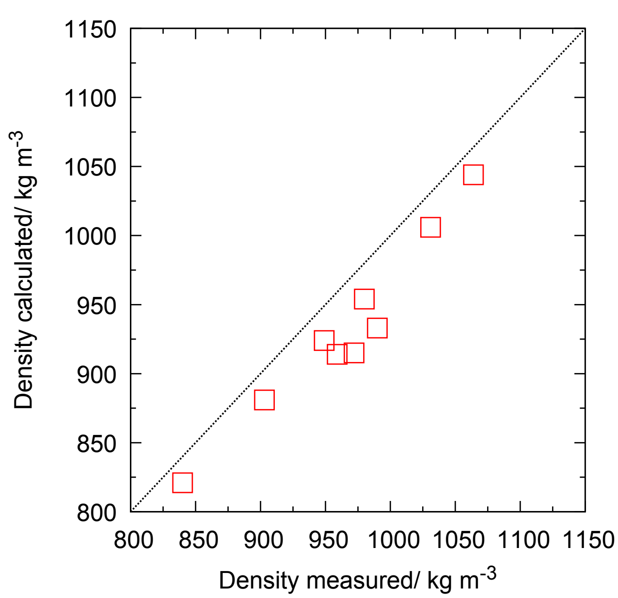

Figure S5: Correlation plot of experimentally determined density and the ones calculated assuming additivities of volumes of the single components. Broken line indicates full correlation between calculated and experimentally determined values.

3 Additional Phase Diagram

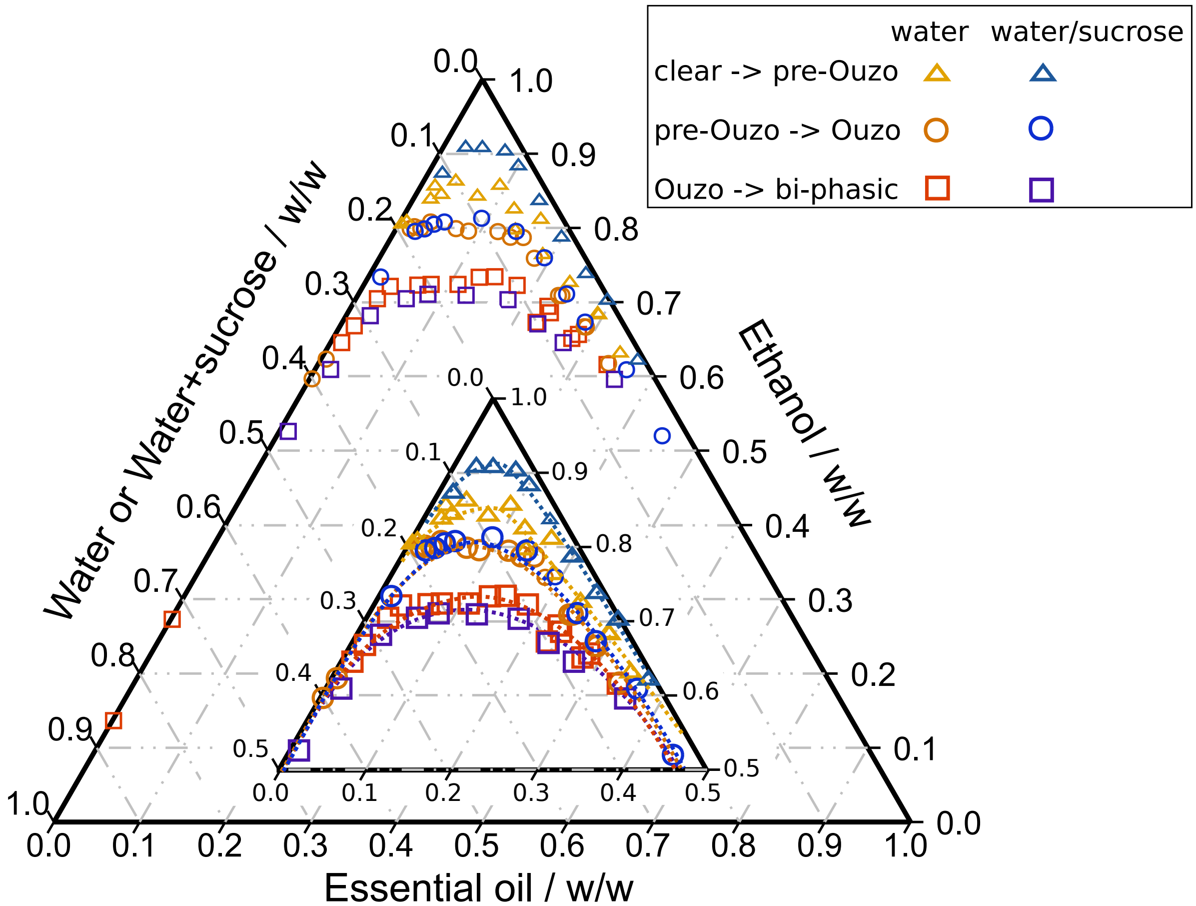

Figure S6: Phase diagram recorded for mixtures of water or of a 33 wt% sucrose in water solution, ethanol, and citrus lemon essential oil extract is given. See full text for further details. Triangles represent transition from the homogeneous to the pre-Ouzo region, circles represent the transition to the Ouzo-region, and squares delimit the region where rapid phase separation occurs. Inset represents enlargement of the ethanol-rich corner of the phase diagram. Concentrations are given in weight fraction. Brocken lines are only a guide to the eyes.

