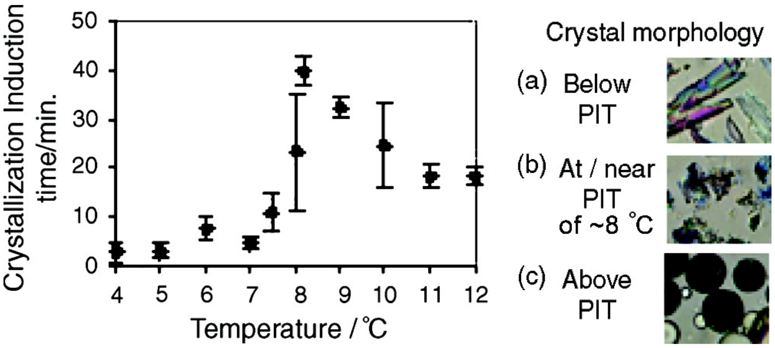
Communication

The Use of Phase-Inverting Emulsions to Show the Phenomenon of Interfacial Crystallization on Both Heating and Cooling

Catherine E. Nicholson, Sharon J. Cooper, Claire Marcellin, and Matthew J. Jamieson

J. Am. Chem. Soc., **2005**, 127 (34), 11894-11895• DOI: 10.1021/ja0526012 • Publication Date (Web): 06 August 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

The Use of Phase-Inverting Emulsions to Show the Phenomenon of Interfacial Crystallization on Both Heating and Cooling

Catherine E. Nicholson, Sharon J. Cooper,* Claire Marcellin, and Matthew J. Jamieson
Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, United Kingdom

Received April 21, 2005; E-mail: sharon.cooper@durham.ac.uk

The ability of water in oil (w/o) emulsions stabilized with nonionic surfactants to undergo a phase inversion to oil in water (o/w) emulsions on cooling is well-known. We exploit this effect and, by using surfactants that promote nucleation, achieve highly anomalous crystallization behavior. In particular, crystallization can be inhibited at the phase-inversion temperature (PIT), allowing systems held at, or near, this temperature to undergo crystallization either on heating or cooling. This new phenomenon is demonstrated for 27.4 wt % aqueous glycine solutions emulsified in 90 wt % decane using Span 20 Tween 20 blends (see Figure 1). On cooling from ambient at 1 °C min^{-1}, the original w/o emulsion inverts at $\sim$7 °C for a 5 wt % total surfactant concentration, comprised of 5% Tween 20 and 95% Span 20. The micrometer−sized aqueous droplets disappear at the PIT, and a more mottled texture develops (see Figure 1b) as the ultralow droplet interfacial tension characteristic of the PIT results in a large increase in the oil−water interfacial area through the continuous formation of numerous small (tens of nanometers), transient self-assembled structures. After holding at 7 °C for 1 min, the system has fully inverted to an o/w emulsion. On further cooling to 5 °C at 1 °C min^{-1}, glycine crystallization begins in the continuous aqueous phase to give elongated β-phase crystals, with the polymorphic form being determined by X-ray diffraction. On heating this colloidal slurry of crystals and w/o emulsion droplets to 10 °C at 1 °C min^{-1} and leaving for 1 min, the system reinverts to a w/o emulsion, and on further heating, crystallization starts again on holding at 24 °C for 5 min, this time producing spherical aggregates of β-phase glycine crystals confined within the regenerated aqueous droplets. Analogous results are obtained for Tween 20 Span 20 blends containing 1 and 10% Tween 20, for decane fractions of $\geq$0.6.

In both the o/w and w/o systems, the nucleation is induced at the droplet interface by the surfactants, as crystals can sometimes be seen growing rapidly from this interface, and the occurrence of the β-phase, rather than the expected α-phase, is consistent with previous studies on glycine crystallization in w/o emulsions stabilized with nonionic surfactants.[1] Indeed, even though the Span 20 is a weaker β-phase nucleator than Tween 20, it is still sufficiently adept to hinder the crystallization of the γ- and α-polymorphs by doping Span 20 emulsions with the cosurfactants AOT and α-aminohexadecanoic acid that promote these phases, respectively. However, significant amounts of α-phase crystals are obtained from Span 20 emulsions containing 13.9 wt % aqueous glycine solutions by adding 5% acetic acid. Crucially, though, crystallization inhibition is still observed at the new PIT of $\sim$0 °C.

