

Supplementary Materials

for the article

Saturated Micellar Networks: Phase Separation and Nanoemulsification Capacity

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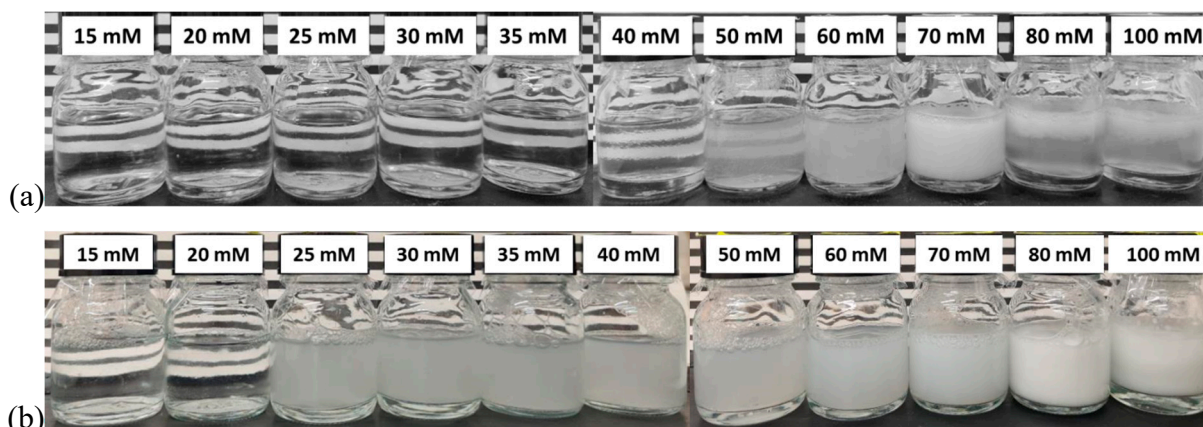


Figure S1. Photographs of 8 wt% 1:1 SDS+DDAO solutions in the presence of: (a) MgCl₂; (b) CaCl₂. The concentrations of added divalent salts are shown on the top of vials.

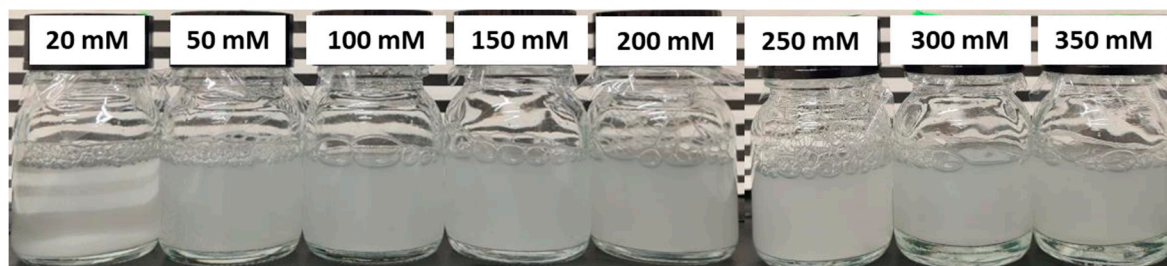


Figure S2. Photographs of 8 wt% 1:1 SLES-3EO+DDAO solutions in the presence of CaCl₂. The concentrations of added CaCl₂ are shown on the top of vials.

Figure S1a shows that the addition of MgCl₂ to mixed 8 wt% 1:1 SDS+DDAO solutions leads to transparent solutions up to 40 mM added MgCl₂ and the surfactant mixtures are salted out for concentrations above 50 mM MgCl₂.

Figure S1b illustrates that all 8 wt% 1:1 SDS+DDAO solutions contain crystals for concentrations of added CaCl₂ above 20 mM.

All mixed 8 wt% 1:1 SLES-3EO+DDAO micellar solutions are turbid with precipitates for added CaCl₂ concentrations above 10 mM, see Figure S2.

In contrast, the saturated micellar phase is observed in 8 wt% 1:1 SDS+CAPB solutions in the presence of MgCl_2 (from 60 mM to 90 mM) and in the presence of CaCl_2 (from 40 mM to 70 mM), see Figure S3.

