Supporting Information:

Pressure Effects on the Nanostructure of Bicontinuous Propane Microemulsions with Extended Surfactants: A SANS Study

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1 Microemulsion Composition

For all microemulsion systems of the type $H_2O/D_2O/NaCl/butyldiglycol$ (A) – *n*-decane/propane (B) – C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na (C), the propane-to--decane ratio was varied while the following parameters were always kept constant:

$$r_{\rm D_2O} = \frac{m_{\rm D_2O}}{m_{\rm D_2O} + m_{\rm H_2O}} = 0.73 \tag{1}$$

$$\psi = \frac{m_{butyldiglycol}}{m_{butyldiglycol} + m_{\rm NaCl} + m_{\rm H_2O}} = 0.05 \tag{2}$$

$$\epsilon = \frac{m_{\rm NaCl}}{m_{\rm NaCl} + m_{\rm H_2O} + m_{\rm D_2O}} = 0.0437 \tag{3}$$

$$\delta = \frac{m_{C_{14-17}-SO_3Na}}{m_{C_{14-17}-SO_3Na} + m_{C_{16-18}-7PO-0.1EO-SO_4Na}} = 0.25$$
(4)

A constant volumetric hydrophilic-to-hydrophobic ratio of

$$\phi = \frac{V_B}{V_B + V_A} = 0.5,\tag{5}$$

corresponding to equal volumes of A and B, is targeted in order to obtain a symmetric microemulsion. Samples with propane were prepared considering filling conditions. Albeit being more compressible than water and *n*-decane, the compressibility of propane is still small compared to other volatile hydrocarbons such as methane, as demonstrated below, which strongly limits the maximum error of the actual (i.e., pressure- and temperature-dependent) ϕ .



Figure S1: Normalized densities ρ/ρ_0 of water, *n*-decane, propane and methane, calculated via data in the NIST database, ^{S1} ρ_0 taken at filling temperature and pressure.

2 Phase Behavior

Phase diagrams of the respective non-deuterated microemulsions were measured as $T(\gamma)$ cuts at constant oil/water ratio in one of our recent works.^{S2} For the SANS studies, surfactant mass fractions (γ) were converted to volume fractions (ϕ_C), given that the switch from H₂O to D₂O would otherwise change the volumetric oil-to-water ratio owing to their different densities. Presence of a one-phase region during the pressure scan was ensured by visually checking the phase boundaries before the measurement. Given the scope of this work as well as the time-consuming nature of these high-pressure phase behavior studies, we therefore limited our investigations to the target surfactant concentration at each propane-to-*n*-decane ratio. The results are compiled in the following. All phase behavior studies were performed in the same high-pressure cell that was used for the subsequent SANS experiment, unless stated otherwise.

Comparison of the D₂O-containing formulations investigated in this work with our previously studied D₂O-free microemulsions^{S2} confirms the pressure-induced shift of phase behavior towards higher or lower temperatures depending on the nature of the oil component, i.e., the propane-to-*n*-decane ratio.

2.1 $H_2O/D_2O/NaCl/Butyldiglycol - n$ -Decane/Propane - C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na (100 wt.% *n*-Decane)

An increase in pressure in the propane-free microemulsion leads to a shift of both phase boundaries to higher temperatures.

Table S1: Pressure-dependent phase transition temperatures of the microemulsion system $H_2O/D_2O/NaCl/butyldiglycol - n$ -decane/propane - C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na, recorded at $f_{propane} = 0.0$ and $\phi_C = 0.058$. ^(a) Measured in a conventional glass test tube, not in the HP-SANS cell.

p / bar	$\underline{2} \rightarrow 1 /^{\circ}\mathrm{C}$	$1 \to \overline{2} /^{\circ}\mathrm{C}$
$1^{(a)}$	46.9	59.6
100	50.5	63.5
220	54.6	69.3
350	58.8	72.1

2.2 $H_2O/D_2O/NaCl/Butyldiglycol - n$ -Decane/Propane - C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na (30 wt.% Propane)

For the system containing 30 wt.% of propane in the oil mixture, the upward phase boundary shift is still observed but less pronounced, especially for the lower phase boundary.

