

Supporting Information

Isothermal Crystallization Kinetics of Sodium Dodecyl Sulfate–Water Micellar Solutions

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Nuclear magnetic resonance (NMR) spectroscopy

¹H NMR spectroscopy was used to monitor for the onset of degradation and the presence of impurities; acquired on a Bruker AV-400 spectrometer. Chemical shifts are reported in parts per million (ppm), coupling constants in Hertz (Hz), and tetramethylsilane (TMS) is the internal standard. To prepare the sample, a few ml of the SDS-H₂O solution in use was dried down in a vacuum desiccator containing silica gel, before being prepared in approximately 0.5 ml of dimethyl sulfoxide-*d*₆ (DMSO-*d*₆), purchased from Merck Millipore. 1-dodecanol (≥98.0% purity) was also purchased from Merck Millipore and used as received; this was run as a reference. The results were analyzed using MestReNova 10.0.2. The spectra for SDS, 1-dodecanol and SDS with 1-dodecanol are provided in Figure S1.

Detection of the degradation product (1-dodecanol) is possible as the ¹H NMR spectra of both molecules have a different chemical shift for the protons in position **D**, when adjacent to either a sulfate headgroup or a primary alcohol. In addition, it is possible to observe the alcohol proton in position **E** for 1-dodecanol when prepared in DMSO-*d*₆. The remaining alkyl chain demonstrates a marginal change in chemical shifts between the two molecules, however this lessens as the deshielding decreases, specifically moving further away from the oxygen-substituted group.