4 Additional SANS patterns

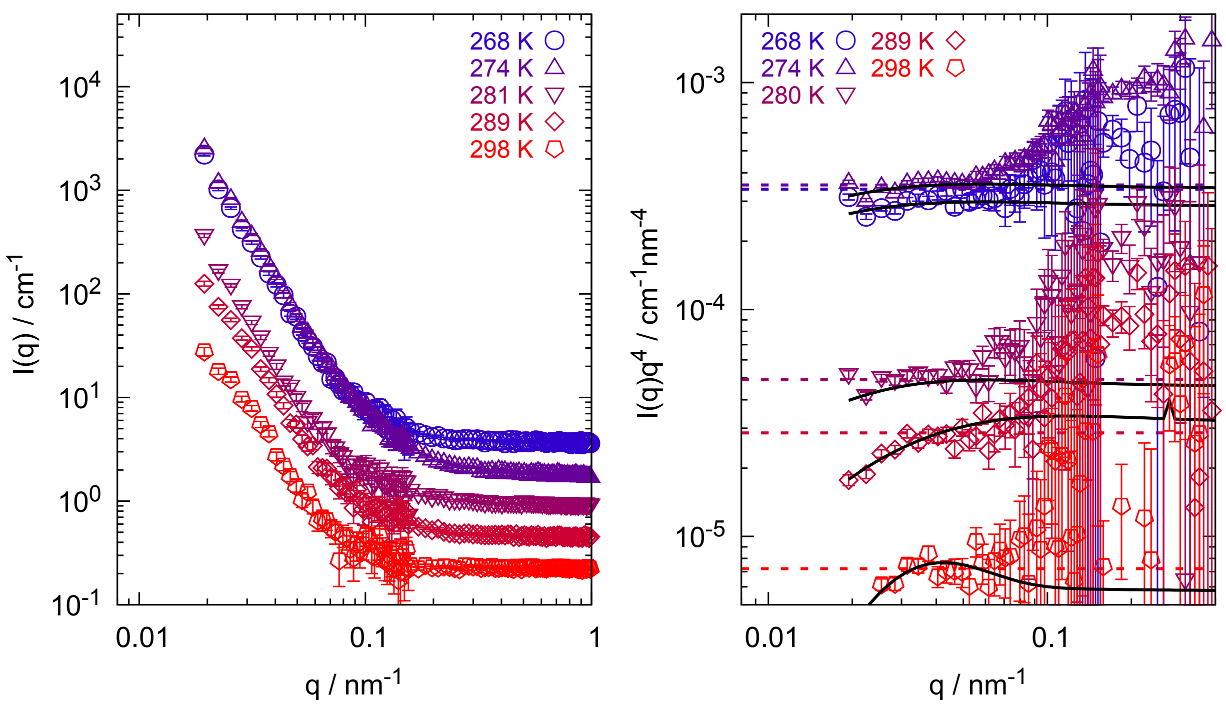

Figure S7: SANS Patterns arising from the sample **LM2**, with a wight fraction composition of 0.21%wt essential oil, 62.2%wt Ethanol, 8.9%wt sucrose, and 28.7%wt water (see Fig. 2 of the main text for location in the pseudoternary phase diagram) recorded at different temperatures. On the left, the scattering intensity is reported as a function of the scattering vector. On the right, the data are reported in the Porod representiation, the full line represents the calculated scattering curve according to a model of polydisperse spheres, the dashed horizontal line represents the Porod constant. See main text for further details. The curves were scaled by successive factors of 2 for improved readability.

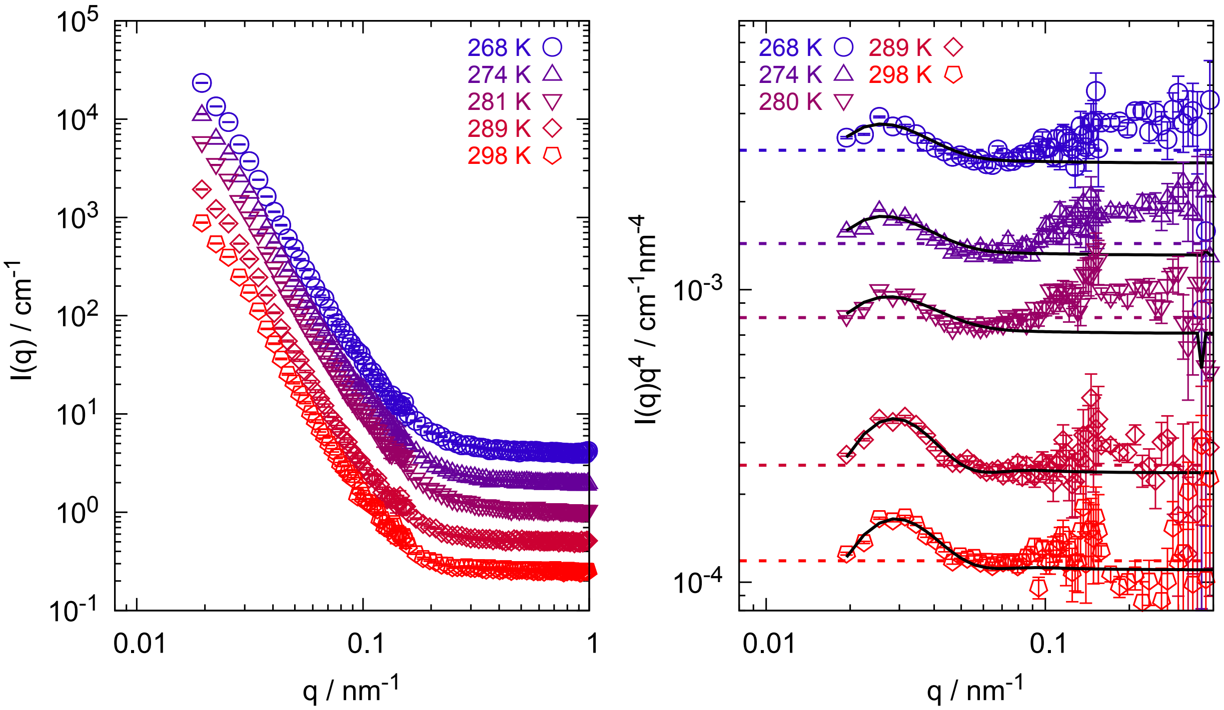

Figure S8: SANS Patterns arising from the sample **LM3**, with a wight fraction composition of 0.14%wt essential oil, 42.1%wt Ethanol, 16.8%wt sucrose, and 41.0%wt water (see Fig. 2 of the main text for location in the pseudoternary phase diagram) recorded at different temperatures. On the left, the scattering intensity is reported as a function of the scattering vector. On the right, the data are reported in the Porod representiation, the full line represents the calculated scattering curve according to a model of polydisperse spheres, the dashed horizontal line represents the Porod constant. See main text for further details. The curves were scaled by successive factors of 2 for improved readability.