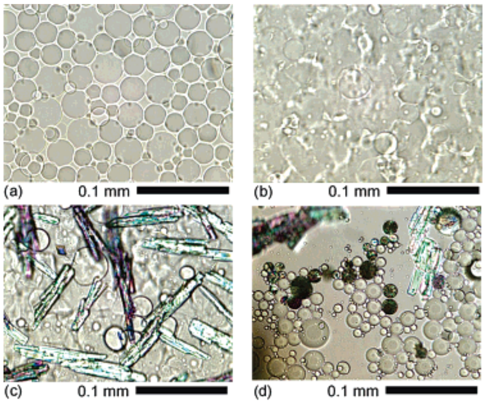


Figure 1. Optical micrographs through crossed polarizers of 27.4 wt % glycine solutions in Tween 20:Span 20 (5:95) 90 wt % decane emulsions: (a) w/o emulsion at $T = 24$ °C; (b) on cooling at 1 °C/min, the system starts to invert at $T = 7$ °C. (c) On further cooling to 5 °C, glycine crystals grow in the o/w emulsion, and (d) on heating at 1 °C/min, the system reinverts, and glycine begins to crystallizes in the w/o droplets on holding at 24 °C.

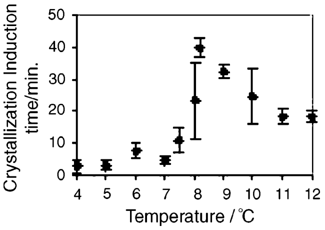


Figure 2. Graph of crystallization induction time, τ, versus temperature for 27.4 wt % glycine solutions in Tween 20:Span 20 (1:99) 90 wt % decane emulsions, showing the maximum in induction time at/near the PIT. Indeed, even at 24 °C, τ is below the value at the PIT, despite the 16 °C temperature increase. For emulsions with an increased proportion (5 or 10%) of the Tween 20 nucleator, the induction times are reduced; however, a maximum induction time is still always observed at/near the PIT.

The inhibitory effect on interfacial crystallization at/near the PIT can readily be shown by holding the systems at different temperatures and comparing the induction times, τ, before crystallization is observed. This is shown in Figure 2 for the Tween 20:Span 20 (1:99) system. At/near the PIT, $\tau \sim 40$ min, while at temperatures flanking this τ falls steeply, and this is the origin of the large error bars on the associated data points since any small temperature fluctuation produces a large variation in τ. τ is the sum of two main time periods: (i) the nucleation time and (ii) the time required for crystal growth of the nuclei to detectable dimensions. For a rate-limiting nucleation step, $\tau = N/J$, where J is the nucleation rate and N is the number of particles per unit volume required for detection of the solid phase, which can be taken as a constant for a given detection technique. The assumption of a rate-limiting nucleation step is justified in our systems since the observable crystal growth proceeds rapidly after the induction period in both the o/w and w/o emulsions; for instance, crystallization within an aqueous droplet is always completed within 2 s.[2] Hence, the maximum in τ obtained at/near the PIT clearly demonstrates the new phenomenon of minimal interfacial nucleation in the vicinity of the PIT.

These findings are unprecedented. An extremely rapid rise in the nucleation rate, J, and hence rapid reduction in τ, is expected on cooling glycine solutions, owing to the associated increase in supersaturation, $\Delta\mu$, the driving force for crystallization.[3] This is

10.1021/ja0526012 CCC: $30.25

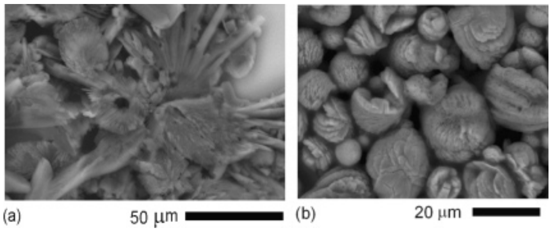


Figure 3. (a) Scanning electron micrographs showing (a) the unusual morphology of glycine crystals grown at the phase inversion for a Tween 20:Span 20 (1:99) system, and (b) the spherical aggregate morphology grown at higher temperatures from the w/o emulsions.