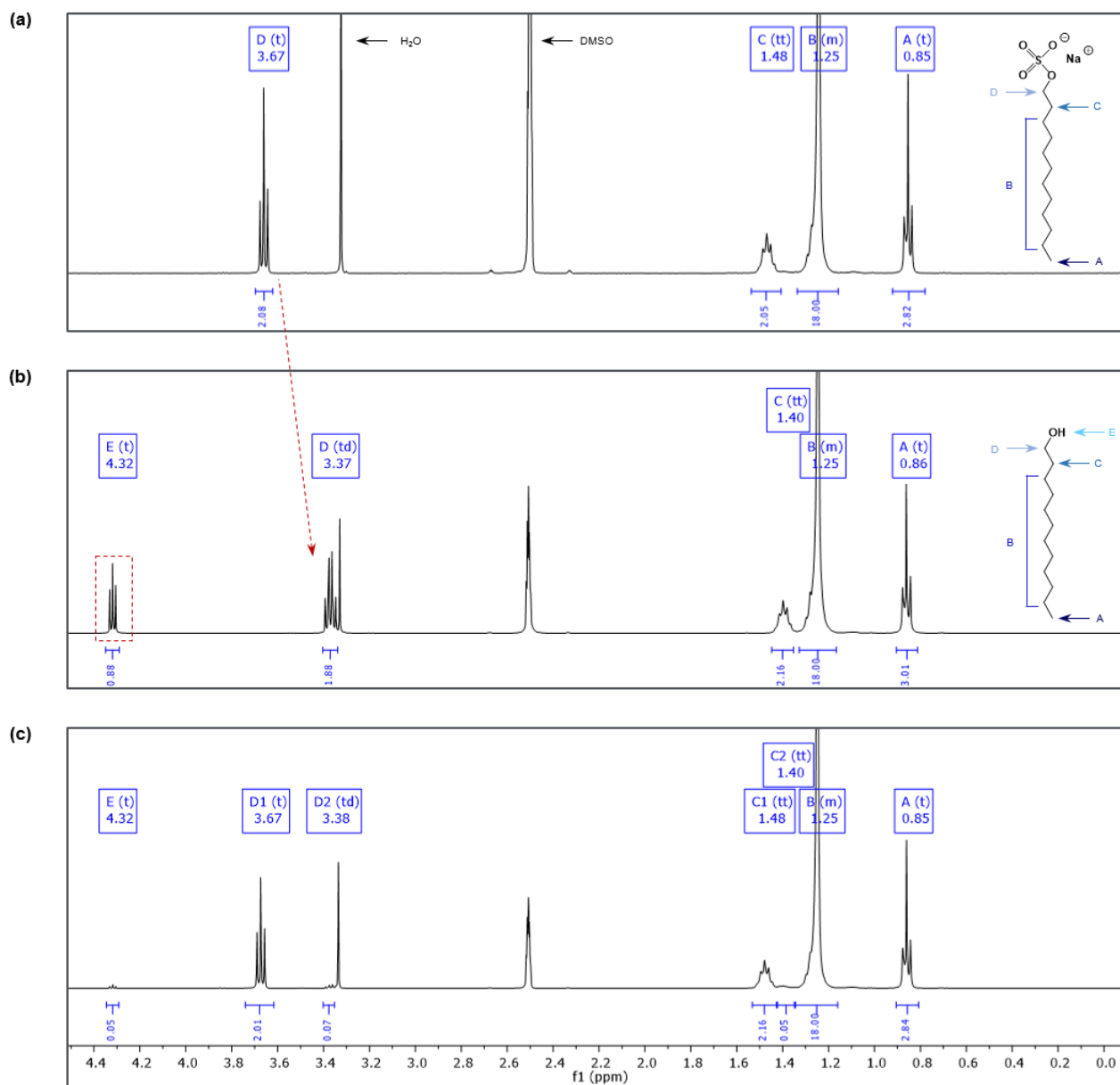


Figure S1. ^1H NMR spectra of (a) SDS, (b) 1-dodecanol and (c) SDS with a small quantity of 1-dodecanol.

(a) ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.67 (2H, t, $J = 6.6$ Hz, **D**), 1.48 (2H, tt, $J = 6.8$ Hz, **C**), 1.25 (18H, m, **B**), 0.85 (3H, t, **A**).

(b) ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 4.32 (1H, t, $J = 5.1$ Hz, **E**), 3.37 (2H, td, $J = 6.6$ Hz, **D**), 1.40 (2H, tt, $J = 6.7$ Hz, **C**), 1.25 (18H, m, **B**), 0.86 (3H, t, **A**).

Optical microscopy image analysis

Image analysis was conducted with ImageJ 1.48v (NIH) as demonstrated in Figure S2. Nucleation densities were estimated manually by computing the number of nuclei within an image, at each time step. Each experiment was typically repeated four times and two representative areas selected for analysis. Within each area (0.2 mm^2), counting was performed three times and averaged. Automated analysis was found to lack accuracy due to the concentrations employed.

For growth analysis, the area(s) covered by the crystals was compared with and without a threshold to ensure that only the crystalline region(s) were selected. The threshold parameters were adjusted across the images and any error with this accounted for. In Figure S2(a) for an image taken at -5°C , the image contrast was adjusted to facilitate with the determination of nuclei, whereas with Figure S2(b) for an image taken at -4°C , the image has been sharpened before applying a threshold. Overall crystalline area fractions were calculated from the ratio of threshold over total area, whereas individual crystal growth analysis was estimated based on the crystal size evolution over time; both the change in area and the change in length of the fastest growing face.

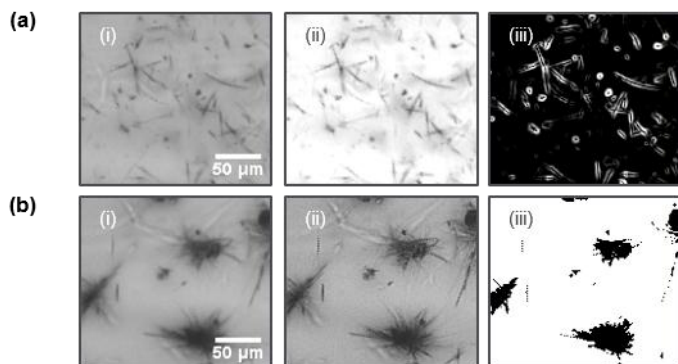


Figure S2. Two examples of the image analysis undertaken for nucleation and growth; the images were acquired with a 10x objective. (a)(i) The original image, (ii) contrast adjustment and (iii) crystal edge detection to determine the number of nuclei. (b)(i) The original image, (ii) sharpened and (iii) with a threshold applied to quantify the crystal area fraction.

