From water-rich to oil-rich gelled non-toxic microemulsions

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S1. Phase diagrams at various ϕ-ratios

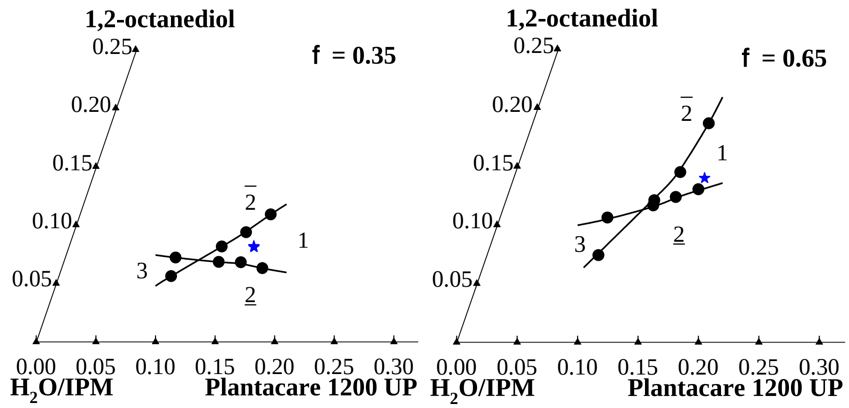

Figure S1. Phase diagrams of the non-toxic system H_2O – isopropyl myristate (IPM) – Plantacare 1200 UP ($C_{12}G_{1.4}$) – 1,2-octanediol at oil-to-water ratios of ϕ = 0.35 and 0.65 at T = 25 °C. The sample compositions of gelled microemulsions for the rheological measurements are marked in blue star.

The phase diagrams of the microemulsions were measured at a fixed oil-to-water ratio ϕ with two variables, namely the surfactant mass fraction γ_C and the co-surfactant mass fraction γ_D. Since the phase inversion is induced by the addition of the co-surfactant,[1–3] the phase diagrams at all ϕ-ratios (Figure S1) have the same trend: along with the addition of 1,2-octanediol, the phase transition has a sequence of $\underline{2} - 3 - \overline{2}$ on the left side of the $\tilde{X}$ point , and $\underline{2} - 1 - \overline{2}$ on the right side of the $\tilde{X}$ point.

S2. Amplitude sweep of water-rich gelled microemulsions

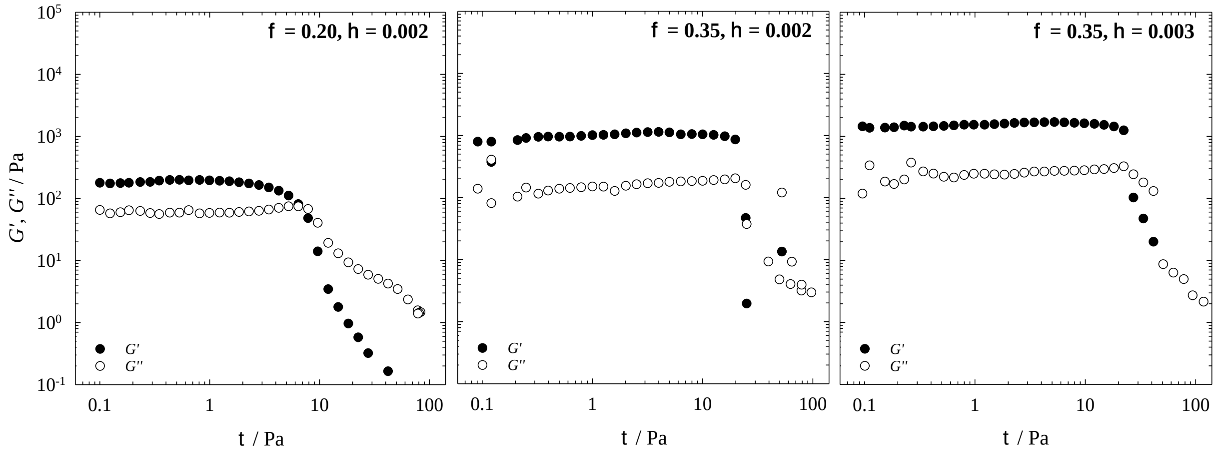

Figure S2. Storage modulus *G'* (filled symbols) and loss modulus *G''* (open symbols) of the gelled microemulsion H_2O – IPM – Plantacare 1200 UP ($C_{12}G_{1.4}$) – 1,2-octanediol in the presence of DBS at T = 25 °C, $\omega = 10\ s^{-1}$ as a function of the shear stress τ with (left) $\phi = 0.20$, $\eta = 0.002$; (middle) $\phi = 0.35$, $\eta = 0.002$; (right) $\phi = 0.35$, $\eta = 0.003$. See Table 2 for sample composition.

