

ESI

Aqueous Foams in the Presence of Surfactant Crystals

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1 Preparation of surfactant solutions/crystal dispersions

Table S1. Aqueous surfactant solutions/crystal dispersions prepared at varying concentrations of SDS and $\text{Mg}(\text{NO}_3)_2$ at room temperature ($T = 20 \pm 3^\circ\text{C}$). Underline denotes precipitation of surfactant crystals.

	Varying [SDS] or $[\text{Mg}(\text{NO}_3)_2]$ /mM
0.1-200 mM SDS	[SDS] = 0.1, 0.2, 0.5, 1, 2, 5, 8, 15, 30, 50, 100, 200
0.1-200 mM SDS in 10 mM $\text{Mg}(\text{NO}_3)_2$	[SDS] = 0.1, 0.2, 0.5, 1, <u>2, 5, 8, 15, 20, 25, 30</u> , 50, 100, 200
0.5 mM SDS in 0.1-200 mM $\text{Mg}(\text{NO}_3)_2$	$[\text{Mg}(\text{NO}_3)_2]$ = 0.1, 0.4, 1, 5, 10, 40, 100
15 mM SDS in 0.1-200 mM $\text{Mg}(\text{NO}_3)_2$	$[\text{Mg}(\text{NO}_3)_2]$ = 0.1, 0.5, 1, <u>3, 5, 7, 10, 30, 50, 100</u>

2 Determination of surfactant concentration in supernatant and sediment

Crystal dispersions were left standing at room temperature ($T = 20 \pm 3 \text{ }^{\circ}\text{C}$) for 2 days. They separated into a clear supernatant and a sediment of concentrated surfactant crystals within a small volume of solution. To determine the actual surfactant concentration in the supernatant and sediment, the volume fractions of the supernatant and sediment (ϕ_{sup} and ϕ_{sed}) were measured after complete sedimentation with:

$$\phi_{\text{sup}} = H_{\text{supernatant}}/H_{\text{total}} \quad (1)$$

$$\phi_{\text{sed}} = H_{\text{sediment}}/H_{\text{total}} \quad (2)$$

where $H_{\text{supernatant}}$, H_{sediment} and H_{total} are the heights of the supernatant, sediment and total height respectively. The variation of ϕ_{sup} and ϕ_{sed} for different crystal dispersions are shown in Figure S1. Following the description in the experimental section, the Epton titration (Figure S2) was carried out to determine the actual surfactant concentration in the supernatant ($[\text{SDS}]_{\text{actual, sup}}$). Taking 20 mL of a crystal dispersion as example ($V_{\text{total}} = 20 \text{ mL}$), the volume of its supernatant and sediment (V_{sup} and V_{sed}) and the total number of moles of SDS (n_{total}) can be calculated from V_{total} , ϕ_{sup} , ϕ_{sed} , and initial SDS concentration ($[\text{SDS}]$). The number of moles of SDS in the supernatant ($n_{\text{SDS, sup}}$) and sediment ($n_{\text{SDS, sed}}$) and the actual surfactant concentration in the sediment ($[\text{SDS}]_{\text{actual, sed}}$) can be calculated using the following equations:

$$\text{Total number of moles of SDS: } n_{\text{total}} = [\text{SDS}] \cdot V_{\text{total}} \quad (3)$$

$$\text{Volume of supernatant: } V_{\text{sup}} = V_{\text{total}} \cdot \phi_{\text{sup}} \quad (4)$$

$$\text{Volume of sediment: } V_{\text{sed}} = V_{\text{total}} \cdot \phi_{\text{sed}} \quad (5)$$

$$\text{Number of moles of SDS in supernatant: } n_{\text{SDS, sup}} = [\text{SDS}]_{\text{actual, sup}} \cdot V_{\text{sup}} \quad (6)$$

$$\text{Number of moles of SDS in sediment: } n_{\text{SDS, sed}} = n_{\text{total}} - [\text{SDS}]_{\text{actual, sup}} \cdot V_{\text{sup}} \quad (7)$$

$$\text{Actual surfactant concentration in sediment: } [\text{SDS}]_{\text{actual, sed}} = n_{\text{SDS, sed}}/V_{\text{sed}} \quad (8)$$

Figure S1. Variation of ϕ_{sup} and ϕ_{sed} measured for crystal dispersions of (a) 2-30 mM SDS in 10 mM $\text{Mg}(\text{NO}_3)_2$ and (b) 15 mM SDS in 3-100 mM $\text{Mg}(\text{NO}_3)_2$.

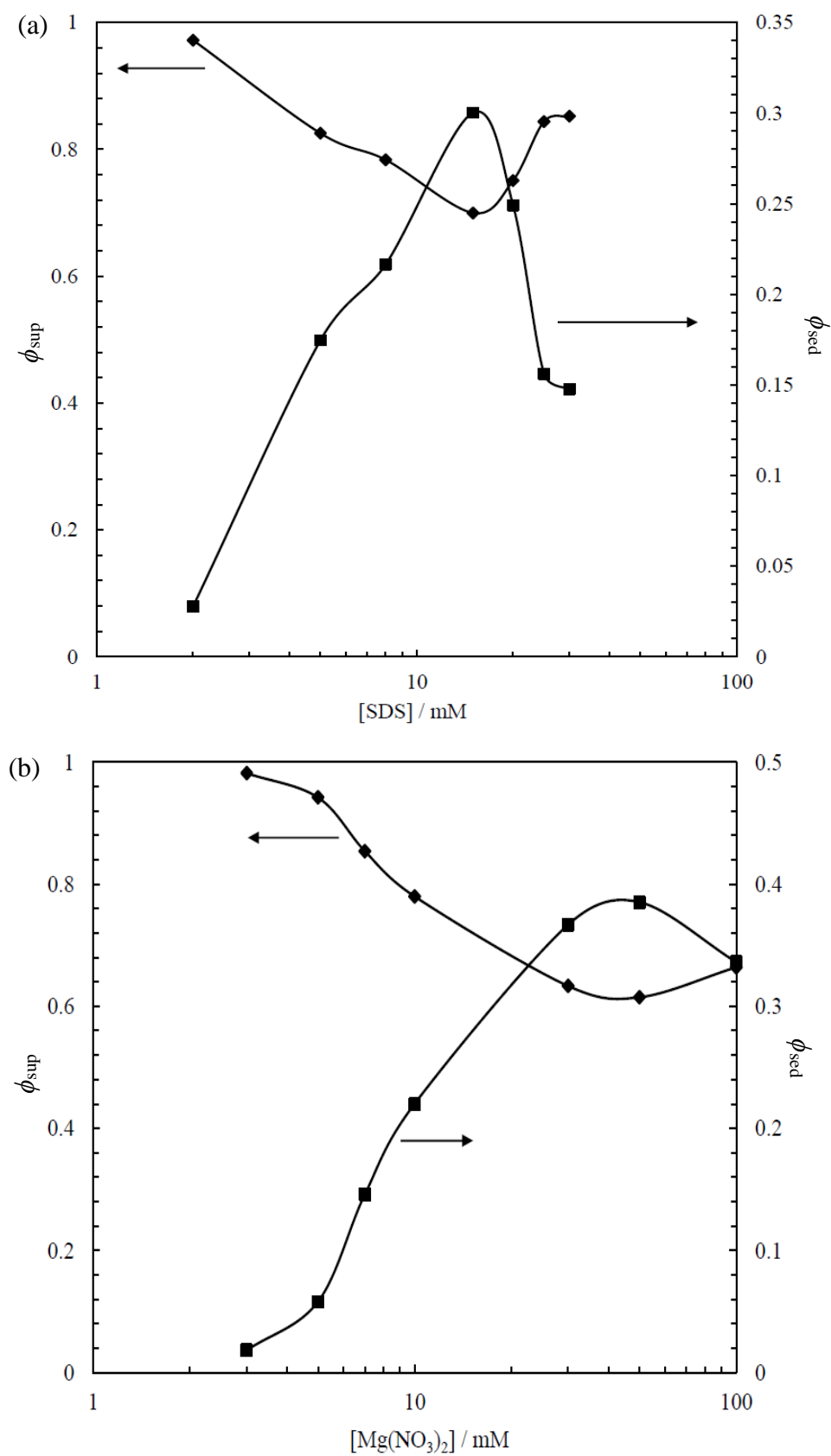
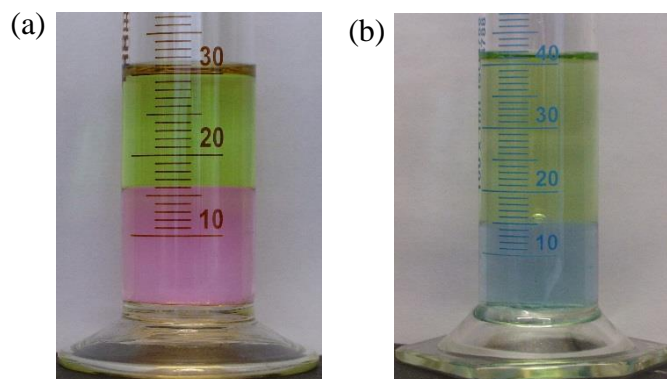


Figure S2. Appearance of water-chloroform mixture (a) before Epton titration and (b) at the end-point.