shown by classical nucleation theory,[4] which predicts J to increase by a factor of $\sim 10^{20}$ between 24 and 8 °C,[5] instead of the observed decrease, since

$$J \propto \exp[-f(\theta)\gamma_{\mathrm{gly-aq}}^{3}/\Delta\mu^{2}]$$

where θ is the contact angle between the critical nucleus and nucleating substrate, *normally* considered a constant for a particular system, $f(\theta) = (2 - 3\cos^2\theta + \cos^3\theta)/4$, and $\gamma_{\mathrm{gly-aq}}$ is the interfacial tension between the glycine critical nucleus and the aqueous medium.

The origin of this highly anomalous behavior is the low droplet interfacial tension, γ_{ow}, that occurs at the PIT, which produces a substantially greater contact angle, θ, between the interface and glycine nucleus, as shown by Young's equation:

$$\cos\theta = \gamma_{\mathrm{ow}} - \gamma_{\mathrm{gly-surf}}/\gamma_{\mathrm{gly-aq}}$$

This increases the activation energy for nucleation, $\Delta G^{*}_{\mathrm{het}}$, as

$$\Delta G^{*}_{\mathrm{het}} = 16\pi\gamma_{\mathrm{gly-aq}}^{3}V_{\mathrm{m}}^{\;2}f(\theta)/[3(kT\Delta\mu)^{2}]$$

where V_{m} is the glycine crystal molecular volume. Hence, the nucleation rate, J, is dramatically decreased according to

$$J \propto \exp(-\Delta G^{*}_{\mathrm{het}}/kT)$$

By using classical nucleation theory and inputting values of $\gamma_{\mathrm{gly-aq}} = 35$ mN m^{-1} [6] and $\gamma_{\mathrm{ow}} = 22$ mN m^{-1} at 24 °C,[7] we can estimate[8] the contact angle to increase from ~61 to 97°; this explains the highly anomalous crystallization kinetics observed.

Furthermore, for very low γ_{ow} values, the droplets can deform/disappear with very little energy cost, which may result in insufficient time for a stable nucleus to form before the transitory interface is disrupted. This kinetic effect will only function in the immediate vicinity of the phase inversion, where γ_{ow} is sufficiently low, if the interface relaxation time is less than the time scale required for nucleation. In contrast, the raising of the contact angle, θ, occurs continuously on cooling to the PIT and will produce nucleation inhibition, provided this effect outweighs that of the concomitant supersaturation increase.[9] Immediately below the PIT, γ_{ow} increases, and so there is a rapid reduction in the induction time, as shown in Figure 2. Consequently, the minimal interfacial nucleation temperature would always be expected to be at, or just above, the PIT.

The crystals that eventually develop at/close to the PIT have an unusual morphology, consisting of spherical needle aggregates with some elongated crystal offshoots (see Figure 3). This aspect is considered in more detail in the Supporting Information.

The strategy of using w/o emulsions stabilized with nonionic surfactants to induce interfacial nucleation provides a relatively simple, tunable method of controlling nucleation rates over a wide temperature range, particularly since the PIT and maximum γ_{ow} values are readily varied by using different oil and surfactant blends. Moreover, this strategy may provide a generic method of controlling w/o emulsion nucleation rates, provided the inhibition mechanism is operative on doping the systems with cosurfactants that direct the nucleation to the required polymorph and morphology.[10] Further studies investigating this aspect are in progress for a range of different crystallizing materials. In addition, the intriguing recent finding[11] that water−oil interfacial tensions can decrease on cooling to ~0 mN m^{-1} in the presence of ionic surfactants, provided the oil surface freezes, suggests that tunable nucleation rates may also be possible using these systems.