Nucleation kinetics

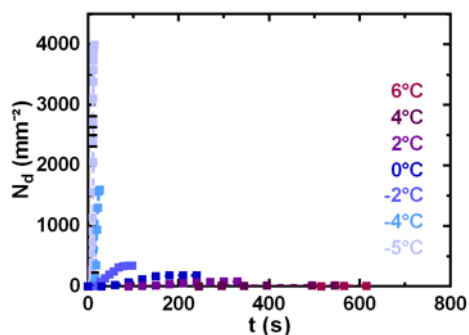


Figure S3. Nucleation density (N_d) as a function of time.

Effect of seeding time and temperature on growth rate estimations at 12 °C

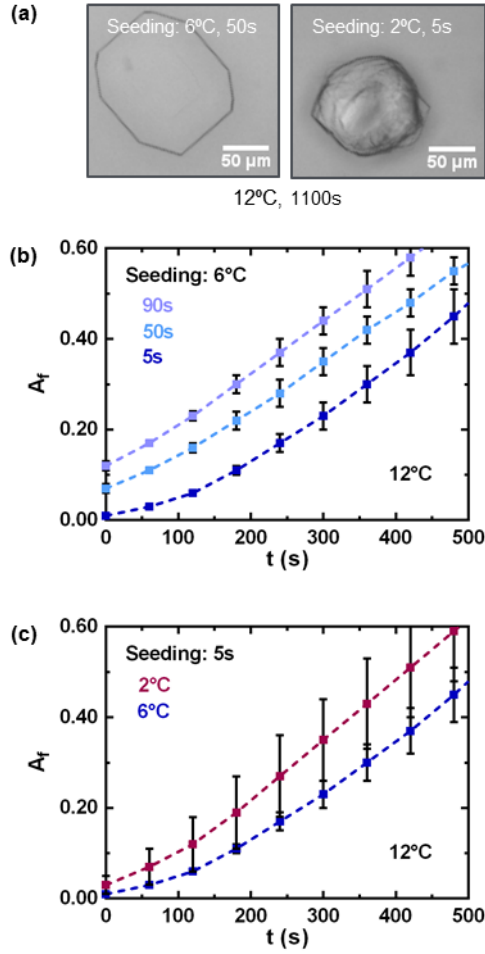


Figure S4 (a) Optical microscopy images of seed crystals generated at 6 and 2 °C, for the times indicated, and subsequently grown at 12 °C. (b) Evolution of the crystal area fraction (A_f) with time for seed crystals generated at 6 °C for 5, 50 and 90 s, and grown at 12 °C. (c) Evolution of the crystal area fraction (A_f) with time for seed crystals generated at 2 and 6 °C for 5s. The crystallization rates (equivalent to growth rates in this case, since only one crystal is present) are robust to variations in hold time and temperature within this range.