3 Cryo-SEM of aqueous foam

A small volume of foam was mounted on an aluminium stub (10 mm in diameter) and plunged in liquid nitrogen ‘slush’ (approximately $-210\text{ }^{\circ}\text{C}$). It was frozen and transferred into a cryogenic preparation chamber (PP3010T Quorum Technologies Ltd.) under a vacuum of 5×10^{-6} mbar. Inside the chamber, the foam sample was fractured horizontally with a built-in blade on a nitrogen gas cooled specimen stage ($-140\text{ }^{\circ}\text{C}$). Sublimation of the surface water (ice) was then performed inside a Zeiss EVO60 SEM chamber at $-75\text{ }^{\circ}\text{C}$ before sputter-coating with a 2 nm thick platinum layer in an argon atmosphere inside the preparation chamber. Cryo-SEM observation was carried out in the Zeiss EVO60 SEM chamber at a voltage of 15 kV and a probe current of 30 pA at $-140\text{ }^{\circ}\text{C}$ and vacuum of 1×10^{-6} mbar under cryogenic conditions. Elemental analysis of sample surfaces was also conducted using an equipped EDX.

4 Determination of *cmc* of SDS at varying $[\text{Mg}(\text{NO}_3)_2]$

Aqueous SDS solutions of 0.1-30 mM were prepared with no $\text{Mg}(\text{NO}_3)_2$ added. Their surface tensions were measured using a Krüss K11 digital tensiometer thermostatted at $20\text{ }^{\circ}\text{C}$. Measurements were performed with the static maximum pull method using a du Noüy ring. Each solution was measured three times separately to confirm the reproducibility. The surface tension was plotted as a function of $[\text{SDS}]$ and the critical micelle concentration (*cmc*) was obtained. In the same way, aqueous solutions of SDS in 0.1 mM, 1 mM, 10 mM and 100 mM $\text{Mg}(\text{NO}_3)_2$ were prepared over the respective surfactant concentration ranges of 0.1-10 mM, 0.1-4.5 mM, 0.1-2 mM and 0.1-1 mM and measured with the tensiometer. The surface

tension of Milli-Q water was measured each time before measurements and it was 72.0 ± 0.2 mN m⁻¹ at 25 °C. The *cmc* values of SDS were determined to be 8 mM, 2 mM, 1 mM and 0.48 mM at Mg(NO₃)₂ concentrations of 0.1 mM, 1 mM, 10 mM and 100 mM respectively.

5 Observation of crystal dispersions

A home-made crossed polarization box was assembled to observe crystal dispersions in crossed-polarized light. It consists of an opaque box, an LED light source, a background polarizing film (polarizer 1) in front of the LED light and another polarizing filter (polarizer 2, Rangers HD MRC SLIM Circular Polarizing Filter) fitted on a camera lens (FinePix HS20EXR, Fujifilm). Upon rotating the polarizing filter on a camera lens (polarizer 2), the viewing field turns from bright to dark to bright recurrently. Extinction is achieved when the viewing field becomes black and darkest. After adjusting polarizer 2 to the extinction position, the glass vial containing a crystal dispersion was placed and photographed between the background polarizing film and camera lens, as shown in Figure S3 below.

Figure S3. Sketch of a home-made light box used to observe samples in crossed-polarized light.

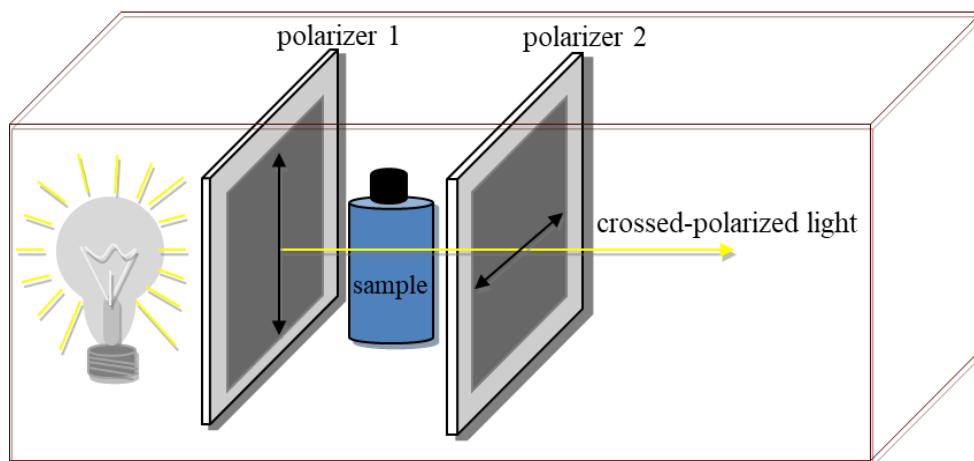


Figure S4. Optical microscopy images of surfactant crystals sampled from aqueous SDS in 10 mM $\text{Mg}(\text{NO}_3)_2$ crystal dispersions at different SDS concentrations given prepared at room temperature ($T = 20 \pm 3\text{ }^\circ\text{C}$).

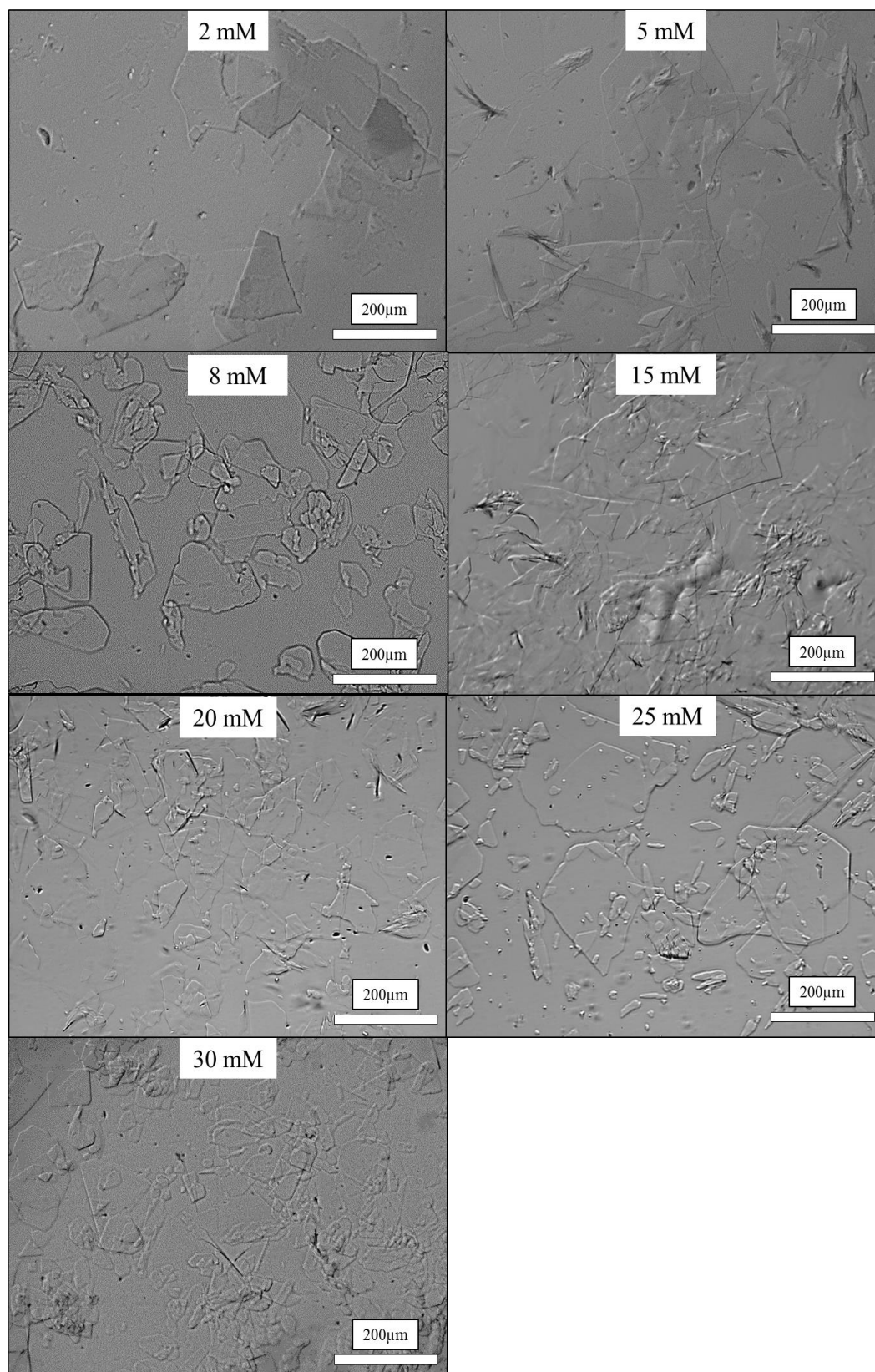


Figure S5. Optical microscopy images of surfactant crystals sampled from 15 mM SDS in $\text{Mg}(\text{NO}_3)_2$ crystal dispersions at different $[\text{Mg}(\text{NO}_3)_2]$ given prepared at room temperature ($T = 20 \pm 3^\circ\text{C}$).