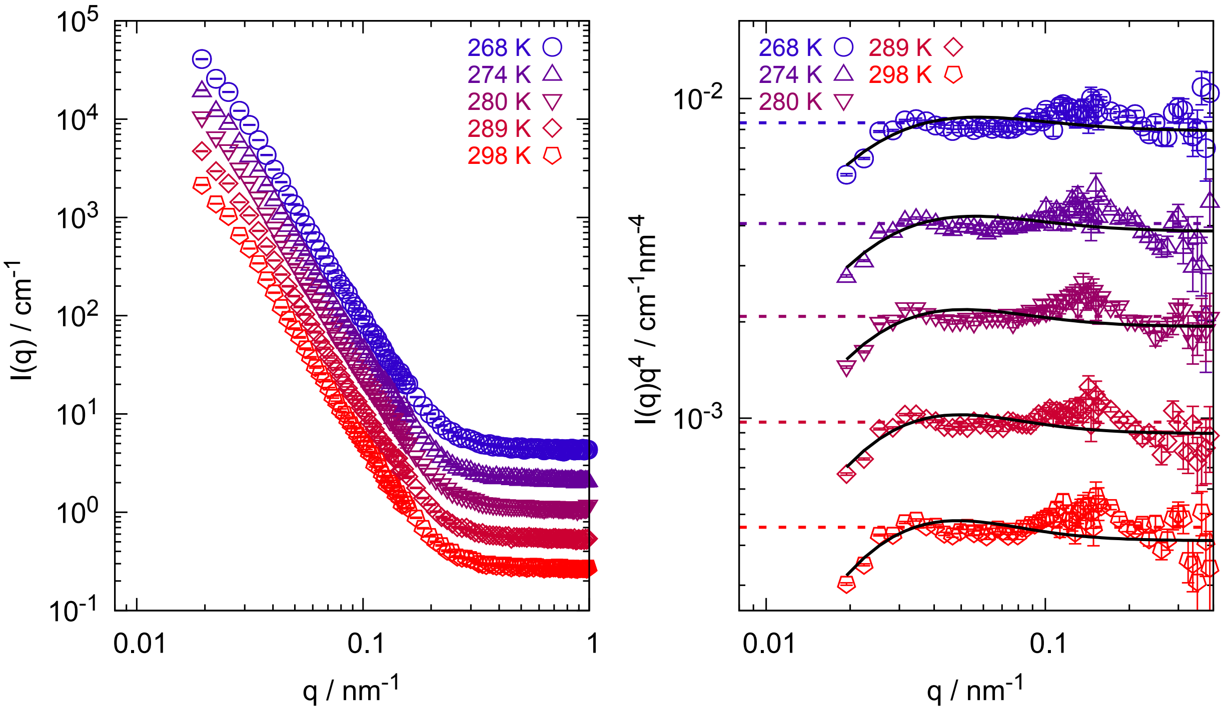

Figure S9: SANS Patterns arising from the sample **LM4**, with a weight fraction composition of 0.07%wt essential oil, 21.4%wt Ethanol, 24.9%wt sucrose, and 53.6% water (see Fig. 2 of the main text for location in the pseudoternary phase diagram) recorded at different temperatures. On the left, the scattering intensity is reported as a function of the scattering vector. On the right, the data are reported in the Porod representiation, the full line represents the calculated scattering curve according to a model of polydisperse spheres, the dashed horizontal line represents the Porod constant. See main text for further details. The curves were scaled by successive factors of 2 for improved readability.

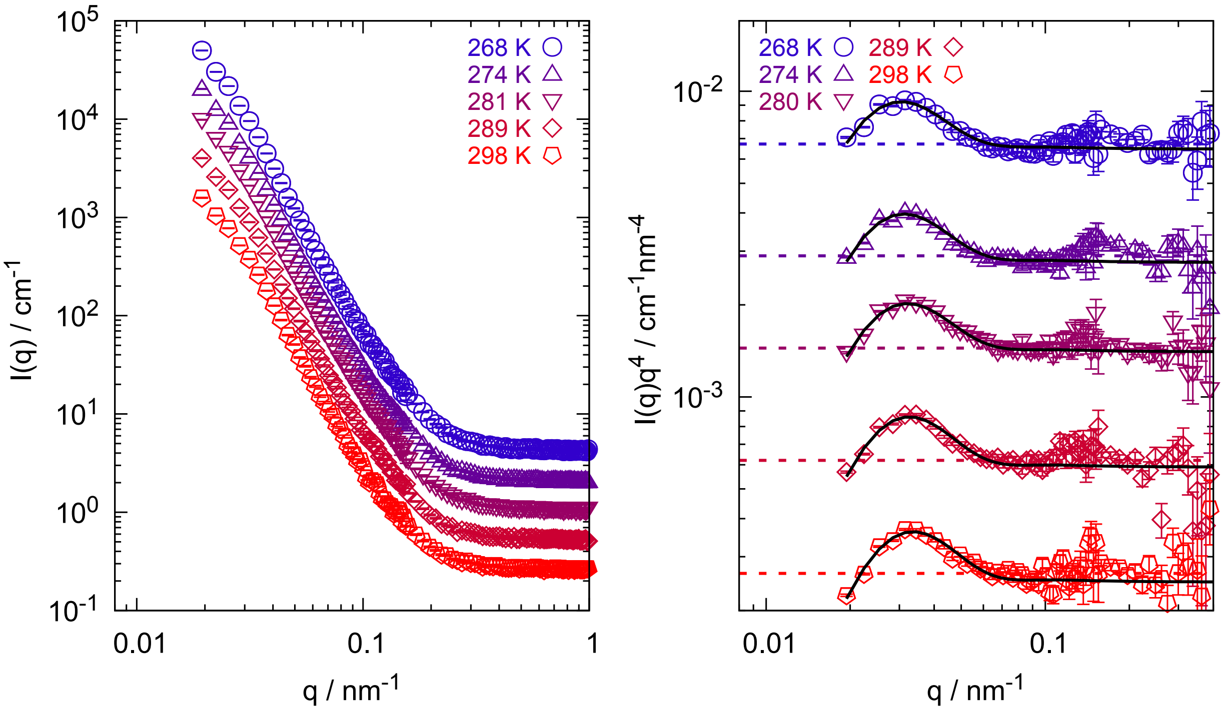

Figure S10: SANS Patterns arising from the sample **LM5**, with a weight fraction composition of 0.10%wt essential oil, 31.7%wt Ethanol, 20.8%wt sucrose, and 47.3%wt water (see Fig. 2 of the main text for location in the pseudoternary phase diagram) recorded at different temperatures. On the left, the scattering intensity is reported as a function of the scattering vector. On the right, the data are reported in the Porod representiation, the full line represents the calculated scattering curve according to a model of polydisperse spheres, the dashed horizontal line represents the Porod constant. See main text for further details. The curves were scaled by successive factors of 2 for improved readability.

