

Interdroplet Heterogeneous Nucleation of Supercooled Liquid Droplets by Solid Droplets in Oil-in-Water Emulsions

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The crystallization of oil droplets in *n*-hexadecane oil-in-water emulsions was monitored by pulsed nuclear magnetic resonance (NMR). The emulsions initially contained an equal mixture of solid droplets and supercooled liquid droplets at either 6 or 8°C. The degree of crystallization in the droplets was determined by measuring the NMR signal 30 μ s after a 90° radio frequency pulse was applied to the sample. The signal from the solid droplets decayed rapidly after the radio frequency pulse, allowing the measured signal to be related to the fraction of liquid droplets. No crystallization was observed in a sample that contained only supercooled liquid droplets, but crystallization was observed when solid droplets of the same material were present. This indicated that crystallization was induced in the liquid droplets by the solid droplets and was most likely caused by interactions between solid and liquid droplets—that is, by interdroplet heterogeneous nucleation. The rate of induced crystallization decreased as the viscosity of the continuous phase was increased and the size of the droplets was increased, but was independent of droplet concentration (20–40%).

KEY WORDS: Crystallization, emulsion, interdroplet nucleation, nuclear magnetic resonance.

Many biological and nonbiological materials consist either partly or wholly as emulsions, or have been in an emulsified form sometime during their production, e.g., pharmaceuticals, foods, cosmetics, fertilizers (1). The physical state of emulsion droplets plays an important role in determining their overall functional properties, such as their stability, rheology and appearance (2–4). Of particular interest is the ability of solid droplets to stabilize whipped foods. Consequently, it is important to investigate the factors that influence the physical state of droplets in emulsions.

The crystallization kinetics of oil dispersed as emulsion droplets are different from those of bulk oil. The temperature at which crystallization begins is often lowered significantly when an oil is homogenized, because the possibility of finding a heterogeneous impurity to catalyze nucleation in a particular droplet is vastly reduced when the oil is divided into a large number of isolated droplets (5). Nucleation in emulsion droplets may therefore be heterogeneous (catalyzed) or homogeneous (uncatalyzed). At least three types of heterogeneous nucleation have been identified in emulsions: (i) bulk nucleation, which is initiated by impurities distributed randomly throughout the volume of the oil (5); (ii) surface nucleation, which is initiated by the oil–water droplet interface (6); and (iii) interdroplet nucleation, which is initiated in a liquid droplet by contact with a solid droplet (7,8).

The rate of interdroplet nucleation depends on the droplet composition and on the chemical structure of the emulsifier used to stabilize the droplets (7,9). It has been proposed that nucleation occurs when droplets come together close enough

for crystals protruding from solid droplets to penetrate into liquid droplets (7). This mechanism could depend on such factors as the frequency of collisions between droplets, the nature of the oil–water interface and the morphology of the crystals. For this reason, we investigated the dependence of the interdroplet nucleation rate on a number of factors that affect the droplet collision frequency, such as the continuous phase viscosity, the droplet concentration and the droplet size.

In previous studies the crystallization of emulsion droplets has been monitored by measuring changes in the ultrasonic velocity of the samples with time (7,9). In this study, a pulsed-nuclear magnetic resonance (NMR) technique was used to monitor crystallization kinetics. This method utilizes the fact that the signal from a sample following a 90° radio frequency pulse decays much more rapidly for solids than for liquids, and, therefore, the different phases can be distinguished. Such a method has been used extensively to monitor crystallization processes in homogeneous liquids (10), but only recently to measure crystallization kinetics within emulsified systems (11–13). Here we use NMR techniques to probe the rate of crystallization induced by interdroplet nucleation in *n*-hexadecane oil-in-water emulsions stabilized by nonionic surfactants (Triton X-100 and Tween 20).

EXPERIMENTAL PROCEDURES

Materials. *n*-Hexadecane, Triton X-100, Tween 20 and sucrose were obtained from the Sigma Chemical Company (St. Louis, MO). Distilled water was used in the preparation of the aqueous phases of the emulsions.

Emulsion preparation. A coarse emulsion premix was prepared by homogenizing weighed amounts of oil (40 wt%) and aqueous phase (60 wt%) together in a high-speed blender (Ultraturrax T25; Janke and Kunkell, Cincinnati, OH). This emulsion was then further homogenized with a high-pressure laboratory valve homogenizer (Rannie Mini-lab 8-30H; Rannie, Copenhagen, Denmark). Samples with different mean droplet sizes were produced by varying the number of times the emulsion was passed through the homogenizer. The aqueous phase of the emulsion consisted of 3 wt% surfactant (either Tween 20 or Triton X-100) in distilled water. The droplet concentration was varied by diluting the 40 wt% emulsion with distilled water. The viscosity of the aqueous phase was varied by adding different amounts of sucrose to the emulsions.