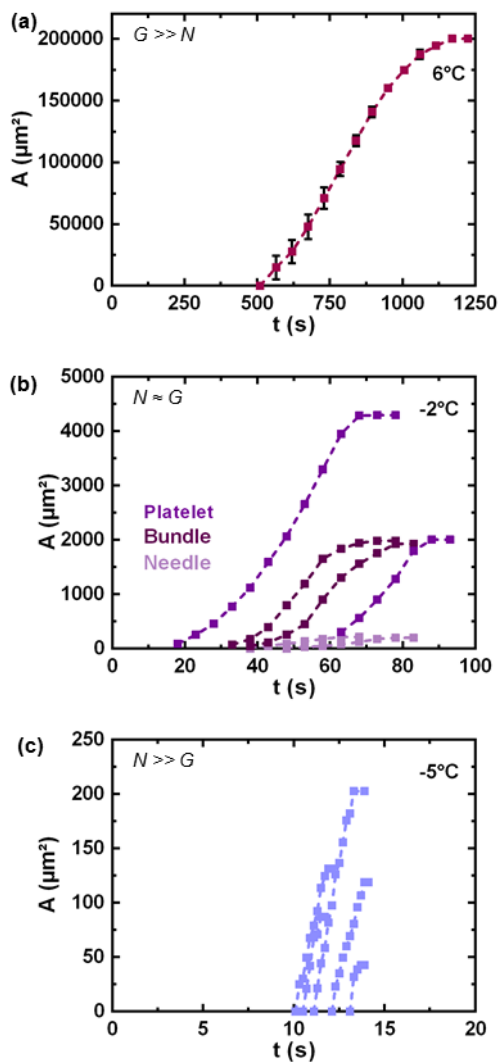


Figure S5. Evolution single crystal area over time for three representative temperatures; when: (a) growth is favored over nucleation ($G \gg N$); 6 °C. (b) $N \approx G$; 2 °C and (c) $N \gg G$; -2 °C. Each line corresponds to an individual crystal within the sample. At the highest temperature only one crystal was observed within the measured sample area. As the nucleation rates decrease with increasing temperature, the size polydispersity increases and we thus prefer to focus on the overall crystalline fraction, calculated instead as shown in Figure S2 above.

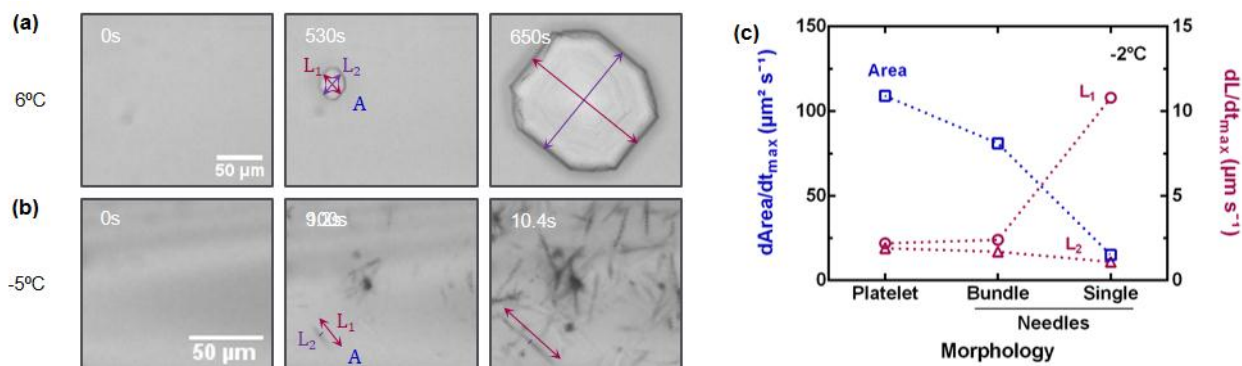


Figure S6. Representative examples of the single crystal analysis at various temperatures. (a) Development of a platelet at 6 °C and (b) isolated needles at -5 °C. (c) Single crystal analysis at -2 °C based on a series of optical images, including those shown in Figure 2(d) of the main paper. Change in single crystal area ($(dArea/dt)_{max}$ – square symbols), the fastest growing face ($(dL_1/dt)_{max}$ – circular symbols) and the slowest growing face ($(dL_2/dt)_{max}$ – triangular symbols) for -2 °C solutions.

For crystals at the same temperature (shown in Figure S4(c) at -2°C), the change in area of an individual crystal ($(dArea/dt)_{max}$) was found to decrease in the order: platelets > needles (bundles) > needles (single). Examining individual faces, however, the growth of the fastest face ($(dL_1/dt)_{max}$) follows the order: platelets < needles (bundles) < needles (single), while the slowest growing face ($(dL_2/dt)_{max}$) remains largely unchanged. Given the predominantly uniaxially growth of needles compared to platelets, their $(dArea/dt)_{max}$ is thus relatively lower, even though the main axis grows faster.