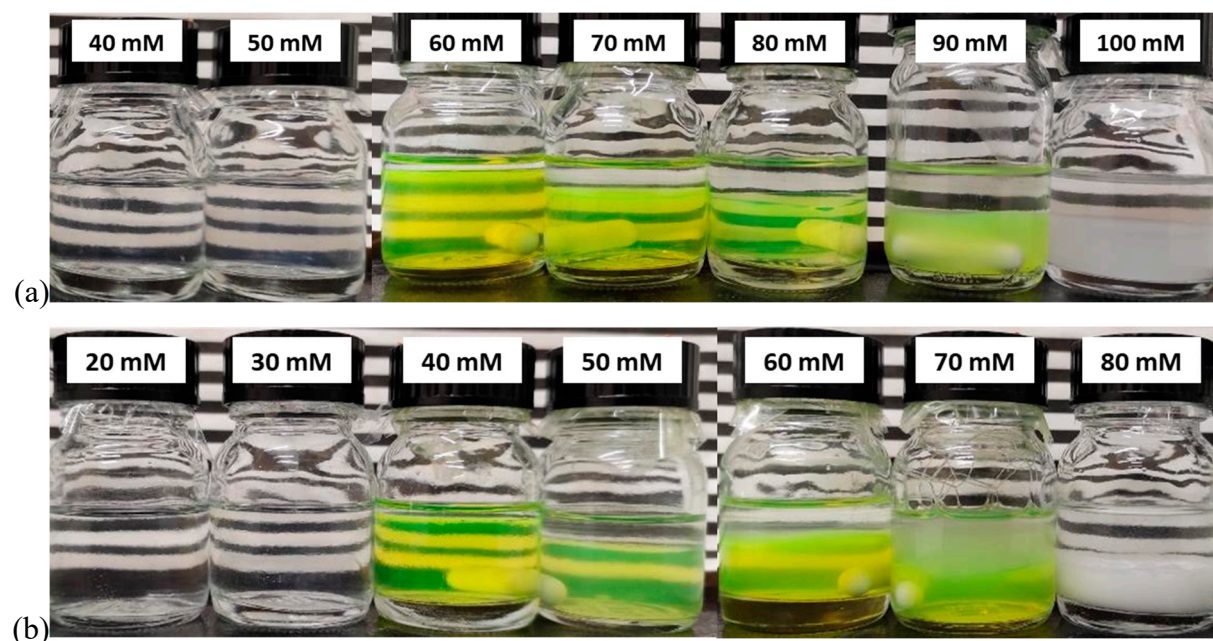


Figure S3. Photographs of 8 wt% 1:1 SDS+CAPB solutions in the presence of: (a) MgCl_2 ; (b) CaCl_2 .



Figure S4a. Confirmation for the bicontinuous nature of the obtained micellar phase in the case of 8 wt% 1:1 SLES-1EO+DDAO + 70 mM CaCl_2 . The solution contains lipophilic and hydrophilic dyes (BODIPY and methylene blue). The physical appearance of the sample

shows that both dyes are mostly in the upper phase. The intensity of the blue color of the supernatant is low, while the upper bicontinuous phase is in intense blue-green color.

After dispersing the aqueous phase in the dark blue phase, one sees again droplets in transmitted light (Figure S4b). In a fluorescence mode, the same droplets are dark, while the background is in green (Figure S4c).

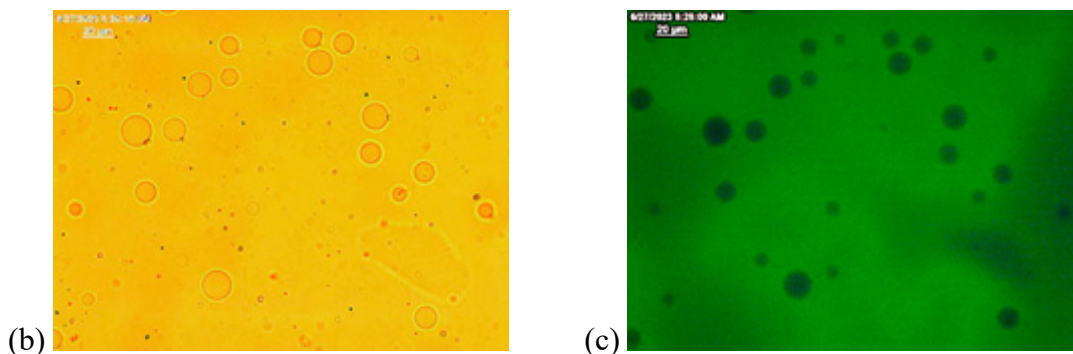


Figure S4b,c. Microscopic images of drops from the lower phase dispersed in the saturated micellar phase in the case of Figure S4a taken in: (b) transmitted light; (c) fluorescence mode.