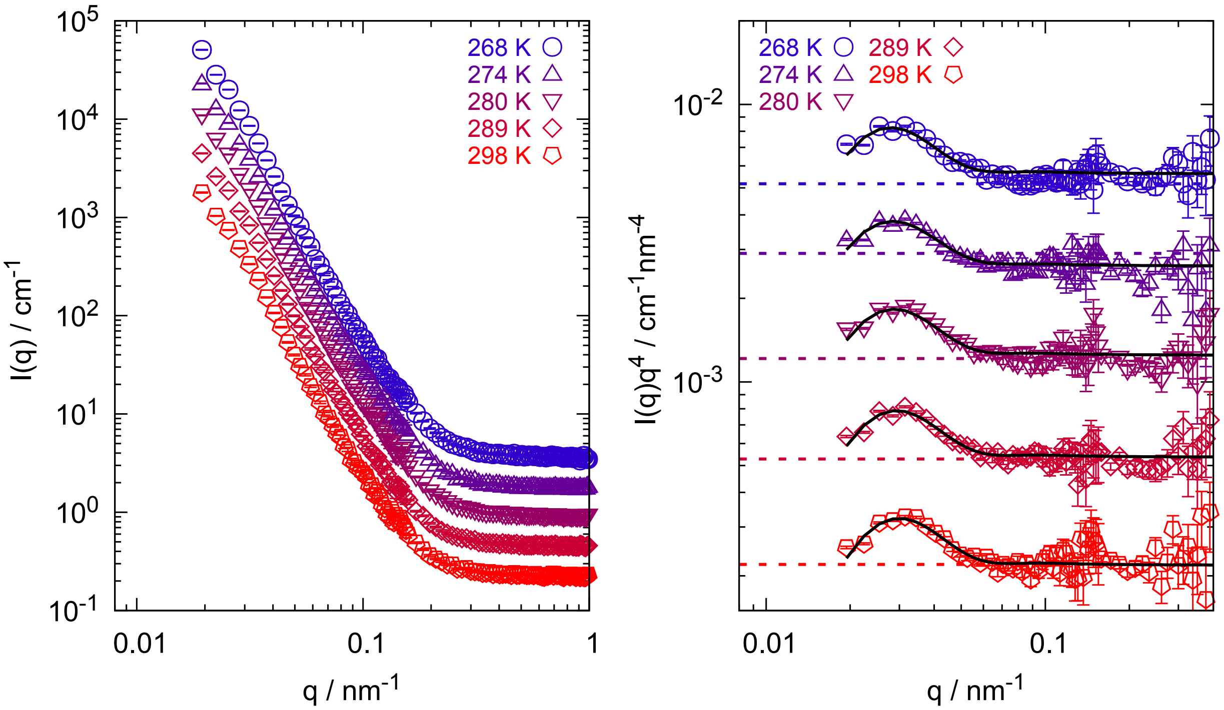

Figure S11: SANS Patterns arising from the sample **LM6**, with a weight fraction composition of 0.10%wt essential oil, 31.2%wt Ethanol, 16.1%wt sucrose, and 52.6%wt water (see Fig. 2 of the main text for location in the pseudoternary phase diagram) recorded at different temperatures. On the left, the scattering intensity is reported as a function of the scattering vector. On the right, the data are reported in the Porod representiation, the full line represents the calculated scattering curve according to a model of polydisperse spheres, the dashed horizontal line represents the Porod constant. See main text for further details. The curves were scaled by successive factors of 2 for improved readability.

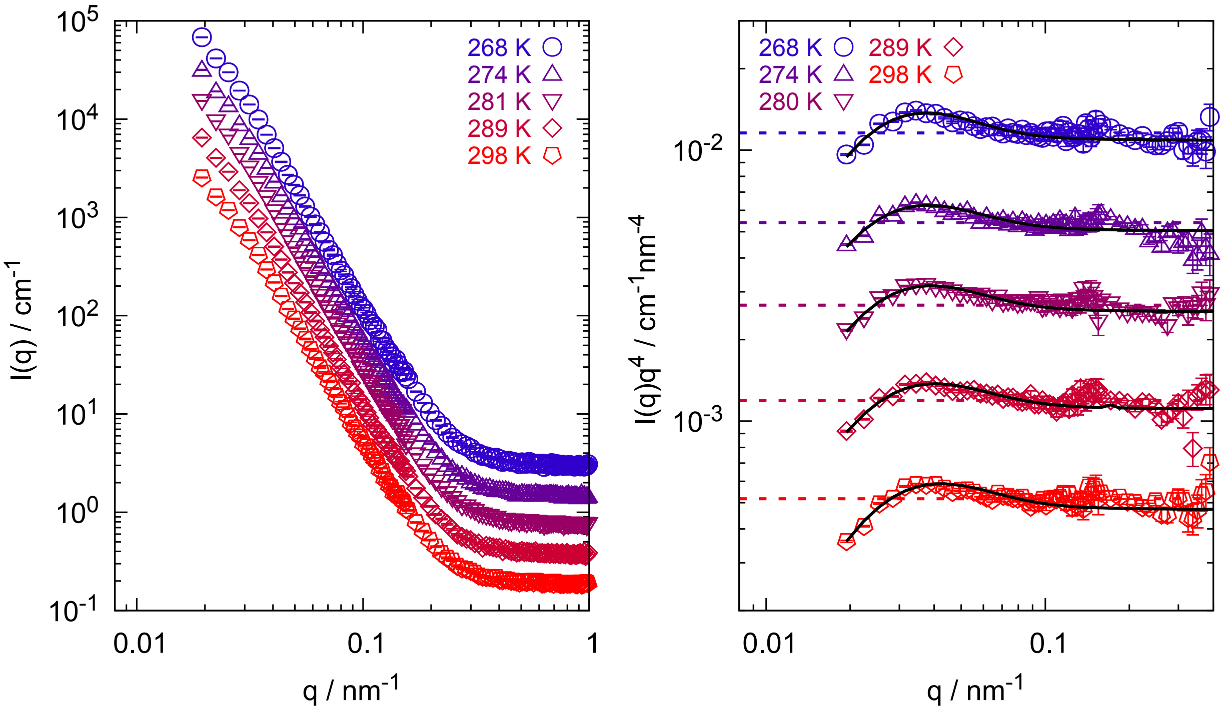

Figure S12: SANS Patterns arising from the sample **LM7**, with a weight fraction composition of 0.10%wt essential oil, 31.7%wt Ethanol, 10.9%wt sucrose, and 57.3%wt water (see Fig. 2 of the main text for location in the pseudoternary phase diagram) recorded at different temperatures. On the left, the scattering intensity is reported as a function of the scattering vector. On the right, the data are reported in the Porod representiation, the full line represents the calculated scattering curve according to a model of polydisperse spheres, the dashed horizontal line represents the Porod constant. See main text for further details. The curves were scaled by successive factors of 2 for improved readability.