Table S2: Pressure-dependent phase transition temperatures of the microemulsion system $H_2O/D_2O/NaCl/butyldiglycol - n$ -decane/propane - C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na, recorded at $f_{propane} = 0.3$ and $\phi_C = 0.042$.

p / bar	$\underline{2} \rightarrow 1 /^{\circ}\mathrm{C}$	$1 \to \overline{2} /^{\circ}\mathrm{C}$
200	33.2	35.0
240	33.2	35.5
290	33.2	37.5
350	34.5	38.9

2.3 $H_2O/D_2O/NaCl/Butyldiglycol - n$ -Decane/Propane - C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na (60 wt.% Propane)

With 60 wt.% of propane, the upper phase boundary remains nearly unaffected by pressure while the lower phase boundary, which borders some lamellar-type phase, shows the opposite behavior of the *n*-decane-rich formulations.

Table S3: Pressure-dependent phase transition temperatures of the microemulsion system $H_2O/D_2O/NaCl/butyldiglycol - n$ -decane/propane - C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na, recorded at $f_{propane} = 0.6$ and $\phi_C = 0.039$. ^(a) Adjacent two-phase region might include a lamellar-type phase. ^(b) Exact T not determined because of similar refractive index of demixed phases.

p/bar	$\underline{2} \to 1 /^{\circ} \mathcal{C}^{(a)}$	$1 \to \overline{2} /^{\circ}\mathrm{C}$
100	26.2	27.8
175	25.7	27.8
240	(b)	27.8
290	(b)	27.8
350	22.2	27.4

2.4 $H_2O/D_2O/NaCl/Butyldiglycol - n$ -Decane/Propane - C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na (100 wt.% Propane)

In the absence of *n*-decane, both phase boundaries are shifted to lower temperatures under pressurization, which is again less pronounced for the upper phase boundary.

Table S4: Pressure-dependent phase transition temperatures of the microemulsion system $H_2O/D_2O/NaCl/butyldiglycol - n$ -decane/propane - C_{16-18} -7PO-0.1EO-SO₄Na/ C_{14-17} -SO₃Na, recorded at $f_{propane} = 1.0$ and $\phi_C = 0.064$. ^(a) Adjacent two-phase region might include a lamellar-type phase.

p / bar	$\underline{2} \to 1 /^{\circ}\mathrm{C}^{(a)}$	$1 \to \overline{2} /^{\circ}\mathrm{C}$
238	28.8	32.9
275	27.3	32.9
350	25.7	32.3

From the pressure-dependent changes of the phase boundaries as a function of the propane-to-*n*-decane ratio, it can be assumed that the transition of the pressure-induced phase sequence inverts somewhere between 45 and 50 wt.% of propane. In excellent agreement, a recent study on the nearly identical D_2O -free microemulsion revealed an inversion with roughly 50 wt.% of propane. S² Deuteration of water does therefore not significantly affect the pressure response of the microemulsion.

3 Small-Angle Neutron Scattering

3.1 Consideration of Multiple Scattering Contributions

In an ideal case, the recorded scattering intensities originate solely from individual scattering processes across the illuminated sample volume. In a real experiment however, multiple scattering contributions are often unavoidable because the sample thickness is not infinitely small and scattered neutrons might be scattered again. Separating single or multiple scattering contributions is intricate because their extent is generally unknown. Multiple scattering consequently affects the reliable analysis of scattering data. It influences both coherent and incoherent scattering, which in the case of microemulsions particularly affects forward scattering intensity $(q \rightarrow 0)$, the Porod regime (intermediate q), and the incoherent background (high q).^{S3–S5} Some authors have therefore introduced factors to incorporate higher-order scattering contributions into their fitting models.^{S6,S7} This approach can be useful because it does not modify the original 1D scattering curves obtained from the raw detector data, but leads to inaccuracies between measurements if parameters such as neutron wavelength or sample thickness are changed because the exact amount of single and multiple scattering processes remains obscure.