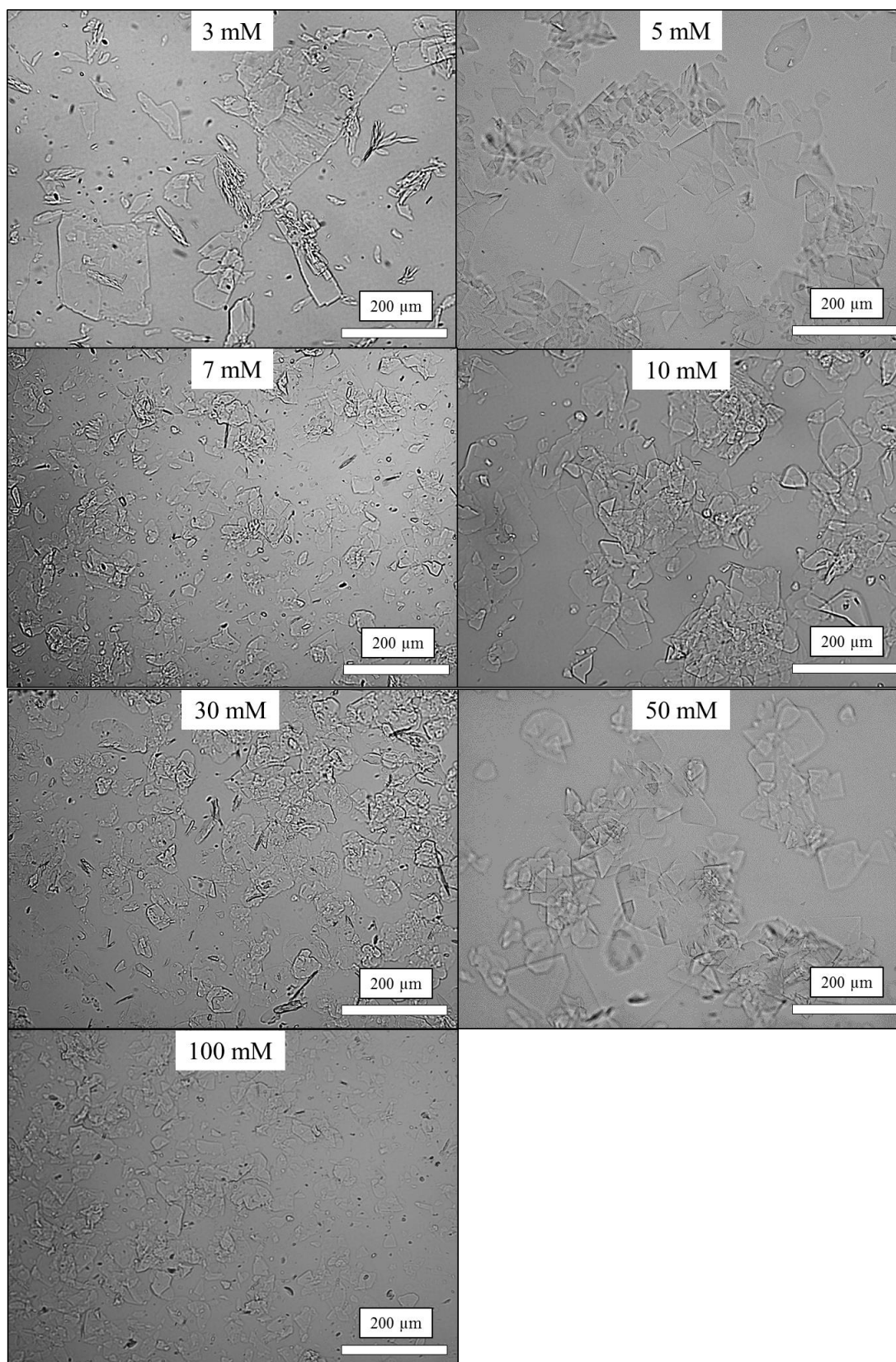


Figure S6. Variation of the average diameter (D) of surfactant crystals precipitated from SDS in 10 mM $\text{Mg}(\text{NO}_3)_2$ crystal dispersions at different surfactant concentrations prepared at room temperature ($T = 20 \pm 3$ °C). The diameters were measured using a Mastersizer 2000 instrument. 1 mL crystal dispersion was added into 120 mL of fresh 10 mM $\text{Mg}(\text{NO}_3)_2$ aqueous solution in a Hydro 2000SM dispersion unit for each measurement. Error bars reflect the result from 3 consecutive measurements.

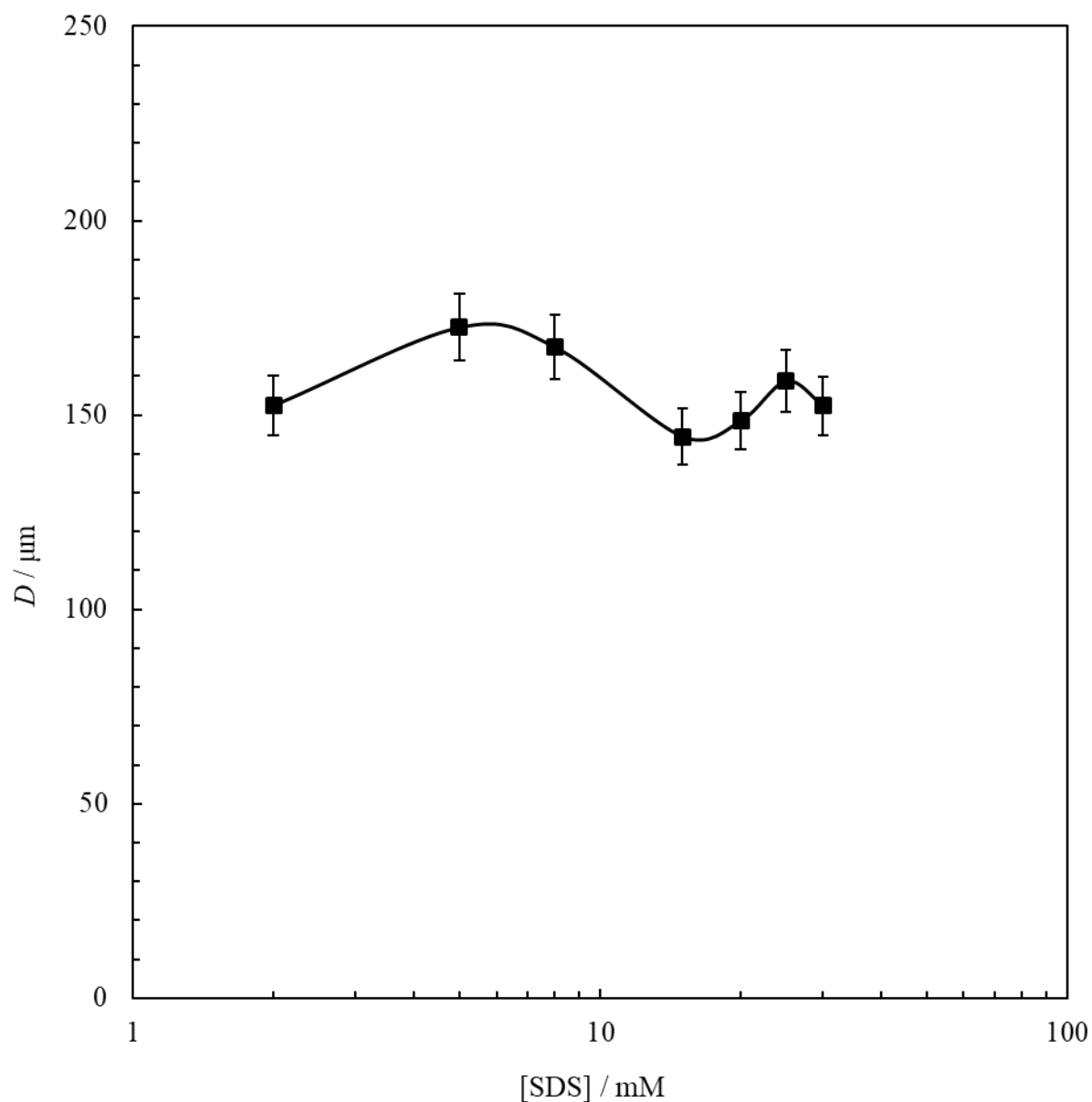
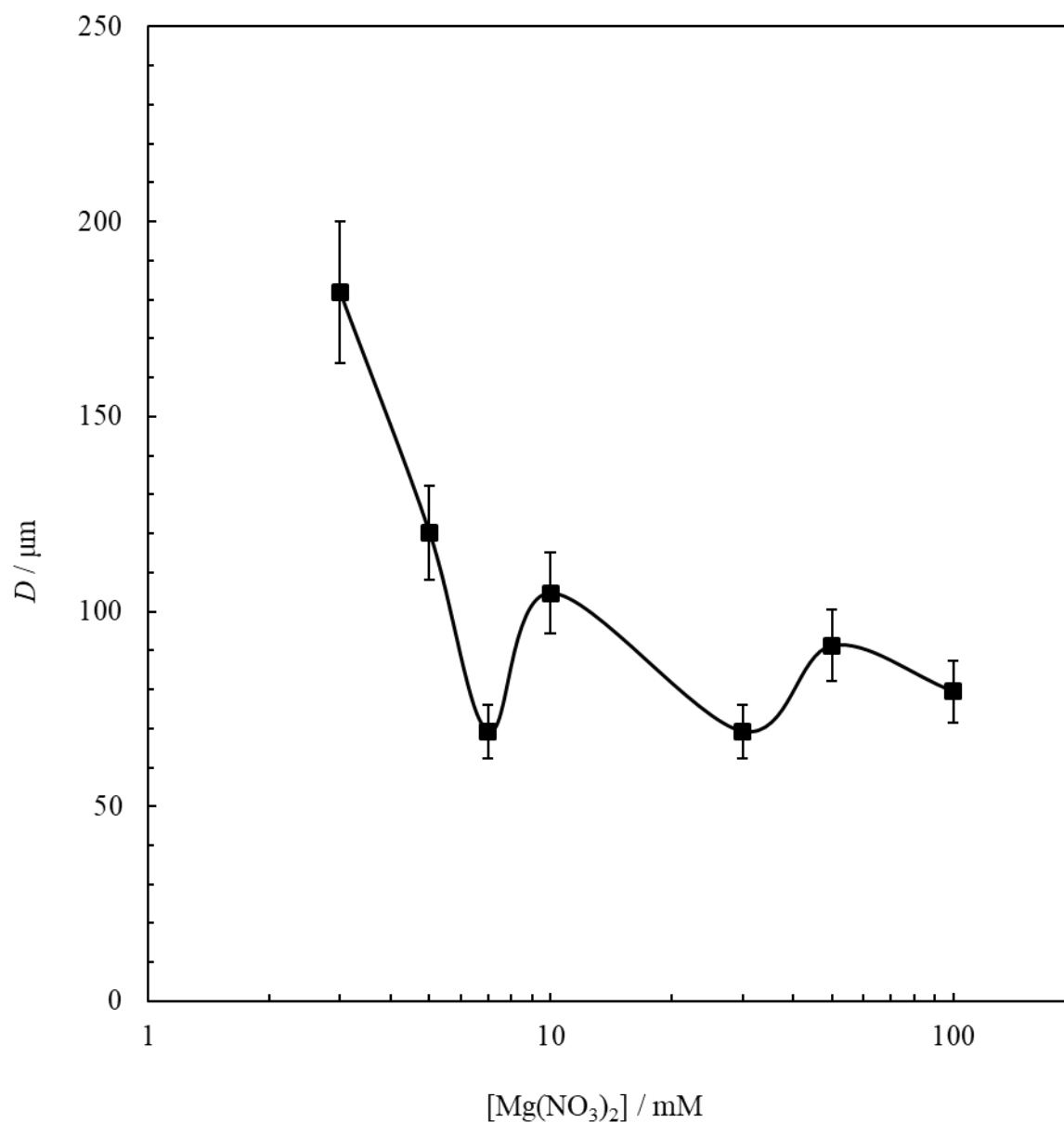