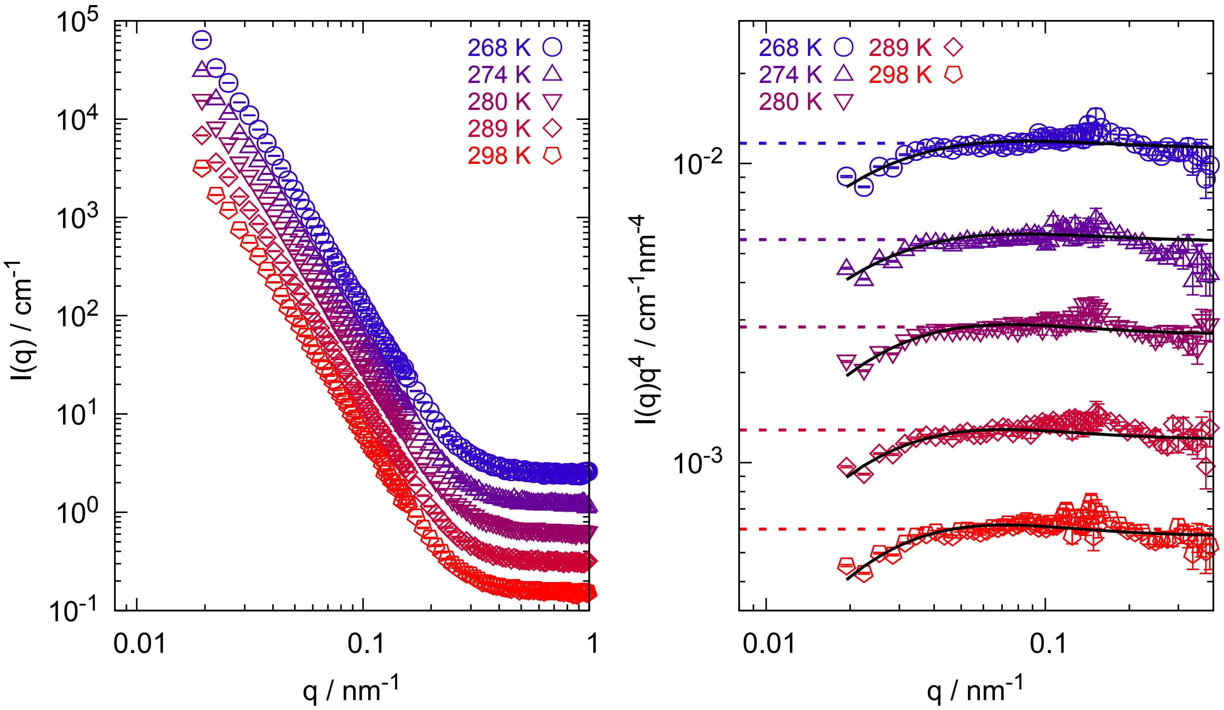

Figure S13: SANS Patterns arising from the sample **LM8**, with a weight fraction composition of 0.10%wt essential oil, 30.9%vol Ethanol, 6.4%wt sucrose, and 62.6%wt water (see Fig. 2 of the main text for location in the pseudoternary phase diagram) recorded at different temperatures. On the left, the scattering intensity is reported as a function of the scattering vector. On the right, the data are reported in the Porod representiation, the full line represents the calculated scattering curve according to a model of polydisperse spheres, the dashed horizontal line represents the Porod constant. See main text for further details. The curves were scaled by successive factors of 2 for improved readability.