In order to mitigate the impact of multiple scattering and to obtain more reliable and comparable data, Frielinghaus et al. introduced the software package MuScatt.^{S5,S8} A two-dimensional Fourier transform is applied to deconvolute and desmear multiple scattering and resolution in reciprocal space, where the multiple scattering correction takes place. The data being treated by MuScatt must be in absolute units of I(q) and must further contain the uncertainties of both I and q, with the latter being specified by the instrumental resolution. Required parameters for the multiple scattering correction are neutron wavelength λ and sample thickness d_{sample} . Multiple scattering effects are more pronounced for higher neutron wavelengths, where the lower kinetic energy of the neutrons enables more interactions with the sample, and for larger sample thicknesses. $S^{4,S8}$ Two additional settings allow for the method of low q extrapolation and whether an incoherent background subtraction should be applied. The use of MuScatt was considered within the scope of the high-pressure measurements, because a correction would facilitate a comparison of high-pressure studies $(d_{sample} = 2 \text{ mm})$ with the ambient pressure reference measurement $(d_{sample} = 1 \text{ mm})$, Hellma cell). Going beyond the scope of this work, this would optimally accomplish a reliable comparison with measurements taken at other wavelengths, with other cuvettes (i.e., sample thicknesses), and generally between different instruments. While *MuScatt* allows to mitigate the impact of multiple scattering, which should generally provide more reliable and comparable data, it directly modifies the original 1D scattering curves obtained from the reduction of raw detector data. Arguments can be put forth whether this kind of data manipulation is beneficial in the sense of being a proper data treatment, or whether it is harmful in the sense of being an improper data alteration that compromises data integrity.

The usage of MuScatt and the subsequent analysis by means of the Teubner-Strey model and Porod's law within the scope of the experiments performed in this work are discussed below, with the microemulsion system H₂O/D₂O/NaCl/butyldiglycol – propane – C₁₆₋₁₈-7PO-0.1EO-SO₄Na/ C₁₄₋₁₇-SO₃Na at T = 30.5 °C and p = 351 bar chosen as an exemplary measurement. All values obtained from the analysis, also for the other investigated specimens, are compiled in Table S5. A direct comparison of original data (obtained via data reduction using the ILL software GRASP)^{S9} and MuScatt-treated data for the same microemulsion system is provided in Figure S2, recorded at a neutron wavelength of $\lambda = 6$ Å and a sample thickness of d = 2 mm. General features of the multiple scattering correction are discussed in the following, outlining advantages and disadvantages that should be considered.



Figure S2: Comparison of original I(q) data obtained from the analysis of the isotropic scattering pattern via $GRASP^{S9}$ (green circles) and I(q) data corrected for multiple scattering contributions via $MuScatt^{S5,S8}$ (gray diamonds) for the microemulsion system H₂O/D₂O/NaCl/butyldiglycol – propane – C₁₆₋₁₈-7PO-0.1EO-SO₄Na/C₁₄₋₁₇-SO₃Na at T = 30.5 °C and p = 351 bar. The incoherent background scattering intensity was subtracted to demonstrate the impact of the data treatment on the high q (low I) data. Peak region analyzed via the Teubner-Strey model^{S10} (red solid lines); high q analyzed with Porod's law, taking into account the diffuseness of the amphiphilic film^{S11,S12} (blue dashed lines).

- 1. MuScatt-treated and original I(q) data are qualitatively uniform with regard to the following features: The correlation peak at q_{max} , the intensity leveling off toward $q \to 0$ (forward scattering intensity I_0) and at high q (incoherent scattering intensity I_{incoh} , subtracted in Figure S2 for the sake of visualization, see below), as well as the q^{-4} decay at intermediate q.
- 2. As anticipated from the removal of additional undesired multiple scattering contributions, the overall scattering intensity becomes lower when applying MuScatt. The impact of the multiple scattering correction is much more pronounced for forward scattering intensity and the incoherent background than for the maximum scattering intensity (I_{max} at q_{max}).
- 3. The position of the characteristic correlation peak (q_{max}) remains essentially the same. Thus, the periodicity d_{TS} is also nearly unchanged. However, the peak becomes notably sharper due to the removal of multiple scattering contributions, leading to a significant increase of the correlation length ξ_{TS} and thus the effective bending rigidity κ_{eff}, while the amphiphilicity factor decreases further (cf. Table S5). Indeed, analyzing the MuScatt data reveals an increase of ξ_{TS} and κ_{eff} by roughly 20 25 %, whereas f_a is reduced by 10 15 %. For the measurements of the n-decane microemulsion at the phase inversion temperature T̃, the slight discrepancy between ambient and high-pressure measurements (cf. Figure 1 and Table 1 in the main manuscript) essentially disappears after the multiple scattering correction (cf. Table S5), in line with our proposition that the influence of an increasing temperature and a higher pressure compensate each other when measuring at the phase inversion temperature.