Figure S7. Variation of the average diameter (D) of surfactant crystals precipitated from 15 mM SDS in $\text{Mg}(\text{NO}_3)_2$ crystal dispersions at different salt concentrations prepared at room temperature ($T = 20 \pm 3 \text{ }^\circ\text{C}$).



6 Foam behaviour of surfactant solutions/crystal dispersions

Figure S8. Variation of initial foam volume (V_{f0}) of aqueous foams generated from 20 mL of 15 mM SDS solutions at room temperature ($T = 20 \pm 3$ °C) as a function of $[\text{Mg}(\text{NO}_3)_2]$. Error bars show maximum deviations of three separate measurements. Inset shows graduated cylinders containing these aqueous foams and a red dashed frame marks foams generated from crystal dispersions.

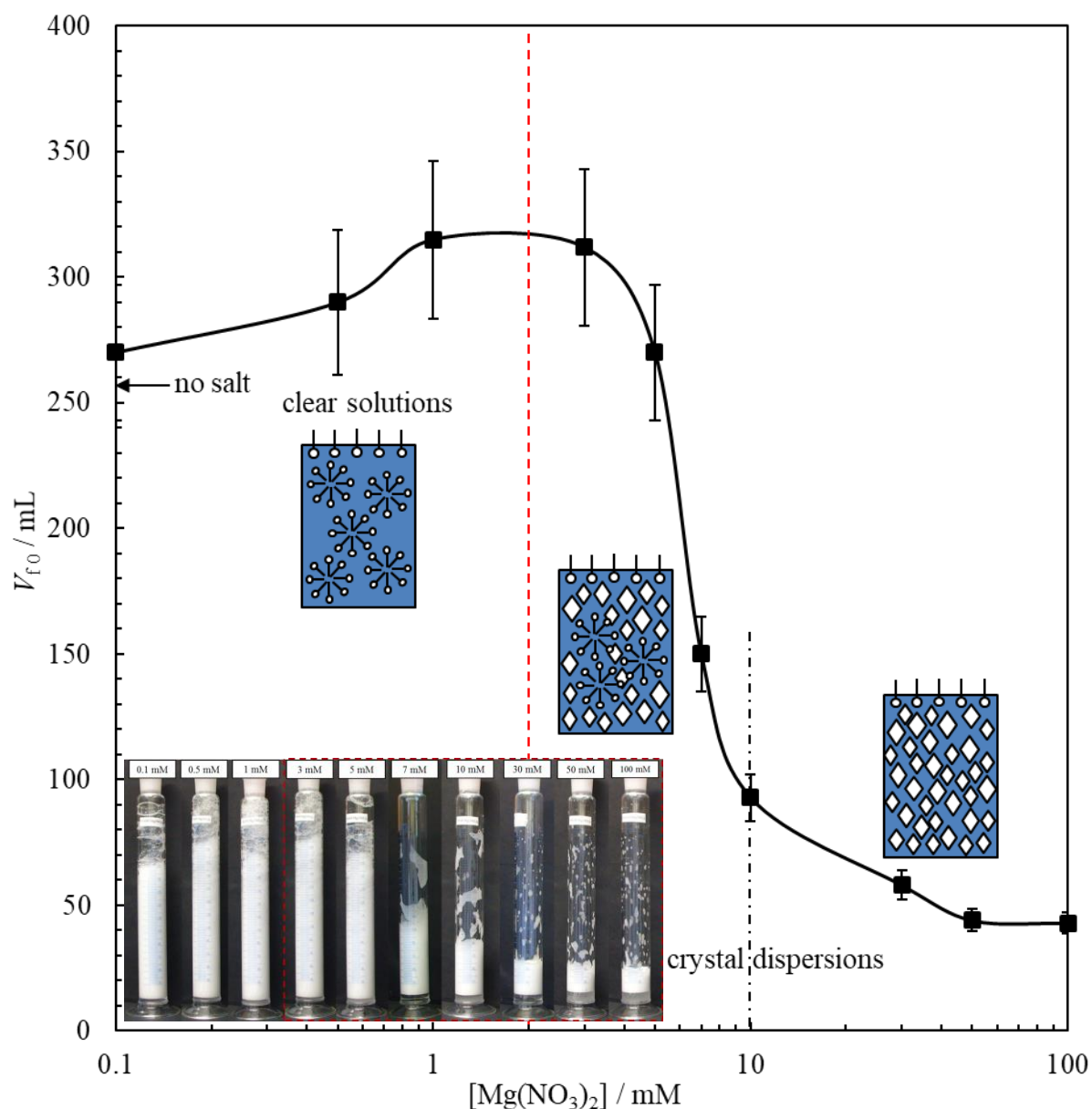


Figure S9. Variation of foam half-life ($t_{1/2}$) of aqueous foams generated from 20 mL of 15 mM SDS solutions at room temperature ($T = 20 \pm 3$ °C) as a function of $[\text{Mg}(\text{NO}_3)_2]$.