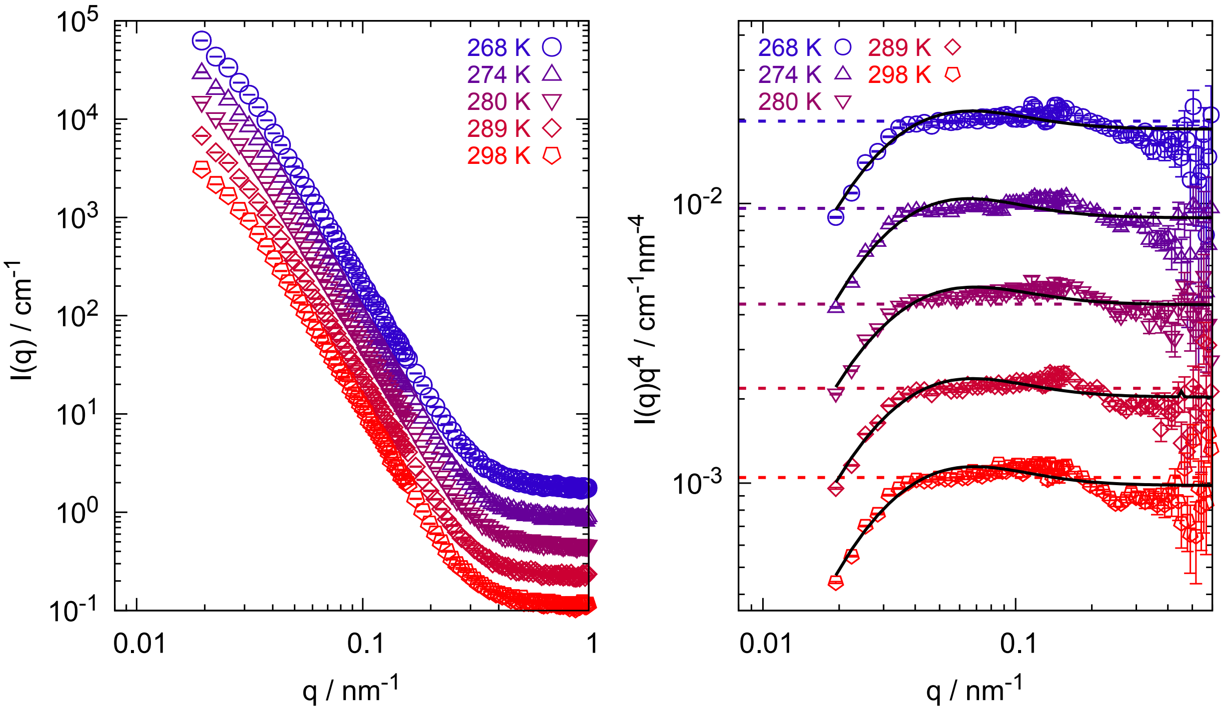

Figure S14: SANS Patterns arising from the sample **LM9**, with a weight fraction composition of 0.10%wt essential oil, 31.6%vol Ethanol, 0.0%wt sucrose, and 68.3% water (see Fig. 2 of the main text for location in the pseudoternary phase diagram) recorded at different temperatures. On the left, the scattering intensity is reported as a function of the scattering vector. On the right, the data are reported in the Porod representiation, the full line represents the calculated scattering curve according to a model of polydisperse spheres, the dashed horizontal line represents the Porod constant. See main text for further details. The curves were scaled by successive factors of 2 for improved readability.

5 Additional SANS results

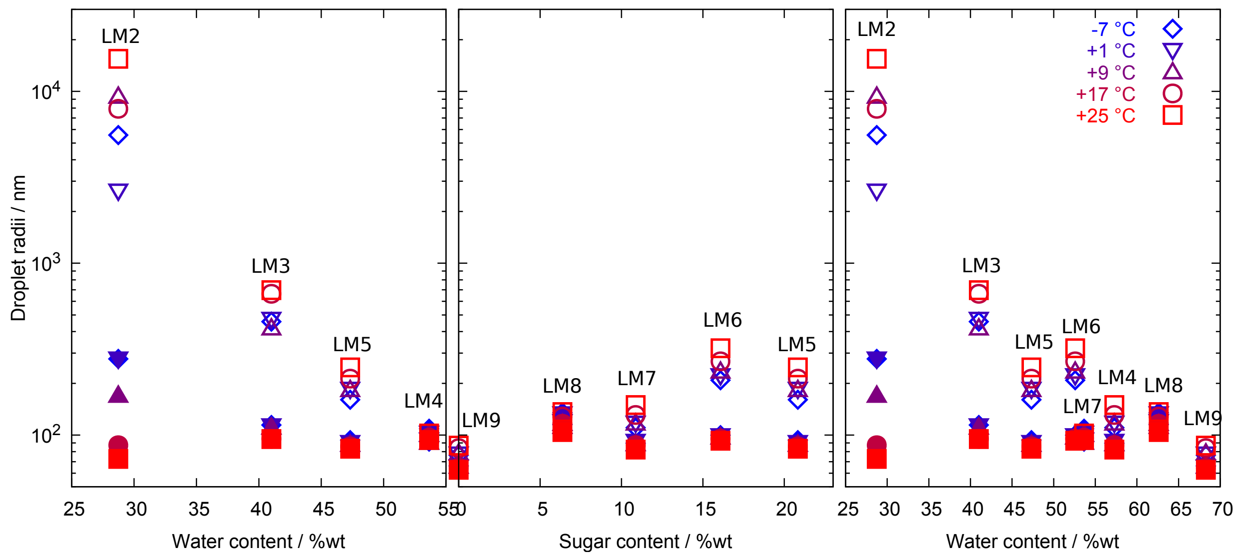

Figure S15: Average droplet size found in the different Limoncello samples by the analysis of the SANS patterns. Empty symbols represents sizes obtained via the Porod analysis under the assumption that the essential oil completely separates into domains dispersed in the water/alcohol/sucrose mixture. Full symbols result from modeling the SANS curves with a polydisperse sphere model, whereby the amount of separated oil was not fixed in the model. See main text for full details. On the left: radii of samples prepared along the dilution line of the ethanolic extract with the sucrose syrup are given as a function of water content; In the center figure: radii of samples prepared at constant oil and ethanol content and variable water and sugar amount are given as a function of sugar content: On the right: radii of all samples are given as a function of water content. The different symbols indicate experiments performed at different temperatures.