Particle size measurements. Droplet size distributions were determined by means of a static light-scattering technique (Malvern MasterSizer S2.01; Malvern, Worcs, United Kingdom). This technique measures the angular dependence of laser light scattered by the droplets in an emulsion. A relative refractive index of 1.08 and an absorptive index of 0.01 were used by the instrument to calculate the droplet size distributions (i.e., a presentation code of 0405). The mean droplet diameter d_{32} of the emulsions are reported as the volume–surface diameter:

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$d_{32} = \sum n_i d_i^3 / n_i d_i^2$, where n_i is the number of droplets with diameter d_i .

NMR measurements. Emulsions (25 g) were contained in glass tubes (180 mm high, 40 mm i.d.), which were stored in a temperature-controlled water bath at 6.0°C ($\pm 0.1^\circ\text{C}$) for the duration of the experiments. At this temperature, the *n*-hexadecane droplets could either be solid or liquid depending on their thermal history (7). Droplets in emulsions, cooled from room temperature to 6°C, remained liquid because of supercooling, whereas those in emulsions that were cooled from room temperature to 0.5°C for 2 h and then heated to 6°C were completely solid (7). For each emulsion, NMR measurements were made on a sample that contained completely liquid droplets, one that contained completely solid droplets and one which contained a 50:50 wt% mixture of the two.

A Bruker Minispec PC 110 spectrometer (Bruker Spectrospin, Ontario, Canada) was used to monitor the extent of crystallization in the emulsion droplets. A tube containing an emulsion was placed in the sample chamber of the spectrometer where it was subjected to a permanent magnetic field (2.3 Tesla). A 90° radio frequency (r.f.) pulse (10 MHz) was then applied to the sample in a direction perpendicular to the permanent field. Immediately after the pulse, the amplitude of the NMR signal from the sample is proportional to the total number of protons in the sample, i.e., from both solid and liquid portions. The amplitude of the signal decreases with time because of spin-spin relaxation by the protons. The relaxation time for solids is much shorter than that for liquids, and so it is possible to distinguish between solid and liquid components by measuring the free induction decay of the signal (10). Phase-sensitive detection and a wide-bandwidth pulse were used in the experiments. The repetition time between pulses was about three seconds, which was sufficiently long to allow nuclei in the samples to return to equilibrium before the next pulse was applied.

The NMR receiver cannot detect a signal from a sample immediately after the applied radio frequency pulse, and so the signal from the solid component will decay appreciably before a measurement can be made. For this reason we only used the signal from the liquid portion of the sample, which can be determined by measuring the amplitude at a time sufficiently long after the r.f. pulse, for the signal from the solid component to have completely decayed. If we assume that the solid droplets do not contribute to the total signal, any difference between the signals obtained from an emulsion containing liquid oil droplets and that containing only solid droplets must arise solely from the liquid oil. We can thus determine the fraction f of crystalline droplets in an emulsion from the equation:

$$\phi = 1 - \frac{S - S_S}{S_L - S_S} = \frac{S - S_L}{S_S - S_L} \quad [1]$$

where S refers to the signal per gram of emulsion sample (i.e., partially crystallized), S_L refers to an emulsion with only liquid oil droplets, and S_S refers to an emulsion with completely solid droplets.

In our experiments, signals were measured at a time 30 μs after the pulse application. For the emulsions containing completely solid droplets, the NMR signal measured

after 30 μs was identical (within experimental error) to that obtained after 70 μs , indicating that the signal from the solid portion of the sample had completely decayed by the measurement time.

Interdroplet nucleation rate and collision frequency. In a previous paper, it was shown that the decrease in the fraction of liquid oil ($1 - \phi$) remaining in the droplets with time can be described mathematically by assuming a binary reaction. This implies that crystallization results from an interaction between one solid and one liquid droplet (8), corresponding to the rate equation:

$$\frac{d(1 - \phi)}{dt} = -K\phi(1 - \phi). \quad [2]$$

Integration yields:

$$\ln\left(\frac{1 - \phi}{\phi}\right) = \ln\left(\frac{1 - \phi_0}{\phi_0}\right) - Kt \quad [3]$$

Here, K is a second-order rate constant, and ϕ_0 is the volume fraction of solidified oil at zero time. The rate constant K can then be calculated from experimental measurements by means of plots of $\ln[(1 - \phi)/\phi]$ vs. time.