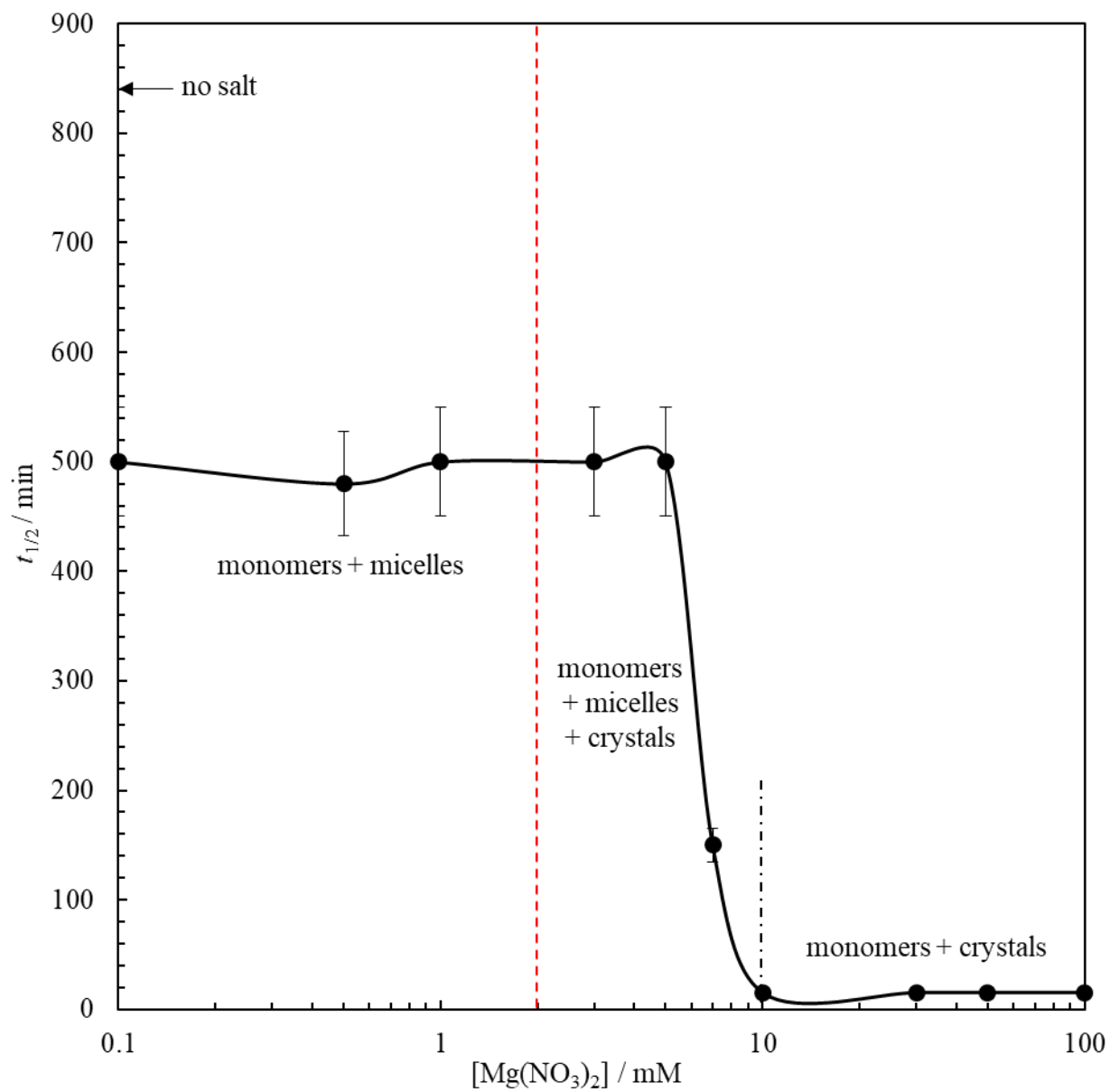


Figure S10. Variation of initial foam volume (V_{f0}) of aqueous foams generated from 20 mL of 0.5 mM SDS solutions at room temperature ($T = 20 \pm 3$ °C) as a function of $[\text{Mg}(\text{NO}_3)_2]$. Inset show graduated cylinders containing these aqueous foams. Surfactant molecules exist as monomers over the whole range of salt concentration.

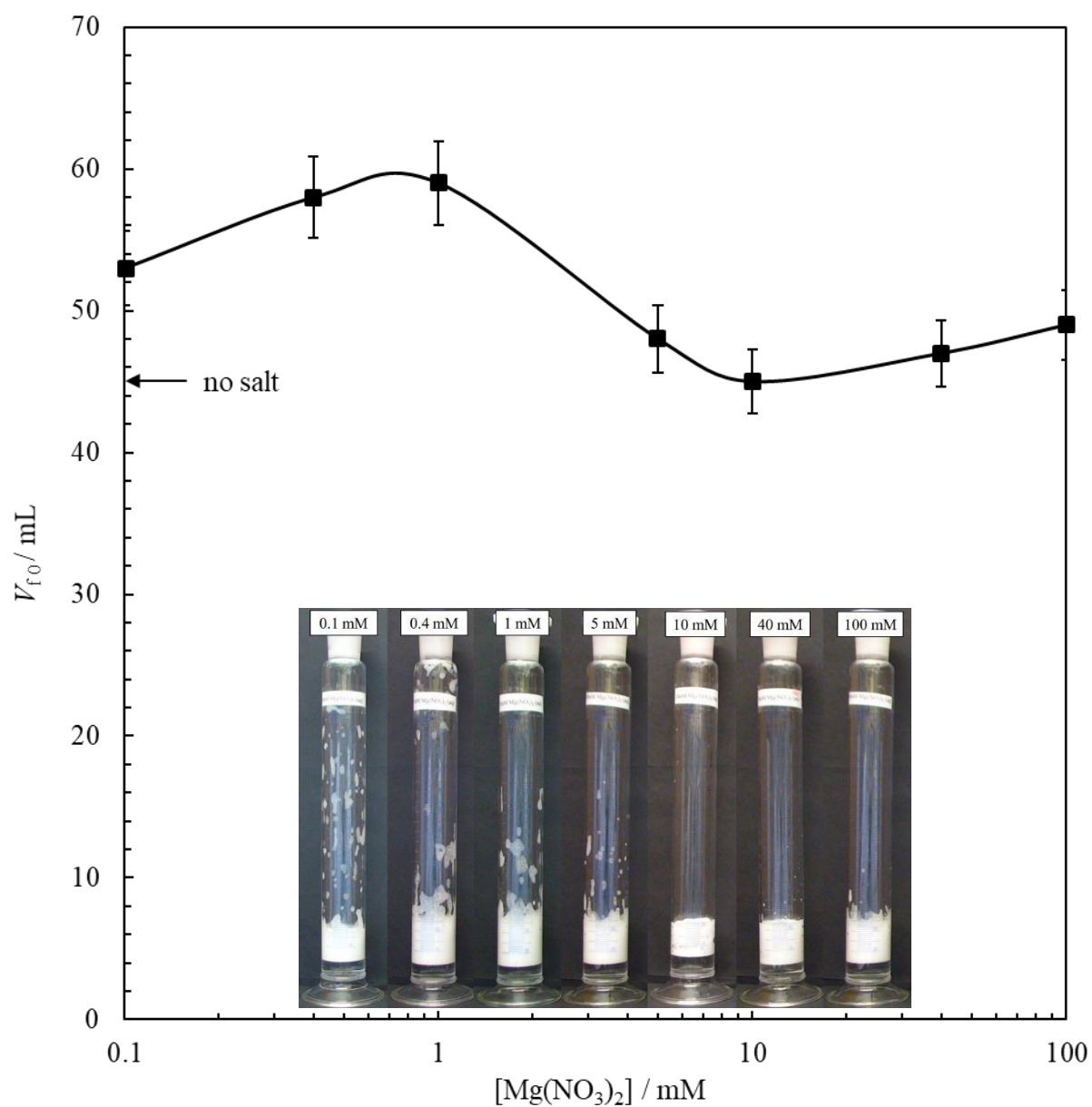


Figure S11. Variation of foam half-life ($t_{1/2}$) of aqueous foams generated from 20 mL of 0.5 mM SDS solutions at room temperature ($T = 20 \pm 3$ °C) as a function of $[\text{Mg}(\text{NO}_3)_2]$. Surfactant molecules exist as monomers over the whole range of salt concentration.