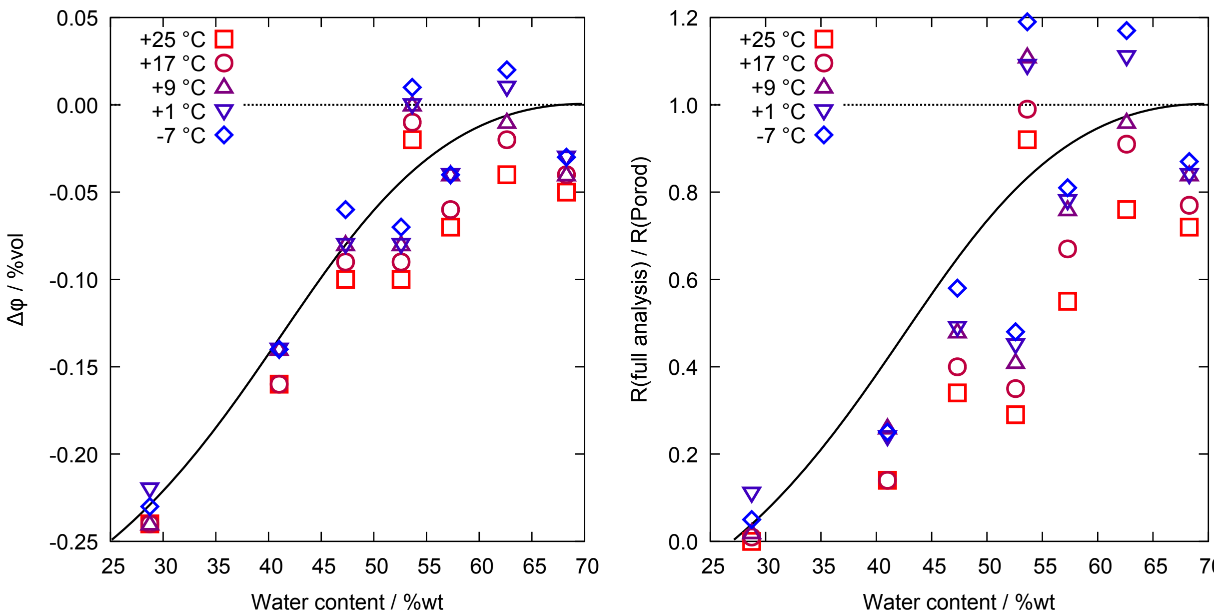

Figure S16: Comparison of fit results from the Porod analysis and the from the description of the SANS curves with polydisperse sphere model. On the left: the difference of the volume fraction of oil droplets as found from the polydisperse sphere model and the value calculated using an oil content of 0.28 %wt in the ethanolic extract, as found by ^{1}H-NMR, is given as a function of the toal water content of the sample. On the right: the ratio between the mean radius resulting from the polydisperse sphere model, defined as the ratio of the third and second moment of the distribution, and the droplet radius obtained from the Porod analysis, is given as a function of the toal water content of the sample. Dashed line indicate consistent results between the two models, full lines indicate the trend and are only a guide for the eyes. All parameters are given in Table S2.

Table S2: Parameters ontained from the SANS data analysis for all samples probed at the different temperatures: the vol% oil is the one calculated assuming a 0.28%vol oil content in the ethanolic extract, $\Delta\rho$ is the scattering contrast between the essential oil droplet and the medium, Σ is the total surface obtained from the Porod analysis, and R_P is the Porod radius (uncertainty on the last significant digit expressed in parenthesis). ϕ, μ, and σ are the parameters obtained from the fit of a model of polydisperse spheres, with ϕ being the droplet volume fraction and μ and σ defining the size distribution; $\langle R^3 \rangle / \langle R^2 \rangle$ is the ratio between the third and second moment of the size distribution. See full text for further details.

Sample	T / K	vol% oil	$\Delta\rho$ / 10^4 nm^{-2}	Σ / cm-1	R_P / nm	ϕ	μ / nm	σ	$\langle R^3 \rangle / \langle R^2 \rangle$
LM2	266	0.24%	5.06	13.2	5600(100)	0.011%	10.9	1.14	277
LM2	274	0.24%	5.02	27.9	2600(100)	0.025%	10.9	1.14	277
LM2	282	0.24%	4.99	7.8	9400(400)	0.004%	14.0	1.00	170
LM2	290	0.24%	4.95	9.3	7900(300)	0.003%	7.1	1.00	87
LM2	298	0.24%	4.91	4.7	15000(600)	0.001%	42.2	0.47	73
LM3	266	0.18%	5.01	118.6	457(5)	0.041%	71.0	0.44	114
LM3	274	0.18%	4.99	115.1	472(5)	0.040%	69.6	0.44	113
LM3	282	0.18%	4.96	129.9	419(5)	0.042%	65.3	0.46	111
LM3	290	0.18%	4.93	82.2	663(10)	0.025%	71.8	0.33	95
LM3	298	0.18%	4.90	78.4	697(10)	0.023%	69.2	0.35	95
LM4	266	0.10%	4.99	335.1	91(1)	0.115%	19.9	0.82	109
LM4	274	0.10%	4.97	327.8	93(1)	0.106%	21.6	0.79	103
LM4	282	0.10%	4.94	339.3	90.8(9)	0.106%	25.0	0.75	101
LM4	290	0.10%	4.92	320.0	96.5(9)	0.095%	27.1	0.71	96
LM4	298	0.10%	4.89	303.1	102.1(9)	0.086%	28.4	0.69	94
LM5	266	0.14%	4.99	268.1	160(1)	0.080%	63.6	0.39	93
LM5	274	0.14%	4.97	233.2	184(2)	0.067%	62.5	0.38	91
LM5	282	0.14%	4.94	235.2	183(2)	0.067%	60.7	0.39	88
LM5	290	0.14%	4.92	203.7	212(2)	0.055%	60.6	0.37	86
LM5	298	0.14%	4.90	175.6	247(3)	0.045%	58.8	0.37	83
LM6	266	0.14%	5.16	207.0	208(3)	0.070%	70.9	0.37	100
LM6	274	0.14%	5.14	194.9	221(3)	0.065%	69.0	0.38	99
LM6	282	0.14%	5.11	184.5	234(4)	0.061%	69.1	0.37	97
LM6	290	0.14%	5.09	162.0	268(5)	0.052%	67.8	0.37	95
LM6	298	0.15%	5.07	136.3	319(6)	0.041%	66.4	0.37	93
LM7	266	0.15%	5.34	403.6	110.3(9)	0.113%	44.5	0.53	90
LM7	274	0.15%	5.31	380.4	117.3(9)	0.109%	42.7	0.55	92
LM7	282	0.15%	5.29	381.3	117.3(7)	0.107%	42.0	0.55	89
LM7	290	0.15%	5.26	342.7	130.8(8)	0.093%	40.0	0.56	87
LM7	298	0.15%	5.23	300.6	149.4(9)	0.075%	38.5	0.55	82
LM8	266	0.15%	5.50	384.4	115.2(7)	0.166%	9.2	1.04	135
LM8	274	0.15%	5.47	370.0	119.9(7)	0.160%	9.7	1.02	133
LM8	282	0.15%	5.44	381.5	116.6(7)	0.136%	13.0	0.93	112
LM8	290	0.15%	5.42	348.6	127.9(8)	0.125%	13.7	0.93	116
LM8	298	0.15%	5.39	328.2	136.1(9)	0.108%	14.6	0.89	104
LM9	266	0.15%	5.69	604.6	76.2(5)	0.125%	21.0	0.68	66
LM9	274	0.15%	5.66	595.4	77.6(5)	0.119%	22.0	0.66	65
LM9	282	0.15%	5.64	589.3	78.5(5)	0.119%	20.1	0.69	66
LM9	290	0.15%	5.61	552.5	84.0(6)	0.110%	20.9	0.67	64
LM9	298	0.15%	5.58	535.4	86.8(6)	0.104%	20.8	0.67	63

Table S3: Parameters ontained from the SANS data analysis for the pseudo-limoncello samples: $\Delta\rho$ is the scattering contrast between the essential oil droplet and the medium, Σ is the total surface obtained from the Porod analysis, and R_P is the Porod radius (uncertainty on the last significant digit expressed in parenthesis). ϕ, μ, and σ are the parameters obtained from the fit of a model of polydisperse spheres, with ϕ being the droplet volume fraction and μ and σ defining the size distribution; $\langle R^3\rangle / \langle R^2\rangle$ is the ratio between the third and second moment of the size distribution. See full text for further details.