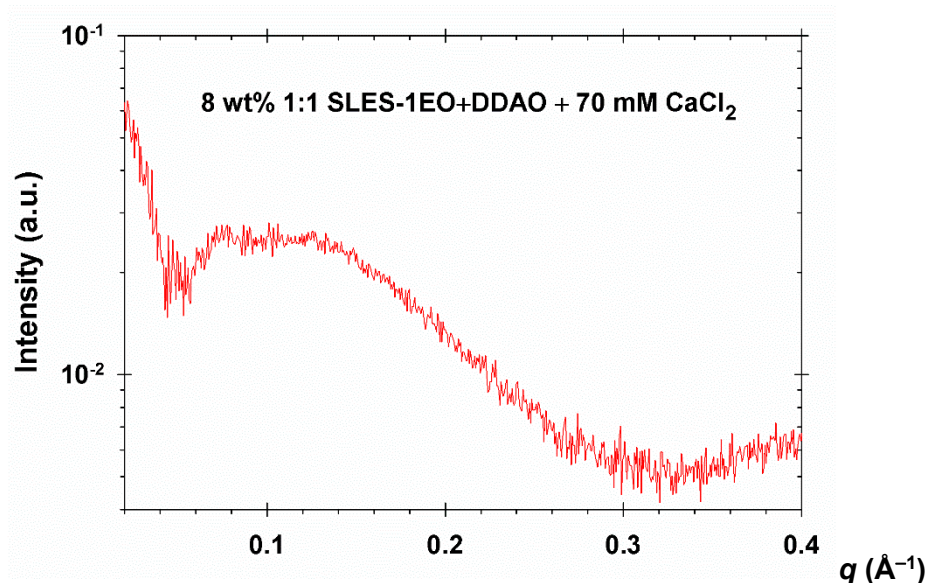


Figure S4d. SAXS spectrum of the phase separated from 8 wt% 1:1 SLES-1EO+DDAO + 70 mM CaCl_2 (see Figure S4a). The shape of spectrum curve does not correspond to any ordered liquid-crystal phase. See the main text for discussions.

Figures S5 and S6 summarize the original experimental data for the apparent shear viscosity, η_{app} , on the applied shear rate, $d\gamma/dt$. In the mixed micellar solution of 8 wt% 1:1 SLES-1EO+DDAO, we added different concentrations of CaCl_2 (Figure S5) and MgCl_2 (Figure S6). In both cases, the viscosities at low shear rates are constants, which correspond to quasi-Newtonian rheological behavior of the solutions. With the rise of the rate of shear

strain, the viscosities decrease – the typical shear thinning rheological behavior of the micellar solutions is observed. The apparent viscosity is inversely proportional to the shear rate. Note, that all solutions with added divalent salt concentrations lower than 10 mM have Newtonian behavior in the studied range of the shear rates – the effect of added divalent salts is not so pronounced as for higher concentrations of added salts.

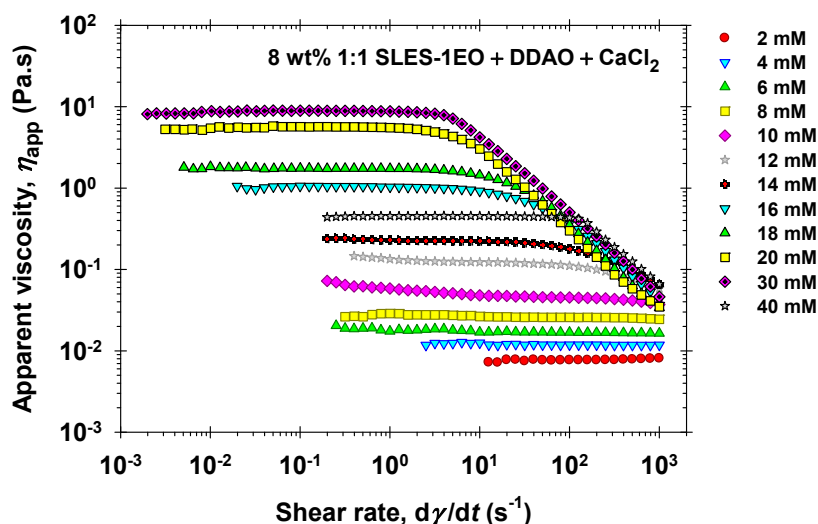


Figure S5. Apparent viscosity as a function of the shear rate for the system 8 wt% 1:1 SLES-1EO+DDAO in the presence of different concentrations of CaCl_2 (the salt concentrations are denoted in the legend of the graph).