Assuming that the induced crystallization arises from interactions between solid and liquid drops, we consider whether the rate of this process is dominated by flocculation kinetics within the bulk phase or by some slower process occurring at the droplet interface. In the former case, the overall rate would depend on the frequency of collisions per unit volume of emulsion (N), the number of droplets per unit volume (n_0) and the fraction of contacts (x) between a solid and a liquid droplet leading to interdroplet nucleation. Hence, if flocculation processes are rate-limiting, the second-order rate constant, K , is given as $K = xN/n_0$.

According to Smoluchowski's theory for fast flocculation kinetics, the frequency of collisions per unit volume, N , is given by:

$$N = 4nDdn_0^2 \quad [4]$$

Here, D is the Brownian diffusion coefficient, n_0 is the number of droplets per unit volume and d is the droplet diameter. For identical spherical particles, $D = kT/3\pi\mu d$, where μ is the viscosity of the continuous phase, k is Boltzmann's constant and T is the absolute temperature. Thus, the flocculation rate becomes:

$$N = \frac{4kTn_0^2}{3\mu} \quad [5]$$

This equation is only strictly applicable to dilute emulsions, but it does give a useful insight into the factors that should affect the collision frequency. Decreasing the number of particles per unit volume (e.g., by decreasing the droplet concentration or increasing droplet size) or increasing the viscosity of the aqueous phase should decrease the number of collisions per unit time. If interdroplet nucleation rates are dominated by flocculation kinetics, these changes would also decrease droplet crystallization rates. We therefore decided to examine the effects of droplet concentration and size and aqueous phase viscosity on the rate of induced crystallization.

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RESULTS AND DISCUSSION

Figure 1 shows the variation in NMR signal with time for three 40 wt% *n*-hexadecane oil-in-water emulsions stabilized by Triton X-100. The signal from the emulsion that contained completely liquid droplets remained constant for the duration of the experiment, which suggests that no crystallization occurred in this sample. Some un-solidified oil was present in the emulsion containing all solid droplets, causing a slight decrease in the signal in the initial stages of the experiment; it took approximately 200 h for complete solidification to occur, after which time the signal remained constant within experimental error (Fig. 1).

Initially, the signal from the emulsion that contained an equal mixture of solid and liquid droplets was midway between those from emulsions containing either only solid or only liquid droplets. The signal decreased with time, which indicated that some of the liquid droplets crystallized. As crystallization was not observed in the sample that contained only liquid droplets, it must be concluded that crystallization was induced in supercooled liquid droplets when solid droplets were present, most likely due to interdroplet heterogeneous nucleation. These results are consistent with effects observed by ultrasound analysis to probe crystallization kinetics within emulsions (7,8).

The fraction of crystalline droplets was determined from the NMR measurements by using Equation 1, and the rate constant K for induced crystallization was then determined from a plot of $\ln[(1 - \phi)/\phi]$ vs. time (Fig. 2). The figure demonstrates the linear dependence of $\ln[(1 - \phi)/\phi]$ on time ($r = 0.995$), therefore supporting earlier results (7,8) that indicate that the crystallization process between the droplets can be described by a binary interaction, as in Equation 2.

Effect of droplet concentration. The variation of solid content with time was determined for a series of emulsions that contained different mass fractions of oil (Fig. 3). The calculated rate constants were not significantly different and varied between approximately 0.0014 h^{-1}

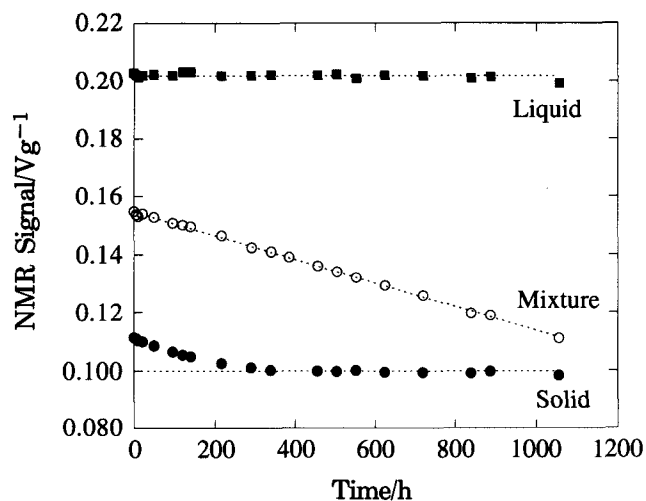


FIG. 1. Variation of nuclear magnetic resonance signal with time for 40 wt% *n*-hexadecane oil-in-water emulsions stabilized by Triton X-100 at 6°C. The three emulsions contained either all solid droplets, all liquid droplets or a 50:50 mixture of solid and liquid droplets.