Amplitude sweeps with a controlled shear stress were carried out to determine the limit of the linear viscoelastic region (LVE region, Figure S2). The limit shear stress for the sample with ϕ = 0.20, η = 0.002 was determined to be τ = 2 Pa, for the sample with ϕ = 0.35, η = 0.002 to be τ = 12 Pa, for the sample with ϕ = 0.35, η = 0.003 to be τ = 14 Pa. One can already see that the sample with ϕ = 0.20, η = 0.002 is a much weaker gel than the two samples with ϕ = 0.35. The sample with ϕ = 0.35, η = 0.003 is slightly stronger than the sample with ϕ = 0.35, η = 0.002 due to the higher gelator concentration.

S3. Hansen solubility parameters (HSPs)

We tested the gelation of the organogelator 1,3:2,4-dibenzylidene-D-sorbitol (DBS) in the individual components of the non-toxic microemulsion (Table S1), namely water, the oil IPM, the co-surfactant 1,2-octanediol, and the oil & co-surfactant mixture (4:1 mass ratio), which has a similar composition with that in our microemulsion. The gel strengths were quickly checked by shaking the test tubes: if the gel was destroyed by the stirring bar with a gentle shake, it is defined as "weak"; if the gel remained still with a hard hit, it is defined as "strong". DBS is insoluble in water at $\eta = 0.001$. DBS forms an instant gel in IPM. However, with $\eta = 0.003$ as the gelator concentration used in the gelled microemulsion, this binary gel is very weak. With an increase to $\eta = 0.005$, DBS forms a strong gel in IPM. The gel is very strong with $\eta = 0.010$. Up to $\eta = 0.006$, DBS is soluble in the co-surfactant 1,2-octanediol. With $\eta = 0.010$, DBS forms a slow but strong gel in 1,2-octanediol. The addition of 20% 1,2-octanediol in IPM weakens the gel strengths and only forms a strong gel at $\eta = 0.010$.

Table S1. The gelation results of DBS in the individual components of the non-toxic microemulsion.

DBS in	H_2O		IPM		1,2-octanediol		IPM & 1,2-octanediol (4:1 mass ratio)	
η	0.001	insoluble	0.003	instant gelation (very weak and transparent gel)	0.003	soluble	0.004	slow gelation (very weak and transparent gel)
	0.003	insoluble	0.005	instant gelation (strong and transparent gel)	0.006	soluble	0.006	slow gelation (very weak and transparent gel)
			0.010	instant gelation (very strong and transparent gel)	0.010	slow gelation (strong and translucent gel)	0.010	slow gelation (strong and transparent gel)

Our microemulsions with varied oil-to-water ratios contain similar amounts of surfactant and co-surfactant, but the amount of water and oil differs. Plotting the gelation results of 1 wt.% DBS in water and IPM on the 3D Hansen space (containing the datasets from [4]), one sees water and IPM on different sides of the sphere.