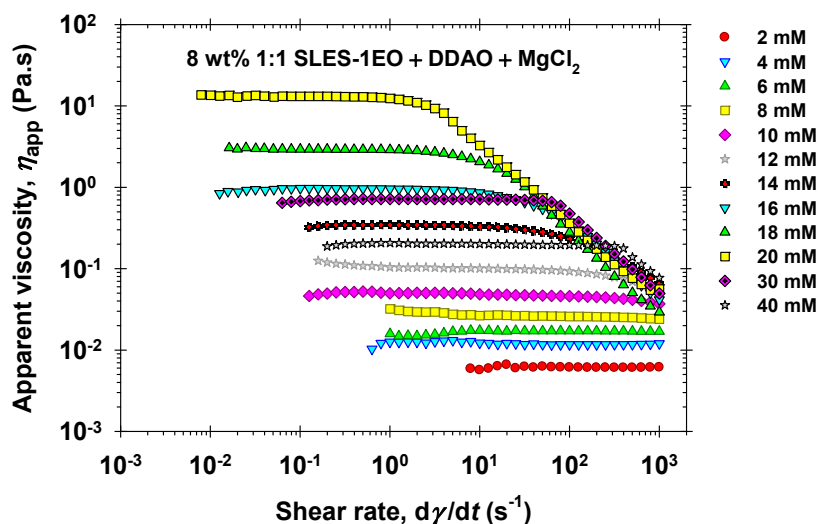


Figure S6. Apparent viscosity as a function of the shear rate for the system 8 wt% 1:1 SLES-1EO+DDAO in the presence of different concentrations of MgCl_2 (the salt concentrations are denoted in the legend of the graph).

Table S1 summarizes the turbidities and pH of 4 wt% individual surfactant solutions in the presence of divalent salts. One sees that all individual solutions are transparent in the range of MgCl₂ and CaCl₂ concentrations up to 120 mM. The only exception is the SDS solutions – these solutions are transparent in the case of 50 mM added MgCl₂ and turbid with crystallites for all other concentrations of added MgCl₂ or CaCl₂.

Table S1. Turbidity and pH of 4 wt% individual surfactant solutions in the presence of divalent salts.

System	MgCl ₂ (mM)	Turbidity (a.u.)	pH	CaCl ₂ (mM)	Turbidity (a.u.)	pH
4 wt% DDAO	50	0.0037	7.52	50	0.0038	7.50
	80	0.0054	7.57	80	0.0023	7.49
	100	0.0025	7.62	100	0.0004	7.48
	120	0.0020	7.64	120	0.0017	7.46
4 wt% SLES-3EO	50	0.0014	5.23	50	0.0036	5.15
	80	0.0034	5.06	80	0.0033	4.97
	100	0.0012	4.97	100	0.0044	4.93
	120	0.0011	4.94	120	0.0055	4.86
4 wt% SLES-1EO	50	0.0025	4.50	50	0.0096	4.39
	80	0.0082	4.31	80	0.0101	4.22
	100	0.0068	4.27	100	0.0110	4.11
	120	0.0092	4.17	120	0.0166	4.05
4 wt% SDS	50	transparent	6.40	50	crystals	6.46
	80	crystals	6.41	80	crystals	6.16
	100	crystals	6.44	100	crystals	5.96
	120	crystals	6.47	120	crystals	5.93

Table S2. Main properties of 8 wt% 1:1 ionic+zwiterionic surfactants in the presence of divalent salts (BMP – bicontinuous micellar phase).

System	Maximum of η_{app} observed at salt conc.		Concentration interval for BMP formation		Salting out concentrations	
	MgCl ₂	CaCl ₂	MgCl ₂	CaCl ₂	MgCl ₂	CaCl ₂
SDS +CAPB	20 (mM)	15 (mM)	60–90 (mM)	40–70 (mM)	> 90 mM	> 70 mM
SDS +DDAO	20 (mM)	20 (mM)	No	No	> 25 mM (crystals)	> 25 mM (crystals)

SLES-1EO +CAPB	30 (mM)	20 (mM)	60–170 (mM)	50–70 (mM)	> 170 mM	> 70 mM
SLES-1EO +DDAO	20 (mM)	30 (mM)	50–70 (mM)	60–80 (mM)	> 70 mM	> 80 mM