On average, higher *individual* crystal growth rates are found with increasing temperature, as the proportion of platelets increases. However, as seen in Figure 5(b) of the main paper, *overall* crystallization kinetics decrease with increasing temperature as the nucleation rate decreases.

Effect of SDS concentration on crystallization kinetics

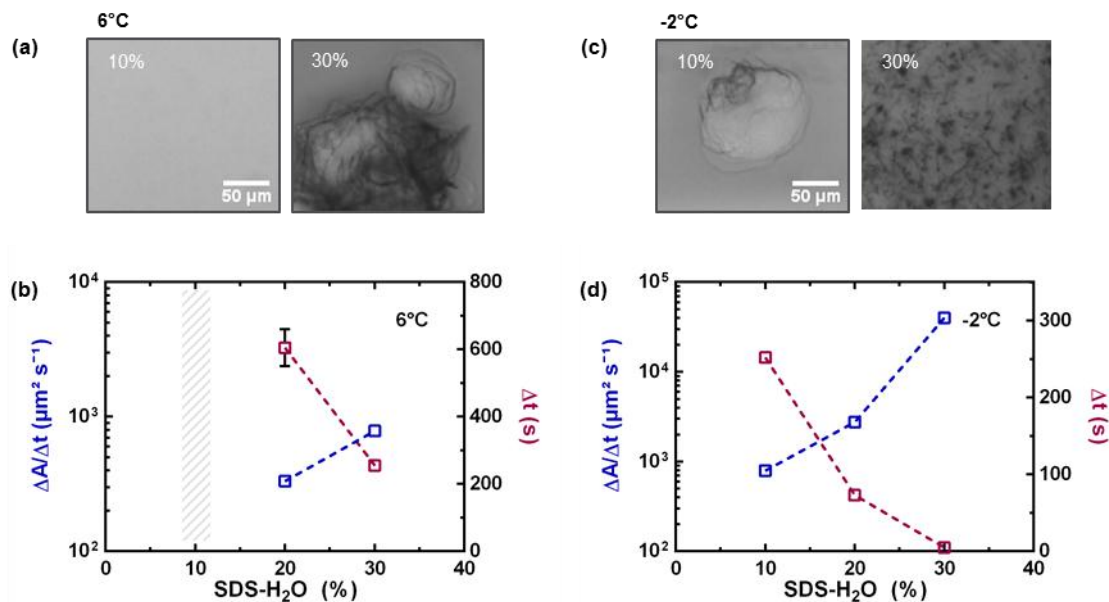


Figure S7. Effect of SDS concentration on the crystallization kinetics for three SDS-H₂O micellar concentrations: 10, 20 and 30%. (a) Optical microscopy images of the predominant crystal habit of 10 and 30% SDS-H₂O solutions held isothermally at 6 °C. (b) Overall rate of crystallization ($\Delta A/\Delta t$ – dark blue, left axis) and duration of crystallization (Δt – dark red, right axis) as a function of concentration. (c) Optical microscopy images for 10 and 30% solutions at -2 °C. (d) Overall rate of and duration of crystallization.

Differential scanning calorimetry (DSC)

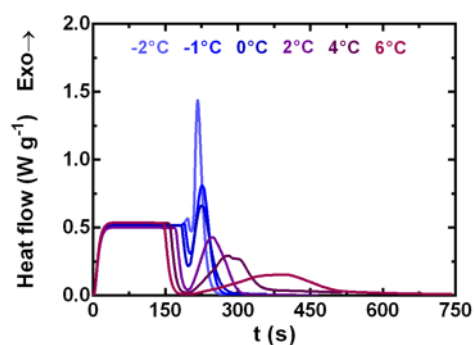


Figure S8. Complete DSC traces of heat flow as a function of time; the sample was cooled at 10 °C min⁻¹ and held isothermally at a set temperature.