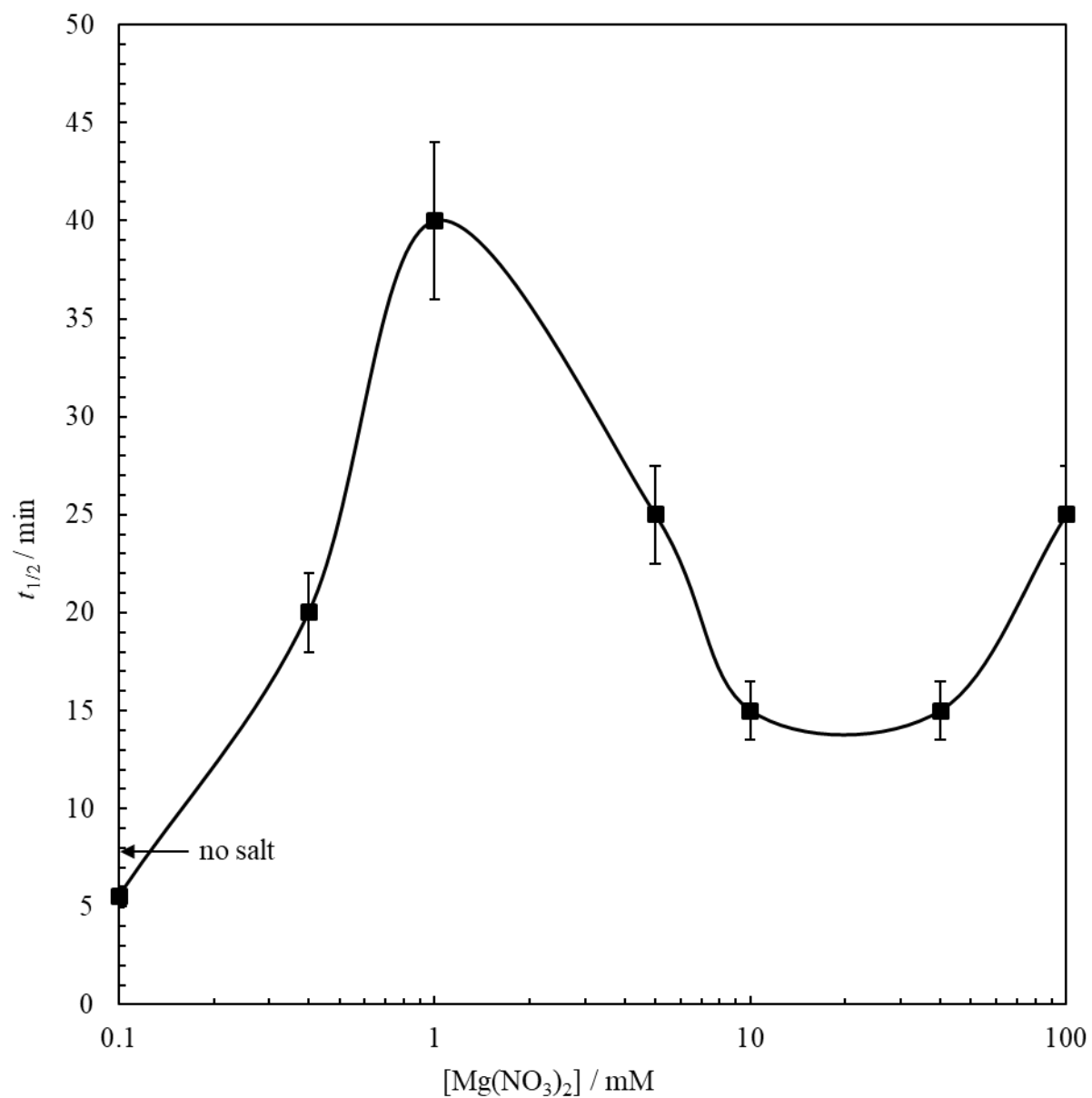


Figure S12. Optical microscope images (or photo' - last row) of aqueous foams at different times generated from a crystal dispersion of 30 mM SDS in 10 mM $\text{Mg}(\text{NO}_3)_2$ at room temperature ($T = 20 \pm 3$ °C).

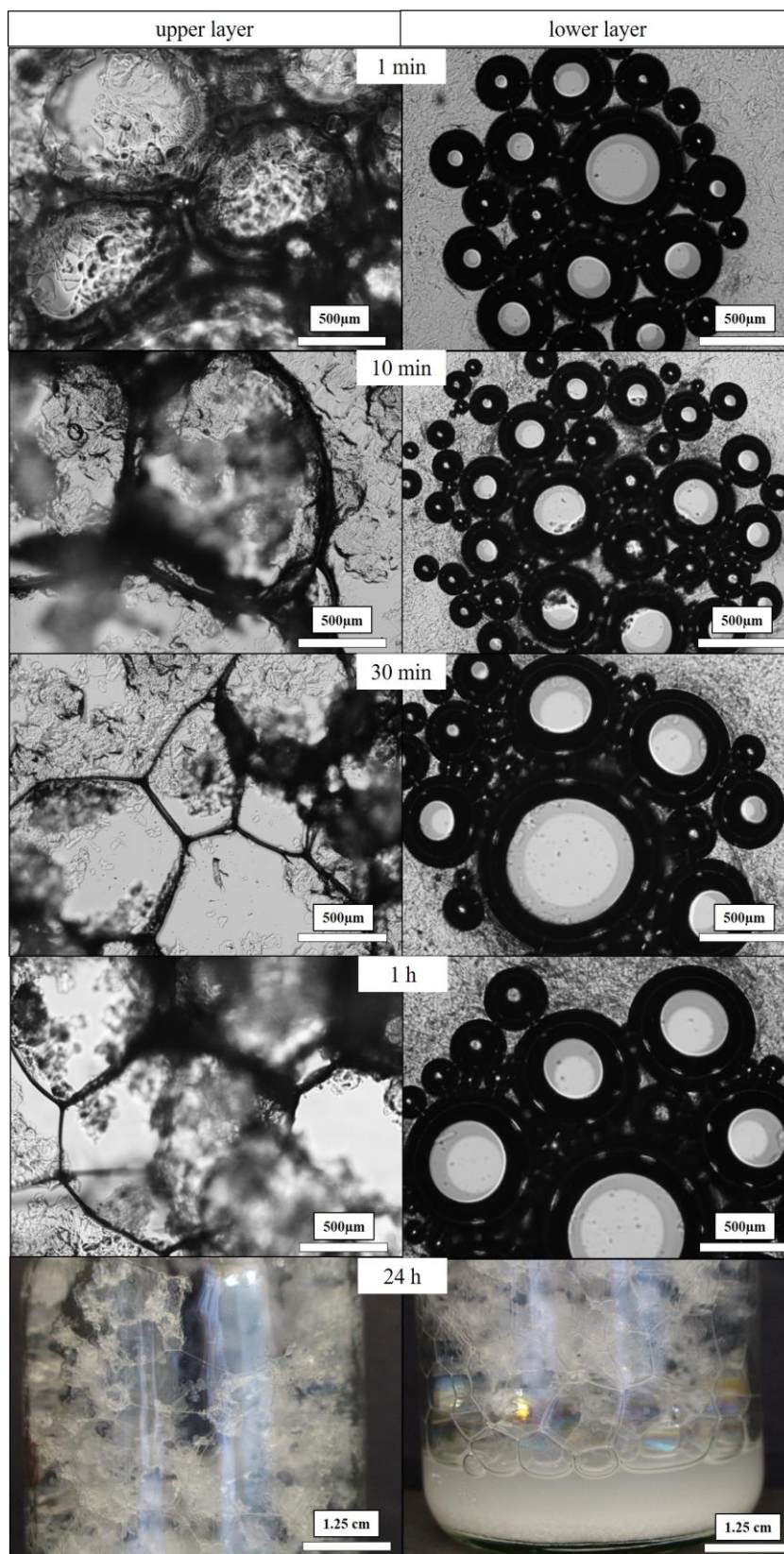


Figure S13. Variation of initial foam volume (V_{f0}) of 20 mL of supernatant, sediment and intact crystal dispersion as a function of actual surfactant concentration. Supernatants and sediments were separated from crystal dispersions of 15 mM SDS in 3-100 mM $\text{Mg}(\text{NO}_3)_2$.