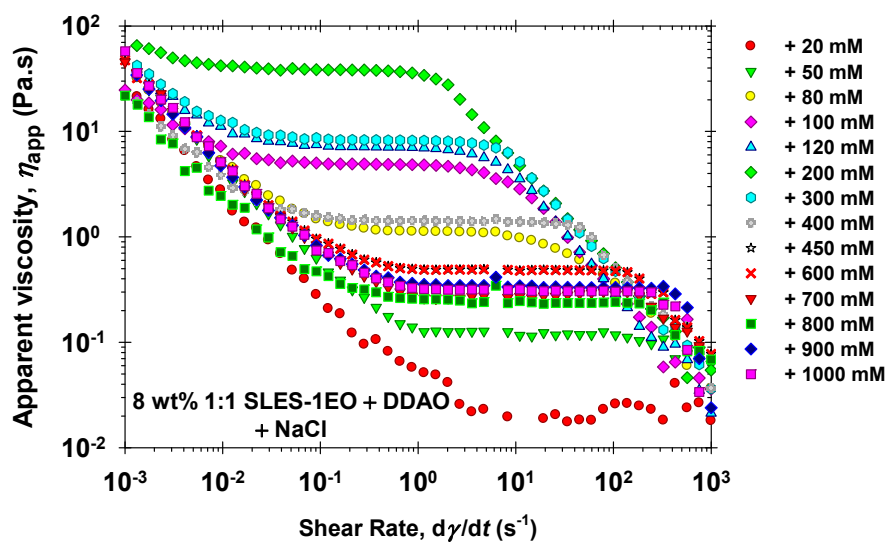
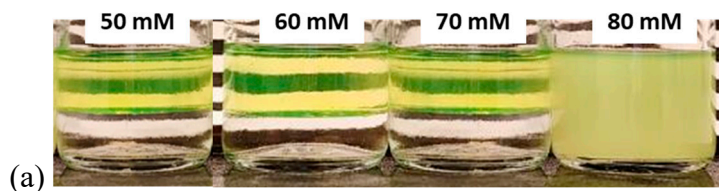


Figure S7. Apparent viscosity as a function of the shear rate for the system 8 wt% 1:1 SLES-1EO+DDAO in the presence of different concentrations of NaCl (the salt concentrations are denoted in the legend of the graph).



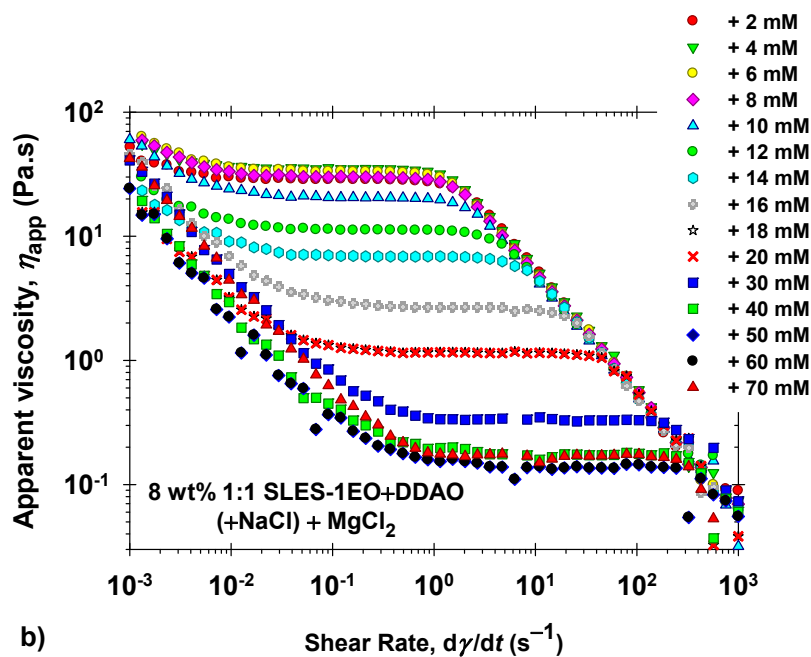


Figure S8. Phase separation (a) and apparent viscosity as a function of the shear rate (b) for the system 8 wt% 1:1 SLES-1EO+DDAO + NaCl in the presence of different concentrations of MgCl₂ (the salt concentrations are denoted in the legend of the graph).