Morphology and nucleation type

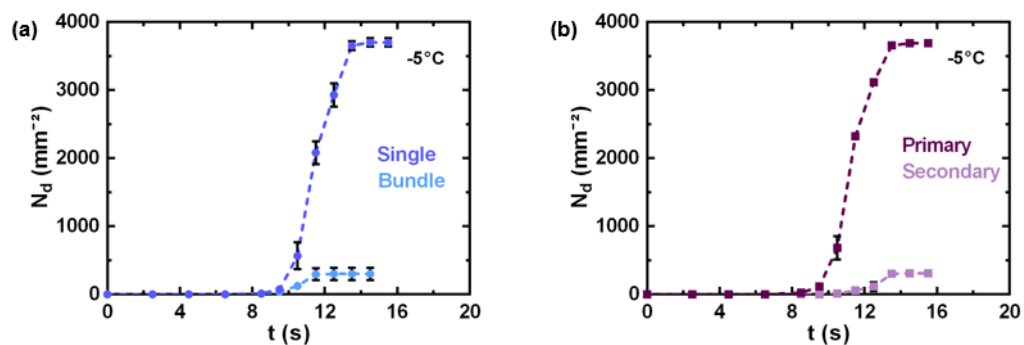


Figure S9 Example of the analysis undertaken to investigate the morphologies and nucleation assignments of 20% SDS- H_2O solutions held isothermally after a cooling quench. The figures are for solutions at -5°C and all parameters are reported against time. (a) Morphologies were broadly assigned as platelets or needles (further classified as bundles or single needles). (b) Nucleation type was classified as primary if growth commenced without the influence of other crystals, or secondary if development ensued from another crystal.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

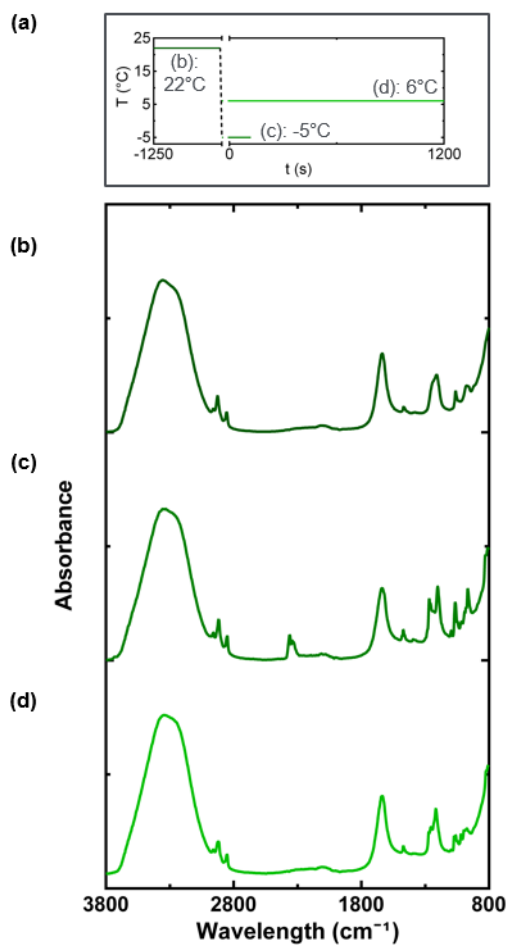


Figure S10. Complete ATR-FTIR spectra to characterize the hydration states of the morphologies observed via optical microscopy. (a) Temperature profiles for spectra (b) to (d). (b) 20% SDS- H_2O micellar solution, conducted as a reference point. (c) Hydrated crystals from rapid cooling to -5 °C. (d) Hydrated crystals from rapid cooling to 6 °C.