- 4. In the *MuScatt*-treated data, the shoulder at $q \approx 2q_{max}$ is significantly less pronounced, but does not vanish completely. Therefore, the high q are shifted to lower intensities, leading to a more or less parallel shift of the Porod fit toward lower I. For the high-pressure measurements, the *MuScatt*-treated values of S/V are around 30 % lower compared to the original untreated data, while the decrease is "only" 20 % for the measurement at 1 bar. In accordance with point 3 above, Table S5 emphasizes that S/V then becomes pressure-independent for both ambient and high-pressure measurements, which suggests that the observed differences outlined in the main manuscript are indeed related to the different sample thicknesses.
- 5. The diffuseness parameter t largely remains unaffected by the multiple scattering correction.
- 6. The desmearing correction leads to a numerical artifact at $q \approx 0.045 \text{ Å}^{-1}$: Here, the overestimated data interpolation of *MuScatt* leads to an offset at the q range where main and side detector overlap.
- 7. At high q, where the scattering intensity is low (emphasized through the subtraction of the incoherent background scattering intensity), the data are much more noisy for the *MuScatt*-treated data.

However, besides the downsides already mentioned in point 6 and 7, it is furthermore not clear to which extent *MuScatt* mitigates multiple scattering contributions not related to sample thickness or neutron wavelength. Lastly and most crucially, the fine line between data treatment and data manipulation blurs. There is no doubt that a multiple scattering correction is highly useful to maintain comparability over a wide range of SANS experiments performed under different conditions (sample thickness, wavelength, instrument), but modifications of original data are always questionable and should thus be taken with caution in order to not compromise data integrity.

Experimentally, the best case scenario would be a reduction of sample thickness and wavelength (spread) in order to minimize multiple scattering contributions, enabling the determination of the true value of S/V. The neutron wavelength can be adjusted in SANS experiments and was deliberately kept at a short wavelength of 6 Å to reduce the impact of multiple scattering; however, the wavelength spread is typically outside the control of the user. Low sample thicknesses can be adjusted by choosing suitable SANS cuvettes, but for specialized setups such as the high-pressure cell used in this work, there might only be one sample thickness available. In our case, the 2 mm sample thickness was necessary to ensure better miscibility and homogeneity of the investigated specimens.

Table S5: Pressure- and temperature-dependent periodicity d_{TS} , correlation length ξ_{TS} and amphiphilicity factor f_a , determined via the Teubner-Strey model, ^{S10} alongside the effective bending rigidity κ_{eff} , ^{S13,S14} for all investigated microemulsions. Specific internal interface S/V determined via Porod's law, considering the diffuseness of the interface t. ^{S11,S12} Geometric prefactor a determined via Equation 7 in the main manuscript. Relative errors are estimated as $\Delta d_{TS}/d_{TS} = 0.02$, $\Delta \xi_{TS}/\xi_{TS} = 0.03$, $\Delta f_a/f_a = 0.015$, $\Delta \kappa_{eff}/\kappa_{eff} = 0.035$, $\Delta (S/V)/(S/V) = 0.1$, $\Delta t/t = 0.1$, $\Delta a/a = 0.1$. (a) 1 bar measurement recorded in a Hellma cuvette.