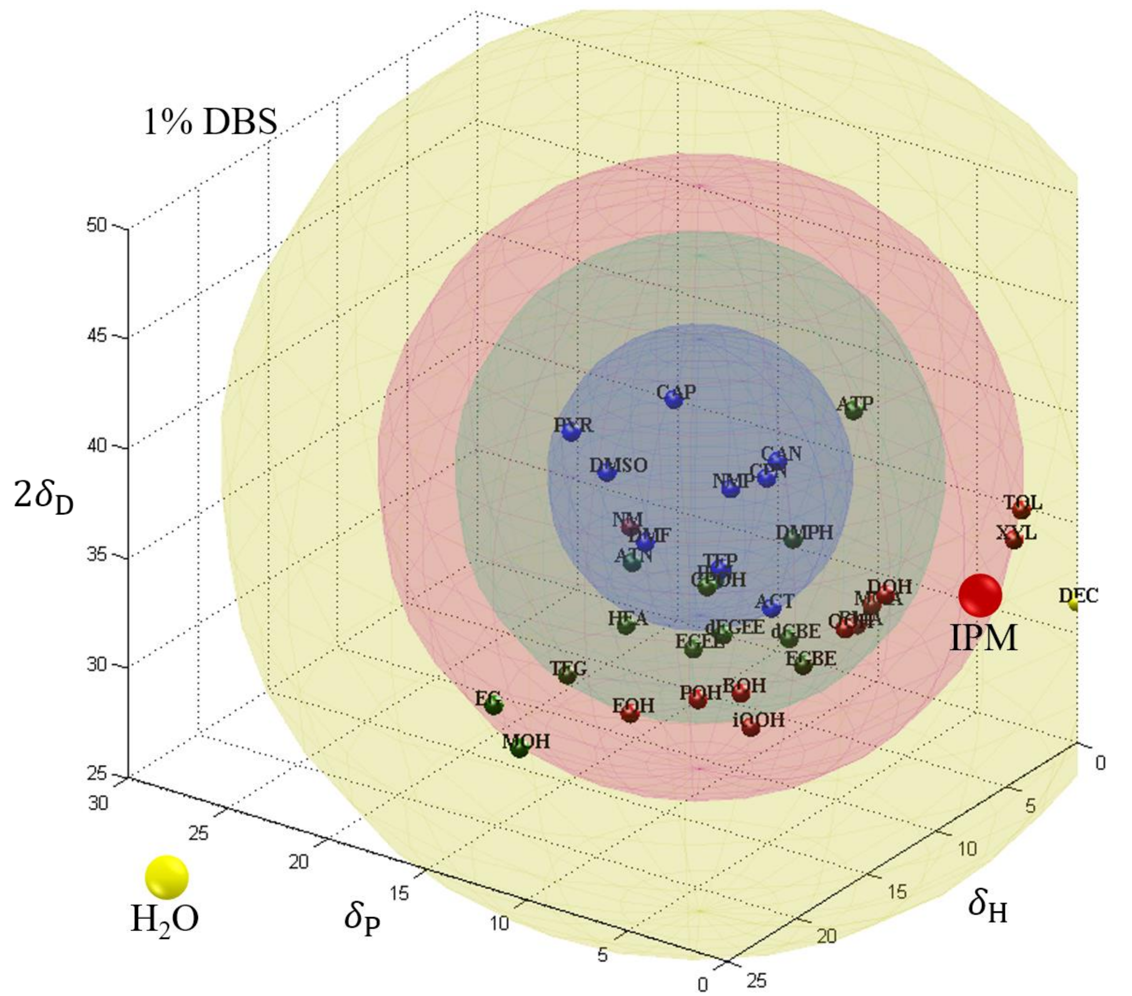

Figure S3. Hansen solubility parameters (HSPs) of DBS (1% weight/volume)[4], water[5], and IPM[6] plotted in the 3D Hansen space. The results show a pattern of concentric spheres, namely the central sol (S) sphere in blue, slow gelation (SG) in green, instant gelation (IG) in red, and insoluble (I) in yellow. The axes represent the three Hansen solubility parameters (δ_D = dispersive, δ_P = polar, and δ_H = hydrogen-bonding interactions).

S4. FFEM image of the water-rich non-gelled microemulsion

To exclude the influence of gel fibers, a non-gelled microemulsion sample with ϕ = 0.20 was additionally investigated to have a clearer view (Figure S3, the composition is marked with red cross in Figure 1, top). It shows polydispersed globular and cylindrical oil droplets in the continuous water domain. The droplet size ranges from 5 to 20nm, the length of cylindrical droplets expands to 30 nm.

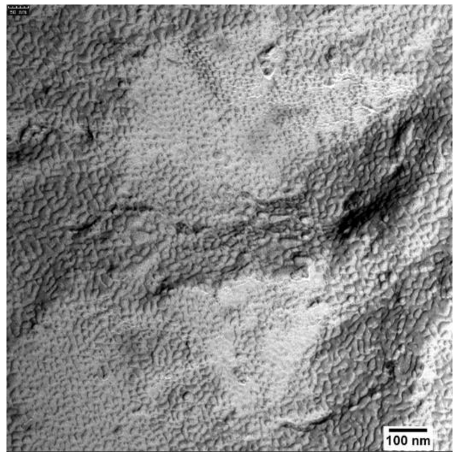

Figure S4. FFEM image of the non-gelled microemulsion H_2O – IPM – Plantacare 1200 UP ($C_{12}G_{1.4}$) – 1,2-octanediol at oil-to-water ratio ϕ = 0.20.

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