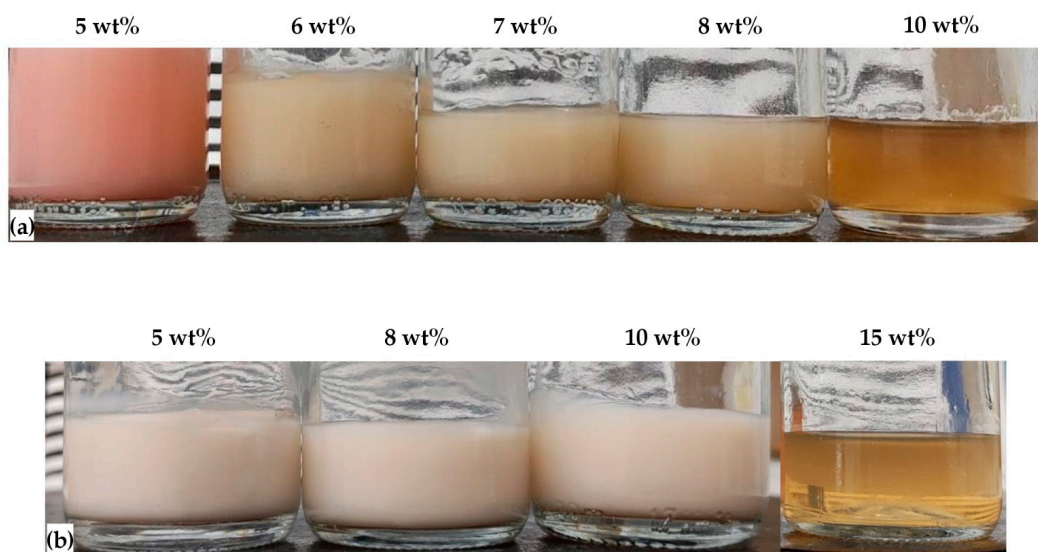


Figure S9. Photographs of the vials containing different concentrations of limonene in the saturated micellar phases separated from solution of: (a) 8 wt% 1:1 SLES-1EO+DDAO + 70 mM CaCl₂; (b) 8 wt% 1:1 SLES-1EO+CAPB + 100 mM MgCl₂. The concentrations of the added limonene are denoted on top of each bottle.

Figure S7 shows the effect of added NaCl to 8 wt% 1:1 SLES-1EO+DDAO micellar solution. Generally, the rheological behavior is analogous to those illustrated in Figures S5 and S6 but the concentrations of added monovalent salt are more than 10 times higher.

Figure S8 summarizes the effect of added MgCl_2 on the behavior of 8 wt% 1:1 SLES-1EO + DDAO micellar solution, when the DDAO sample contains the same amount of NaCl as the used CAPB sample.

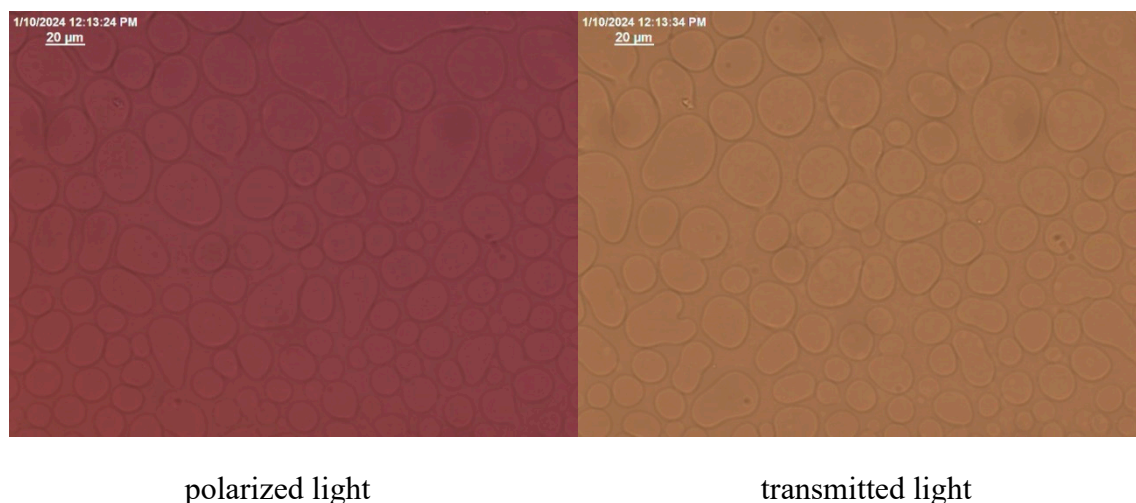


Figure S10. Microscopic images of 8 wt% 1:1 SLES-1EO+DDAO + 70 mM CaCl_2 solution obtained in polarized and transmitted light using optical microscope Axiolmager M2m.