Oil Composition	ϕ_C	p/bar	$T/^{\circ}C$	$d_{TS}/\text{\AA}$	$\xi_{TS}/\text{\AA}$	f_a	κ_{eff}/k_BT	$S/V/10^{-3}\text{\AA}^{-1}$	$t/\text{\AA}$	a
100 wt.% n-decane	0.058	$1^{(a)}$	56.1	573	359	-0.88	0.53	4.4	4.3	5.0
		101	57.0	578	356	-0.87	0.52	4.4	6.0	5.1
		221	61.9	579	362	-0.88	0.53	4.5	6.0	5.2
		353	65.1	577	350	-0.87	0.52	4.5	6.0	5.2
100 wt.% n-decane	0.058	101	60.6	583	358	-0.87	0.52	4.5	6.5	5.2
		141	60.6	579	365	-0.88	0.54	4.5	6.5	5.2
		180	60.6	579	367	-0.88	0.54	4.6	6.5	5.3
		221	60.6	583	358	-0.87	0.52	4.6	6.5	5.4
		260	60.6	581	337	-0.86	0.49	4.6	6.5	5.3
		300	60.6	588	315	-0.84	0.45	4.6	6.0	5.4
		353	60.6	594	292	-0.81	0.42	4.6	6.0	5.5
30 wt.% propane,	0.042	200	34.9	768	407	-0.83	0.45	3.9	5.5	6.0
70 wt.% n-decane		240	34.9	766	419	-0.84	0.47	4.0	5.5	6.1
		290	34.9	765	411	-0.84	0.46	4.0	5.5	6.1
		351	34.9	766	396	-0.83	0.44	4.0	5.5	6.1
60 wt.% propane,	0.039	101	27.0	846	403	-0.80	0.41	3.8	4.5	6.4
40 wt.% n-decane		175	27.0	835	399	-0.80	0.41	3.8	4.5	6.3
		240	27.0	830	403	-0.81	0.41	3.8	4.5	6.3
		291	27.0	820	404	-0.81	0.42	3.8	4.5	6.2
		350	27.0	820	423	-0.83	0.44	3.8	4.5	6.2
100 wt.% propane	0.064	243	30.5	536	191	-0.67	0.30	5.8	5.5	6.2
		260	30.5	530	199	-0.70	0.32	5.8	6.0	6.1
		275	30.5	536	208	-0.71	0.33	5.8	6.0	6.2
		294	30.5	536	218	-0.74	0.35	5.8	5.5	6.2
		312	30.5	527	229	-0.76	0.37	5.8	5.5	6.1
		351	30.5	531	243	-0.78	0.39	5.8	5.5	6.2

3.2 Subtraction of Incoherent Background Scattering

As discussed in the main manuscript, the scattering intensity levels out toward the highest experimental q, with the remaining intensity resulting from incoherent background scattering, I_{incoh} . If this incoherent background is subtracted, the intensity falls off further toward $I \rightarrow 0$, with the decay being even steeper due to the diffuseness of the interfacial film, as visualized below in Figure S3. The value of I_{incoh} has a strong influence at high q, where the incoherent scattering contribution outweighs the coherent scattering contribution and thus strongly impacts the values of S/V and t obtained from the Porod analysis. Due to this sensitivity to the absolute intensity, the background-corrected coherent scattering intensities $I(q)-I_{incoh}$ were used for the analysis. For the sake of visualization of the measured intensities and to avoid data overlap at extremely low intensities at high q, as visible in Figure S3, the incoherent background was subsequently re-added to the fits for all plots presented in the main part of the manuscript.



Figure S3: Pressure-dependent bulk contrast SANS curves with subtracted incoherent background scattering intensity I_{incoh} , displaced by a factor of 10 (lowest pressure unscaled) Left: Microemulsion system containing 100 wt.% *n*-decane, recorded isothermally at T = 60.6 °C and $\phi_C = 0.058$. Right: Microemulsion system containing 100 wt.% propane, recorded isothermally at T = 30.5 °C and $\phi_C = 0.064$. For all data, the peak region was analyzed via the Teubner-Strey model^{S10} (red solid lines); high *q* were analyzed with Porod's law, taking into account the diffuseness of the amphiphilic film^{S11,S12} (blue dashed lines).