In conclusion, we demonstrate the phenomenon of minimal interfacial nucleation in phase-inverting systems for the first time and show that the minimal interfacial nucleation temperature is expected to be at, or just above, the PIT. The morphology of crystals grown at/near the PIT is also unusual. This methodology provides considerable control over nucleation rates and may offer a paradigm shift in controlled crystallization strategies through the use of tunable contact-angle nucleators.

Acknowledgment. The authors thank Dr. M. R. Wilson for useful discussions, and EPSRC for funding for M.J.J. and C.E.N.

Supporting Information Available: Details of the emulsion preparation, optical microscopy and X-ray diffraction studies, and further discussion on the different crystal polymorphs and morphologies. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Allen, K.; Davey, R. J.; Ferrari, E.; Towler, C.; Jones, M. O.; Pritchard, R. G. *Cryst. Growth Des.* **2002**, *2*, 523−527.
(2) The numerous, small (tens of nanometers), transient self-assembled structures present at the PIT could adhere onto the growing nucleus and impede crystal growth. Individual surfactant molecules could also adsorb and cause some growth inhibition. However, we do not expect these to be dominant processes in this system, because the high glycine concentration of 27.4 wt % aids rapid crystal growth, droplet adhesion is not observed on any of the crystals, and the final morphologies reflect the normal aqueous morphologies of β-glycine, albeit that the PIT crystal morphology has mixed o/w and w/o crystal formation character. Furthermore, if growth inhibition was prevalent at the PIT, then the relative nucleation rate would increase, and we would expect a greater density of crystals to be produced, which is also not observed.
(3) $\Delta\mu = kT\ln(c/c_{\mathrm{sat}})$, where c and c_{sat} are the actual and saturation solute concentrations, respectively.
(4) For a summary of classical nucleation theory, see: Sigsbee, R. A.; Pound, G. M. *Adv. Colloid Interface Sci.* **1967**, *1*, 335−390.
(5) A θ value of 61°, consistent with the observed nucleation rate at 24 °C, is used for this calculation, together with values of $\gamma_{\mathrm{gly-aq}} = 35$ mN m^{-1} [6] and $\gamma_{\mathrm{ow}} = 22$ mN m^{-1}. However, irrespective of the precise value used, a dramatic increase in nucleation rate is always predicted.
(6) The $\gamma_{\mathrm{gly-aq}}$ value has not been determined. However, a value of 40 mN m^{-1} has been given for glycine in aqueous ethanol solutions. See: Walton, A. G. *Formation and Properties of Precipitates*; Wiley and Sons: New York, 1967. The greater solubility of glycine in water compared to that in ethanol is expected to provide an interfacial tension value lower than this.
(7) The interfacial tension values for this Tween 20/Span 20 (1:99) system have not been determined. However a γ value of 22.2 mN m^{-1} at 22 °C has been given for Span 20 at the decane−water interface. See: Peltonen, L.; Hirvonen, J.; Yliruusi, J. *J. Colloid Interface Sci.* **2001**, *240*, 272−276.
(8) This calculation results in a rather low value of $\gamma_{\mathrm{gly-surf}} \sim 5$ mN m^{-1}, which may reflect the inability of classical heterogeneous nucleation theory to model interfacial crystallization in emulsions.
(9) This effect leads to the occurrence of a smaller maxima in the induction time at ~15 °C for our 27.4 wt % aqueous glycine solutions.
(10) The miscibility of the nucleation-promoting cosurfactant with Span 20 is likely to be a key parameter in the success of this strategy. For examples of interfacial crystallization induced in microemulsions and emulsions by doping with surface-active additives, see: (a) Jamieson, M. J.; Nicholson, C. E.; Cooper, S. J. *Cryst. Growth Des.* **2005**, *5*, 451−459. (b) Davey, R. J.; Hilton, A. M.; Garside, J.; de la Fuente, M.; Edmondson, M.; Rainford, P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1927−1933. (c) Kaneko, N.; Horie, T.; Ueno, S.; Yano, J.; Katsuragi, T.; Sato, K. *J. Cryst. Growth* **1999**, *197*, 263−270.
(11) Sloutskin, E.; Bain, C. D.; Ocko, B. M.; Deutsch, M. *Faraday Dicuss.* **2005**, *129*, 339−352.

JA0526012