Sample	T / K	vol% oil	$\Delta\rho$ / 10^4 nm^{-2}	Σ / cm-1	R_P / nm	ϕ	μ / nm	σ	$\langle R^3\rangle / \langle R^2\rangle$
LM-EO1	298	0.40%	5.85	2.28	52900(600)	0.001%	12.9	0.829	72
LM-EO2	298	0.32%	5.65	12.0	7900(90)	0.005%	52.6	0.613	135
LM-EO3	298	0.24%	5.46	65.0	1090(4)	0.023%	64.6	0.473	113
LM-EO4	298	0.18%	5.34	383	142.9(3)	0.119%	54.1	0.499	101
LM-EO5	298	0.13%	5.22	426	90.5(2)	0.139%	32.8	0.677	103

6 Interfacial tension

The interfacial tension between distilled lemon essential oil and water/ethanol/sucrose mixtures was measured using the drop shape analysis method. In particular, two experiments were performed using a H_2O (21 wt%), Ethanol (47 wt%), and sucrose (32 wt%) solution (density: 1.031 g cm^{-3}) and a D_2O (21 wt%), Ethanol (47 wt%), and sucrose (32 wt%) solution (density: 1.0703 g cm^{-3}). A density of the essential oil of 0.841 g cm^{-3} was used. The measurement was repeated on 10 drops giving an average value of 4.1 mN m^{-1} with D_2O and 5.0 mN mmN m^{-1} with H_2O. The picture of the drop is shown in Fig. S18.

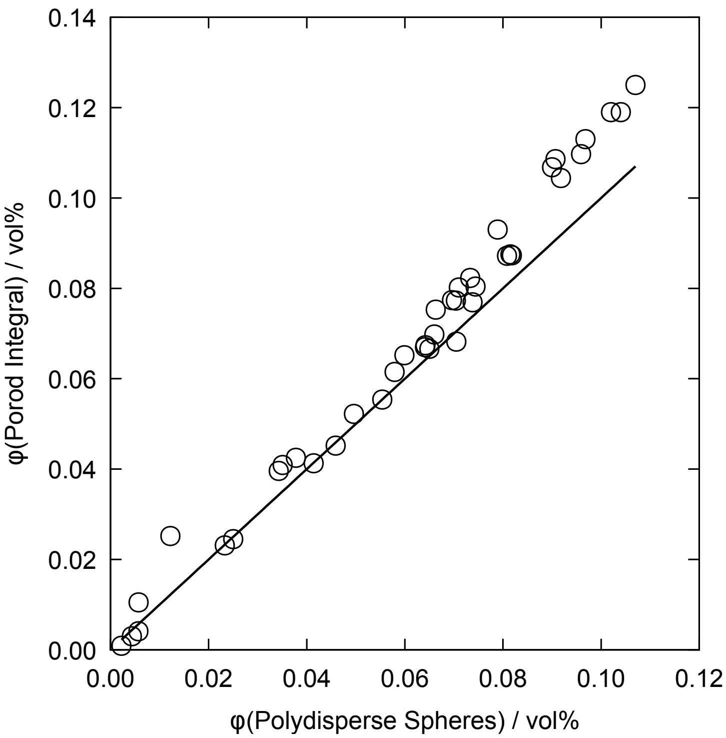

Figure S17: Correlation plot of essential oil volume fraction determined by the Porod invariant analysis and obtained from the full analysis of the SANS data with the polydisperse sphere model. Full line indicates full correlation between calculated and experimentally determined values.

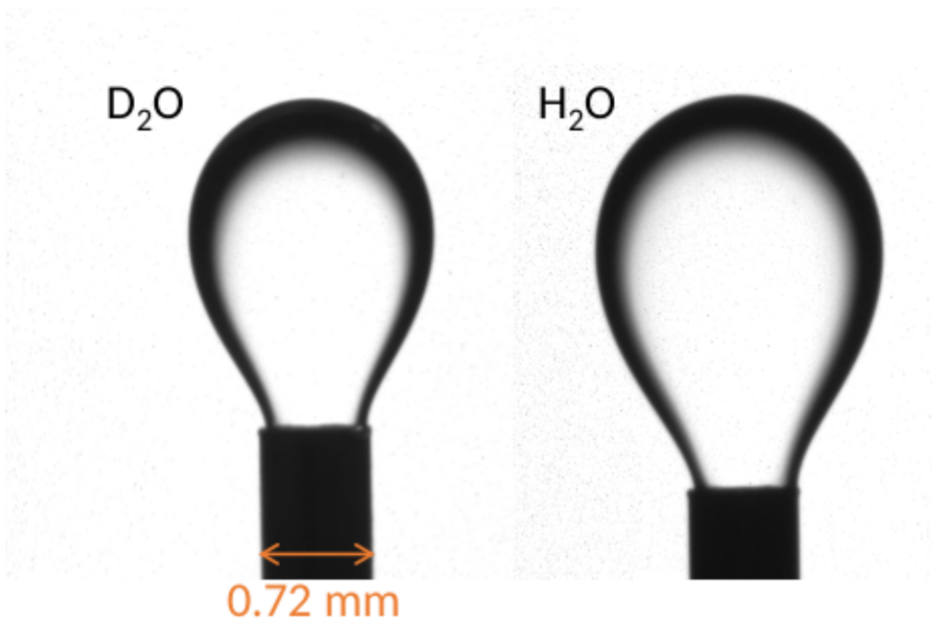

Figure S18: Emergent drop picture of lemon essential oil in D2O and H2O obtained. The interfacial tension is calculated from the drop shape profile analysis using the Young-Laplace equation

References

(S1) Clará, R. A.; Marigliano, A. C. G.; Sólimo, H. N. Density, Viscosity, and Refractive Index in the Range (283.15 to 353.15) K and Vapor Pressure of α-Pinene, d -Limonene, (±)-Linalool, and Citral Over the Pressure Range 1.0 kPa Atmospheric Pressure. *J. Chem. Eng. Data* **2009**, *54*, 1087–1090.