3.3 Analysis with the Teubner-Strey Model

The peak region of all scattering profiles was analyzed with the Teubner-Strey model by treating the bicontinuous domains, characterized by a specific length, as non-rigid domains.^{S10} The Teubner-Strey model is derived from Landau theory, for which the Landau free energy, obtained from an order parameter expansion of the free energy density using gradient terms, provides the scattering intensity distribution I(q) under consideration of the free energy change resulting from fluctuations of the order parameter. In the equation

$$I(q) \propto \frac{1}{a_2 + c_1 q^2 + c_2 q^4},$$
(6)

the coefficient c_1 of the order parameter expansion gives rise to a correlation peak for $c_1 < 0$ (with $a_2 > 0$ and $c_2 > 0$). Fourier transform of Equation 6 removes proportionality and yields

$$I(q) = \frac{8\pi \langle \eta^2 \rangle c_2 / \xi_{TS}}{a_2 + c_1 q^2 + c_2 q^4},\tag{7}$$

where ξ_{TS} is the correlation length and $\langle \eta^2 \rangle$ describes the mean square fluctuations of the scattering density under consideration of the volume fractions of the respective components. Modifying these equations with more descriptive fit parameters provides the fitting function used for the analysis of the scattering data, with

$$I(q) = \frac{I_0}{\left(1 - \frac{I_0}{I_{max}}\right) \left(\frac{q^2}{q_{max}^2} - 1\right)^2 + \frac{I_0}{I_{max}}},$$
(8)

where I_{max} is the maximum scattering intensity and I_0 is the forward scattering intensity. These fitting parameters can be related to the order expansion coefficients a_2 , c_1 and c_2 with

$$a_2 = I_0^{-1} \tag{9}$$

$$c_1 = -2q_{max}^2 c_2 \tag{10}$$

$$c_2 = q_{max}^{-4} \left(I_0^{-1} - I_{max}^{-1} \right), \tag{11}$$

which are then used for the determination of the length scales d_{TS} (periodicity) and ξ_{TS} (correlation length), as outlined in the main manuscript.

3.4 Dependence of Periodicity on Surfactant Volume Fraction

Considering all high-pressure SANS results provided in the main manuscript demonstrates that the periodicity d_{TS} (i.e., the size of water and oil nanodomains), listed in Table 1, essentially remains pressureindependent for a constant propane content. As expected, d_{TS} changes as a function of the propane-to*n*-decane ratio due to the different surfactant volume fractions used for each measurement, given that the propane concentration was found to affect the solubilization capacity of the surfactant ^{S2} and ϕ_C was always targeted in proximity to the respective \tilde{X} point, while still allowing for pressure variations without leaving the one-phase region. The inverse proportionality of periodicity and surfactant concentration, $d_{TS} \propto \phi_C^{-1}$, is predicted by several geometric models of the bicontinuous structure ^{S15,S16} and experimentally confirmed in literature. ^{S17} Consequently, if oil and water are fully solubilized by the amphiphile in each case, a smaller ϕ_C will result in larger oil and water subdomains because less surfactant is present in the specimen and the bulk phases effectively swell. In order to gauge whether the exact value of d_{TS} can be traced back solely to differences in the amphiphile concentration, a normalized, reduced periodicity $d_{TS,norm}$ is introduced according to