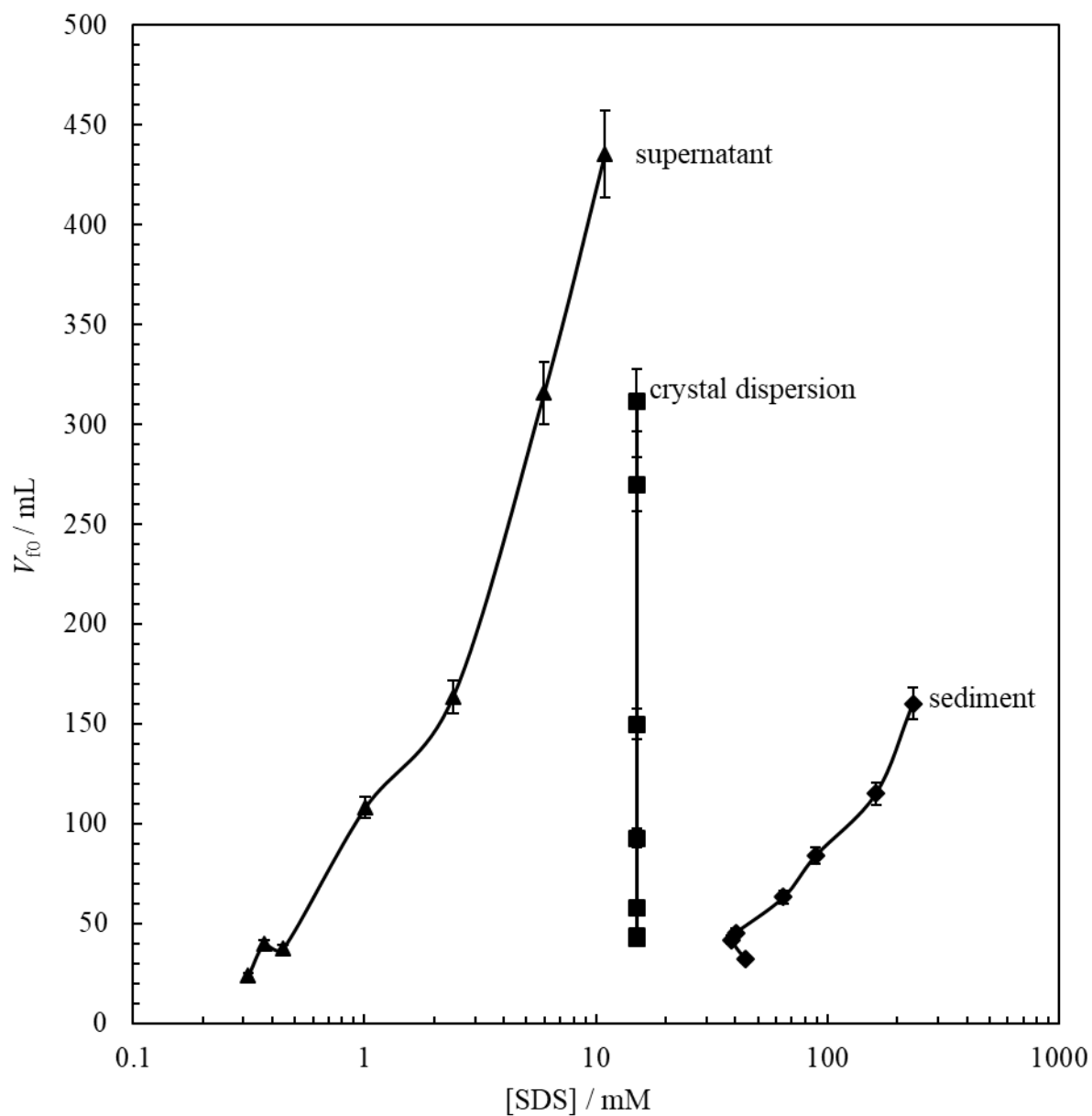


Figure S14. Variation of calculated (dashed line) and experimental (solid line) initial foam volume (V_{f0}) of 20 mL of intact crystal dispersion as a function of $[\text{Mg}(\text{NO}_3)_2]$.

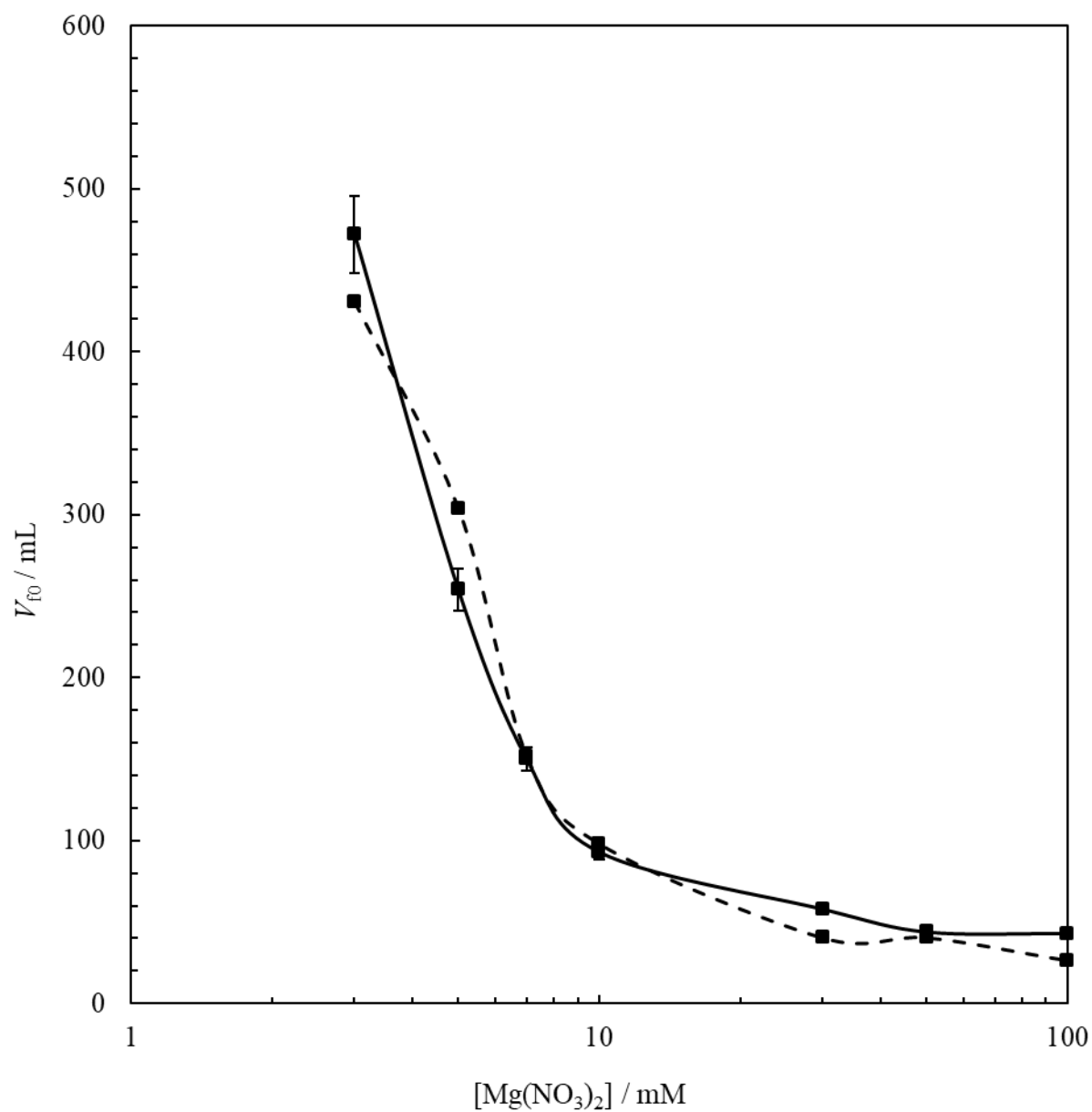


Figure S15. Variation of foam half-life ($t_{1/2}$) of 20 mL of supernatant, sediment and intact crystal dispersion as a function of actual surfactant concentration. Supernatants and sediments were separated from crystal dispersions of 15 mM SDS in 3-100 mM $\text{Mg}(\text{NO}_3)_2$.

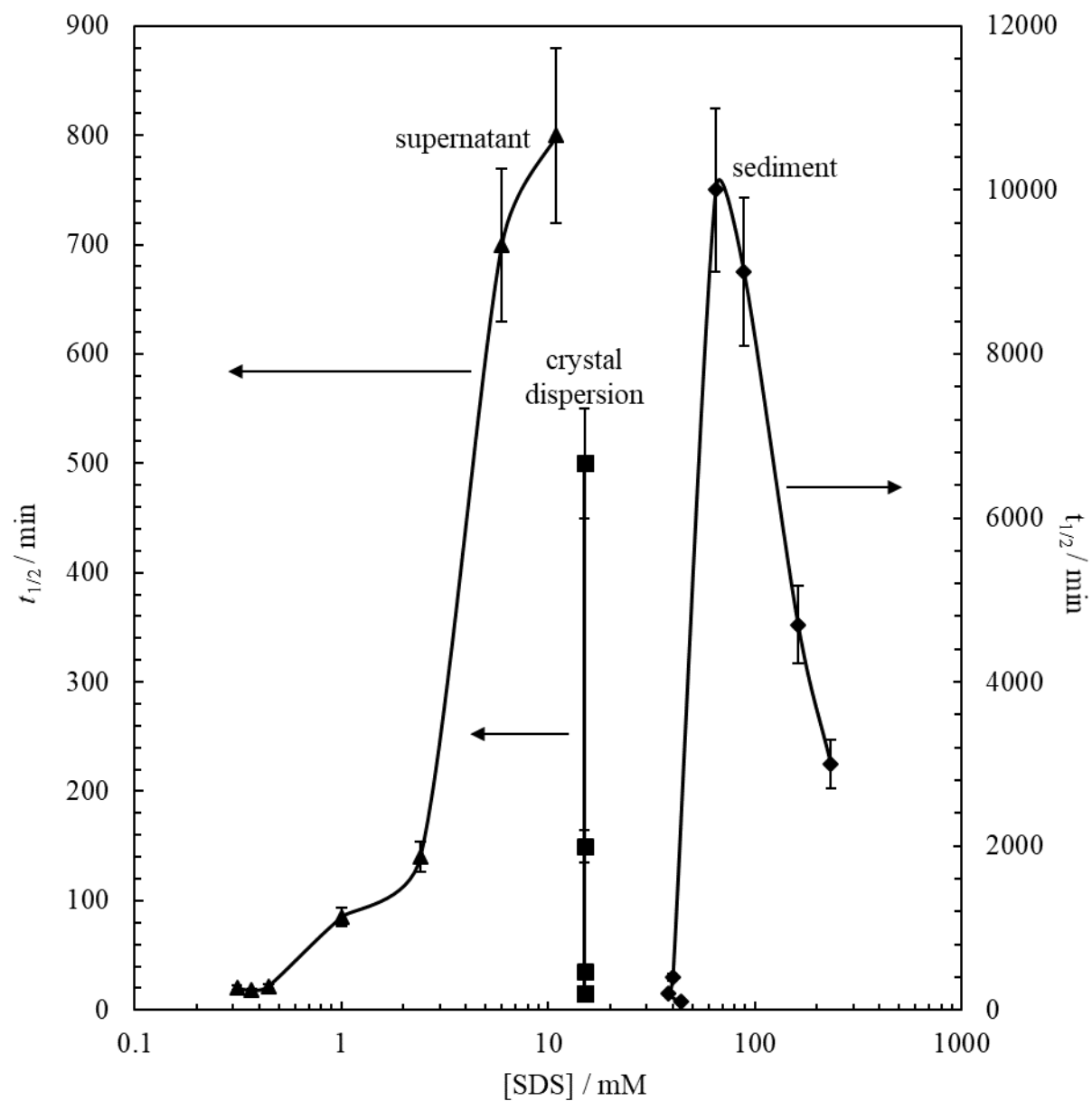


Figure S16. Crossed-polarised microscope images of foams generated from (left) crystal dispersions of 15 mM SDS in two $[\text{Mg}(\text{NO}_3)_2]$ and (right) corresponding sediments. Images were taken just after preparation. An increased coverage of surfactant crystals on bubbles in foams prepared from sediment is confirmed.