Other concentrations

The temperature range investigated extends below the freezing point of H₂O, therefore the possible crystallization of H₂O was considered. Samples of H₂O in capillary tubes were prepared according to the procedure outlined in the main text. Whilst all of the crystals observed are hydrates, these are rich in SDS, containing >94% SDS by weight.¹ As the investigation solutions have an overall SDS content between 10 and 30%, it is assumed that as a result of crystallization, the liquor is ‘pure’ H₂O. Two additional concentrations near the critical micelle concentration (cmc) of SDS (0.23% at 25 °C)² and ten-fold higher, 0.2 and 2% SDS-H₂O respectively, were studied to understand both the impact on crystallization when a large excess of H₂O is present and to determine whether H₂O crystallizes in these systems, over the relevant time window. The optical microscopy images for the three additional concentrations are provided in Figure S7.

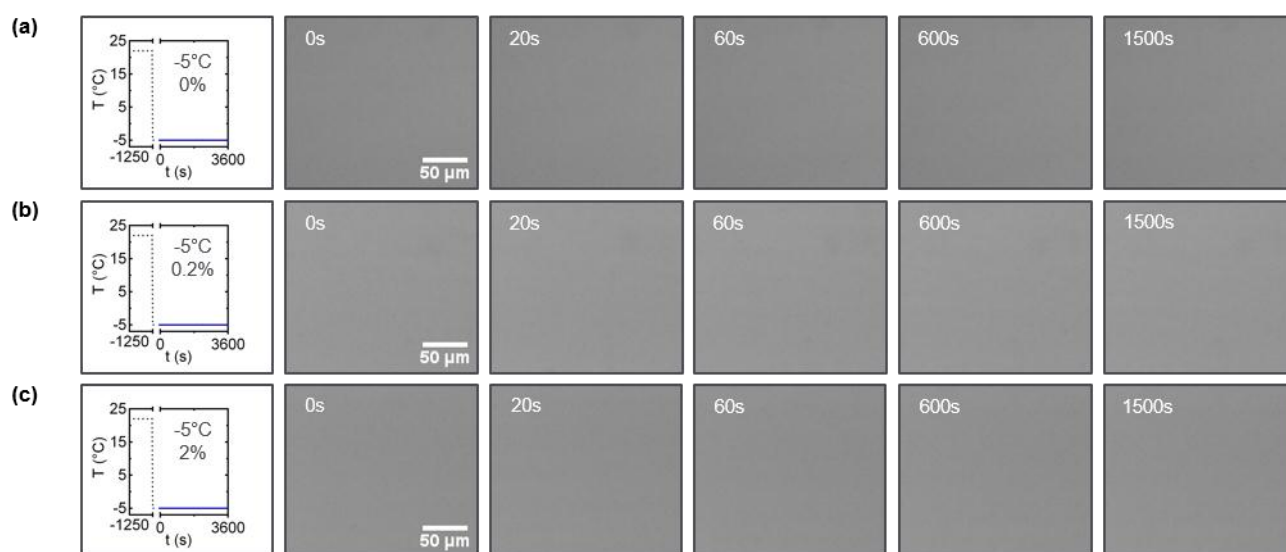


Figure S11. Optical microscopy images of H₂O and SDS-H₂O solutions over 3600 s at -5 °C; the implemented thermal profile is shown on the left panels. (a) H₂O. (b) 0.2% SDS-H₂O. (c) 2% SDS-H₂O. The solutions were equilibrated for 20 min, rapidly cooled at 50 °C min⁻¹ to -5 °C and held isothermally for the stated time interval.

For 20% SDS-H₂O at -5 °C, t_{ind} is 7.8 ± 1.0 s and Δt is 6.7 ± 0.6 s. By contrast, H₂O crystallization was not observed in the 0 to 2% SDS-H₂O solutions over an isothermal hold. It was thus concluded that, for the timescales in question, H₂O crystallization is not observed. Additionally, at these very low concentrations of SDS, 0.2 and 2%, SDS crystallization is also not noted over these timescales.

References

- (1) Kékicheff, P.; Grabielle-Madelmont, C.; Ollivon, M. *J. Colloid Interface Sci.*, **1989**, *131*, 112–132.
- (2) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; NSRDS-NBS 36; U. S. Department of Commerce: Washington, DC, 1971.