$$d_{TS,norm} = \frac{(d_{TS}\phi_C)_p}{(d_{TS}\phi_C)_{ref}},\tag{12}$$

taking d_{TS} of the non-pressurized (1 bar), gas-free *n*-decane microemulsion system as reference (ref) for normalization. Figure S4 confirms that this expression can indeed be used to scale the d_{TS} obtained at different oil ratios, surfactant volume fractions, and pressures against the measurement at ambient conditions. This proves the independence of d_{TS} on both pressure and oil ratio and emphasizes that the surfactant volume fraction is a suitable normalization parameter. In theory, it would be even better to use the surfactant volume fraction in the interface, $\phi_{C,i}$, since ϕ_C by definition also includes the amount of surfactant that might be monomerically dissolved in water or oil. However, from surface tension measurements we know that the critical micelle concentration of the utilized surfactants is low; additionally, the monomeric solubility of ionic surfactants in hydrophobic oils is generally low as well. Thus, the approximation $\phi_C \approx \phi_{C,i}$ is precise enough, as confirmed by Figure S4. This might no longer be the case for non-ionic surfactants, which typically have a much higher monomeric solubility in oils.^{S18} Indeed, the two studies attributing pressure-induced deviations of the water-in-propane droplet radius^{S19} or the periodicity in balanced CO₂ microemulsions^{S20} to an altered monomeric solubility of the surfactant were stabilized by a non-ionic surfactant.



Figure S4: Top: Schematic representation of the inverse proportionality of periodicity d_{TS} and surfactant volume fraction ϕ_C . Bottom: Pressure-dependent reduced periodicity $d_{TS,norm}$, normalized with the respective ϕ_C against the 1 bar measurement of the *n*-decane microemulsion.

3.5 Azimuthal Analysis of the Scattering Patterns

Bicontinuity of the investigated microemulsions was expected based on previous phase behavior and electrical conductivity studies S^2 and subsequently confirmed through the characteristic features of the SANS curves recorded near the \tilde{X} point close to the phase inversion. Even with small pressure-induced shifts away from \tilde{T} , utilizing equal volumes of water and oil ensures that those shifts do not result in a pronounced qualitative change of the scattering curves. Radial averaging was thus well-suitable for data analysis, given that the azimuthal angle χ should not have any noticeable effect on the recorded scattering intensity. In this light, it is interesting to consider the follow-up measurement at a pressure of 200 bar – located outside of the target measurement range – in the microemulsion system containing only propane as the oil.



Figure S5: Radially averaged pressure-dependent bulk contrast SANS curves for the microemulsion system containing 100 wt.% propane, recorded isothermally at T = 30.5 °C and $\phi_C = 0.064$. Curves are displaced by a factor of 10 (200 bar unscaled). Peak region analyzed via the Teubner-Strey model^{S10} (red solid lines); high q analyzed with Porod's law, taking into account the diffuseness of the amphiphilic film^{S11,S12} (blue dashed lines). The measurement at 200 bar, measured outside of the one-phase region, no longer exhibits the typical features of bicontinuous microemulsions and was thus excluded from the analysis. Inset: Unscaled close-up of the peak region with linear I axis. Fits are omitted for better visibility.

As visible from Figure S5, the radial analysis over the full azimuthal range reveals that the scattering profile at 200 bar no longer exhibits the typical correlation peak, instead showing an increasing scattering intensity toward $q \rightarrow 0$ and two smaller local peaks at intermediate q. The unusual shape of the scattering curve was not observed for any other pressure or propane-to-*n*-decane ratio and renders the data unsuitable for an analysis with the Teubner-Strey model. Considering the phase diagrams we recently recorded for the propane microemulsion utilizing the same surfactants^{S2} as well as those of other propane microemulsions in literature, ^{S21,S22} the shape of the scattering curve gives rise to the assumption that a transition toward a lamellar phase, or some multi-phase region containing this lamellar phase, has taken place.

In order to validate this hypothesis, scattering data of selected pressures in the propane microemulsion system were analyzed as a function of the azimuthal angle χ . Figure S6 shows the 2D scattering patterns at 200 bar, at an intermediate pressure of 260 bar, and at the highest pressure of 351 bar. For the two higher pressures, the scattering pattern is clearly isotropic. In contrast, an anisotropic scattering pattern is found

for the lowest pressure. Subsequently, the scattering data was azimuthally represented as a function of the scattering angle around the respective peak regions (white circles). Utilizing the elliptical fit function

$$I(\chi) = \frac{I_{max}}{\sqrt{\cos^2\left(\chi - \chi_{max}\right) + \left(\frac{I_{max}}{I_{min}}\right)^2 \cdot \sin^2\left(\chi - \chi_{max}\right)}}$$
(13)

suggested by Fischer et al.,^{S23} the azimuth-dependent scattering intensities $I(\chi)$ were analyzed as a function of the azimuthal angle χ . Here, I_{max} is the scattering intensity at χ_{max} and $\chi_{max} + 180^{\circ}$, while I_{min} is the scattering intensity at $\chi_{max} + 90^{\circ}$ and $\chi_{max} + 270^{\circ}$. The values of I_{max} and I_{min} can be used further to calculate the alignment factor AF via^{S23}

$$AF = \frac{I_{max} - I_{min}}{I_{max} + I_{min}}.$$
(14)