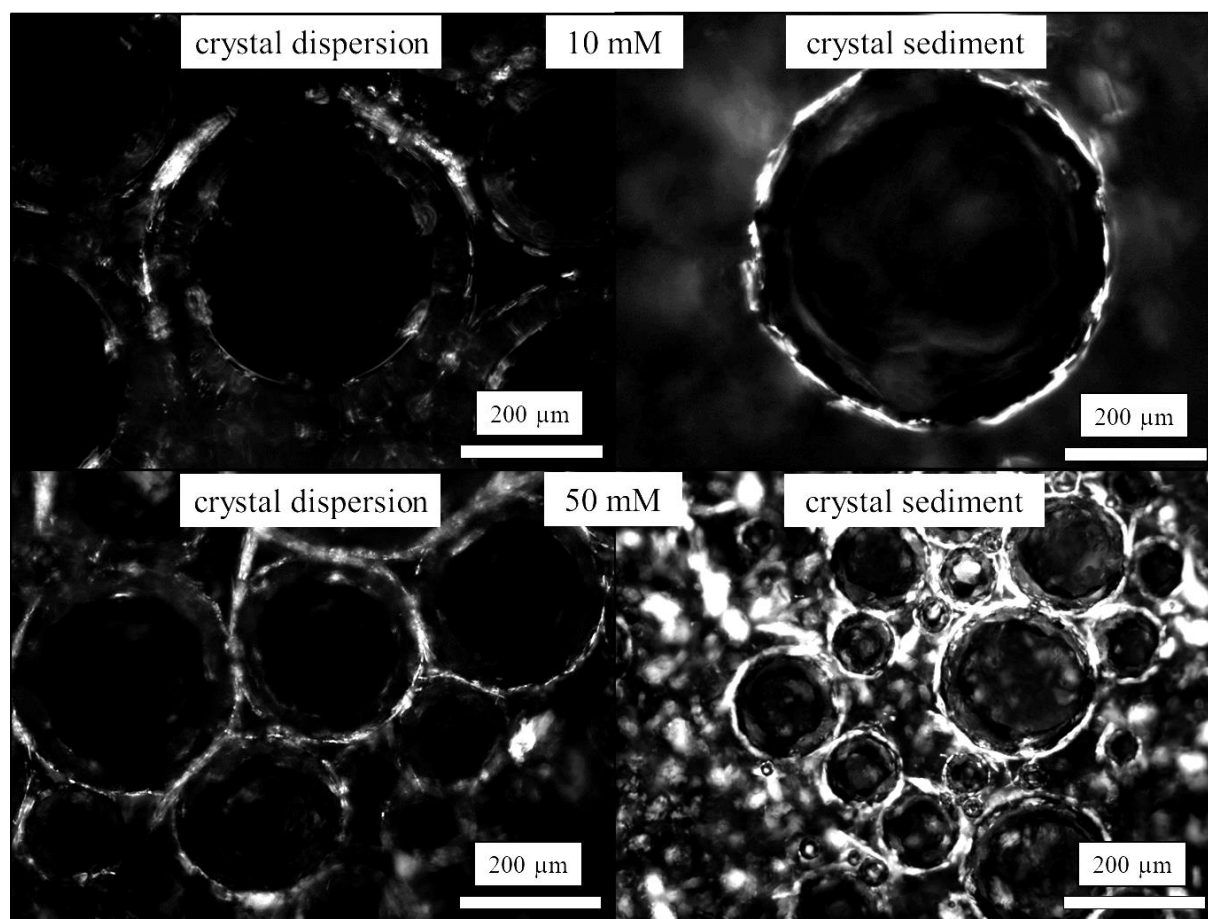


Figure S17. Variation of the average diameter (D) of surfactant crystals in dispersions of 30 mM SDS in 10 mM $\text{Mg}(\text{NO}_3)_2$ after sonication at an amplitude of 100% for different times.

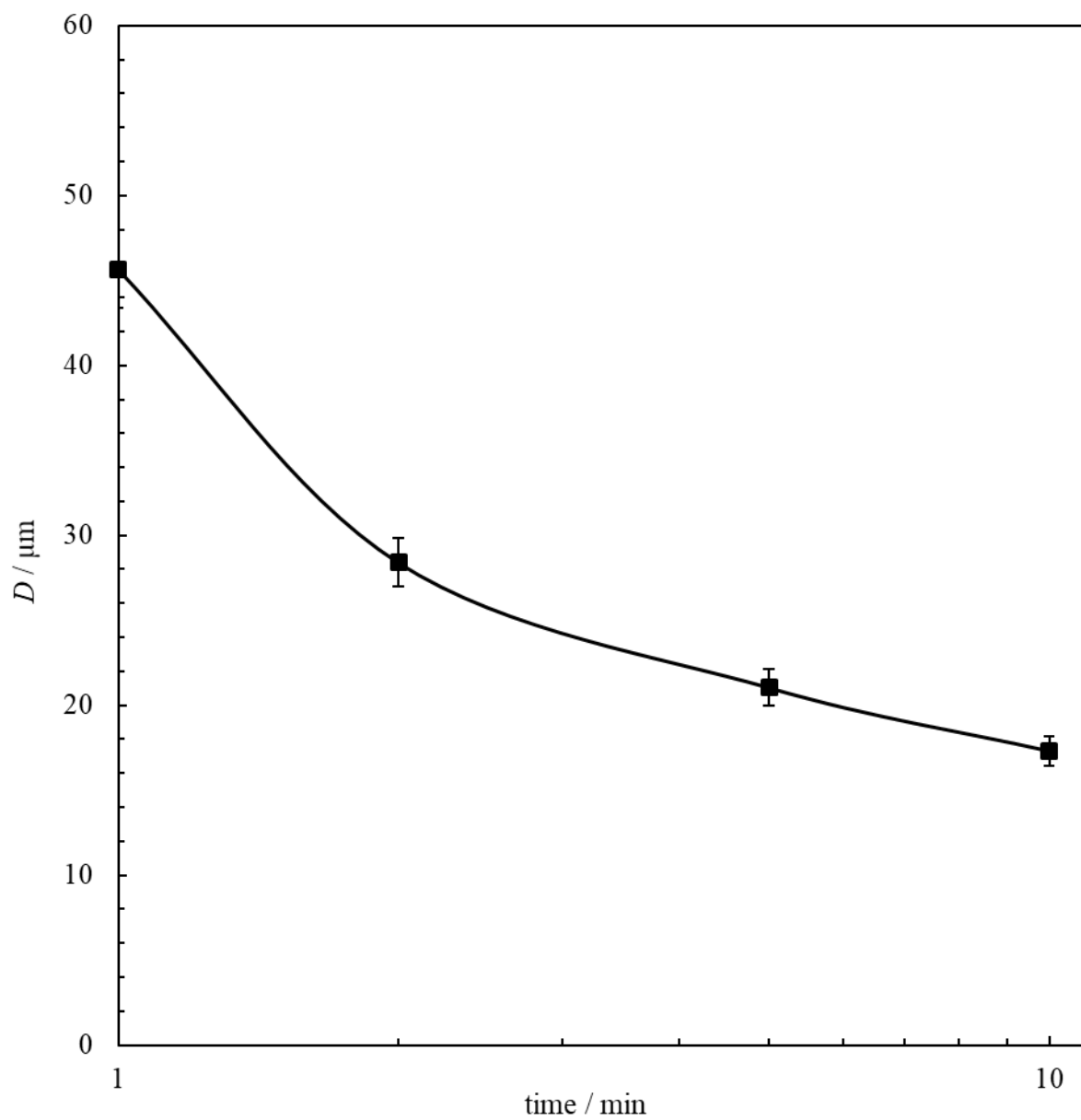


Figure S18. Variation of the average diameter (D) of surfactant crystals in dispersions of SDS in 10 mM $\text{Mg}(\text{NO}_3)_2$ prepared after rapid cooling. For comparison, the variation in size of crystal dispersions prepared at room temperature ($T = 20 \pm 3^\circ\text{C}$) is also plotted.