For a perfectly isotropic scattering pattern of interwoven oil/water domains in a sponge-like bicontinuous structure, $I_{max} = I_{min}$, and therefore AF = 0. For an anisotropic scattering pattern, $I_{max} \neq I_{min}$ and therefore AF > 0. All fitting parameters are given in Table S5.



Figure S6: Top: Pressure-dependent 2D scattering pattern of the microemulsion containing 100 wt.% propane, recorded at T = 30.5 °C. Bottom: Azimuthal analysis of the scattering patterns around the respective peak region.

The bottom part of Figure S6 shows the $I(\chi)$ data for the three pressures. As expected, only the scattering intensity for the lowest pressure of 200 bar depends on χ . For this pressure, two intensity peaks in close proximity to 90° and 270° are observed (cf. Table S5), proving the presence of lamellar sheets stacked

perpendicular to the plane defined by neutron path and z axis. Keeping the same intensity scale as for the two higher pressures, the relative increase of the scattering intensity around these azimuthal angles is only weakly visible; thus, a modified grayscale scattering pattern is shown to emphasize the strong anisotropic signal. For the isotropic scattering patterns at 260 and 351 bar, $I_{max} \approx I_{min}$, and thus the elliptical fit becomes unsuitable. Quantifying the degree of anisotropy, the alignment factor AF was determined. Indeed, $AF \ll 0.01$ is obtained for the isotropic patterns of the two higher pressures, while $AF = (0.38 \pm 0.01)$ for the measurement at 200 bar. Such high alignment factors have been previously reported in microfluidic-SANS experiments on the shear-induced sponge-to-lamellar transition. ^{S23,S24}

The azimuthal analysis of the scattering patterns thus corroborates the hypothesis of a transition toward an anisotropic lamellar-like phase when crossing the lower phase boundary in propane-rich microemulsions. Considering that the pressure-induced shift of the phase boundaries at isothermal conditions can lead to a shift outside of the one-phase region, the increasing scattering intensity toward $q \rightarrow 0$ is attributed to demixing of the sample. Given that lower pressures limit the solubilization capacity of the short-chain propane and the mutual solubility of propane and surfactant, it can be assumed that the lamellar phase is water-rich and coexists with some oil-rich phase.

Table S6: Fitting results of the azimuthal analysis of selected scattering patterns in the propane microemulsion. ^(a)The high error reflects the unsuitability of an elliptical fit for isotropic scattering patterns since $I_{max} \approx I_{min}$, which therefore evidences the bicontinuous structure. ^(b)No errors given due to extremely small AF.

p/bar	q / Å	$I_{max} / \mathrm{cm}^{-1}$	$I_{min} / \mathrm{cm}^{-1}$	I_{max}/I_{min}	$\chi_{max} /^{\circ}$	AF
$200 \\ 260 \\ 351$	0.0245-0.0277 0.0088-0.0121 0.0097-0.0126	816 ± 1 4860 ± 5 4830 ± 6	$367 \pm 1 \\ 4835 \pm 5 \\ 4803 \pm 7$	$\begin{array}{c} 2.232 \pm 0.008 \\ 1.005 \pm 0.003 \\ 1.005 \pm 0.003 \end{array}$	91.4 \pm 0.1 95.6 \pm 10.0 ^(a) 90.6 \pm 10.9 ^(a)	$\begin{array}{c} 0.38 \pm 0.01 \\ \ll 0.01^{(b)} \\ \ll 0.01^{(b)} \end{array}$

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