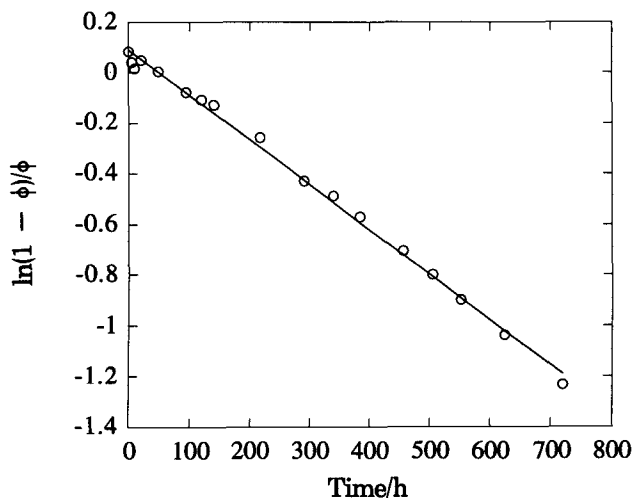


FIG. 2. Time dependence of the fraction of solidified droplets ϕ with time at 6°C for a 40 wt% *n*-hexadecane oil-in-water emulsion stabilized by Triton X-100 initially and containing an equal mixture of solid and liquid droplets.

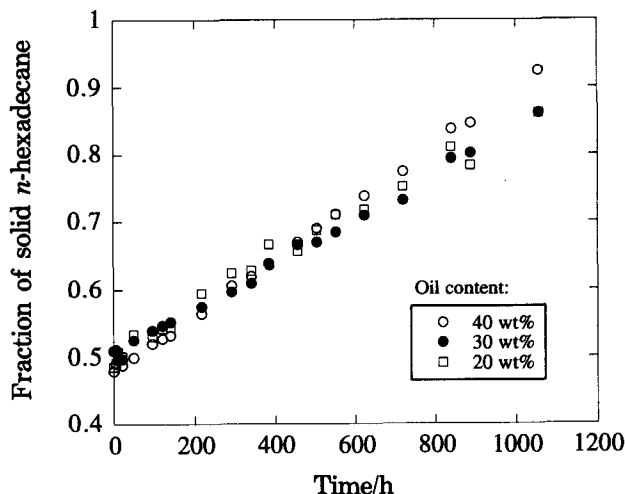


FIG. 3. Time dependence of the fraction of solidified droplets with time at 6°C for *n*-hexadecane oil-in-water emulsions stabilized by Triton X-100 and containing different concentrations of oil droplets.

and 0.0018 h^{-1} . The insensitivity of the rate of interdroplet nucleation to droplet concentration suggests that the interdroplet nucleation rate may not be dominated by the rate of collision between droplets (Equation 5). The emulsions used in these experiments had similar droplet sizes, and therefore, the mass fraction of oil is proportional to n_0 . The collision frequency should therefore increase by four times as the droplet concentration doubles, and yet, such an increase was not observed in the overall crystallization rate.

Equations 4 and 5 were derived for dilute emulsions, and are not strictly applicable to the concentrated systems used in this work. The diffusion coefficient of a droplet in an emulsion decreases as the concentration of droplets increases, as droplet motion is hindered by neighboring droplets (14). In addition, Equation 4 does not account for multiple particle effects, i.e., more than two particles being involved in an encounter. Unfortunately, the

crystallization kinetics of more dilute emulsions could not be measured by the NMR technique because there was only a small difference in the NMR signal from an emulsion containing completely solid droplets and one containing completely liquid droplets. This small difference leads to larger errors in the measurements of the signal from the liquid oil component.

The concentration effects mentioned above may partially counteract the increase in collision frequency expected when the particle concentration is increased in dilute emulsions. However, a droplet in a 40% emulsion will have a diffusivity that is approximately 40% of that for a droplet in a 20% emulsion (14), and, thus, we would still expect a factor of almost two increase in the collision frequency as we double the droplet concentration (Equation 4). Hence, it is possible that the relative insensitivity of induced crystallization rate to droplet volume fraction

observed in our experiments arises because droplet collision is not the rate-limiting step in the overall process.

Effect of aqueous phase viscosity. Equation 5 predicts that as the viscosity is increased the rate of floc formation should decrease because the frequency of collisions is inversely related to the viscosity. A series of 30 wt% hexadecane oil-in-water emulsions stabilized by Triton X-100 were therefore prepared that had different concentrations of sucrose (22–30 wt%) added to the aqueous phase. This additional sugar increases the viscosity up to eightfold. Figure 4 shows that the increased viscosity does indeed decrease the crystallization rate. Also plotted on the figure is the predicted decrease in crystallization rate obtained from Equation 5, showing how the rate measured with no added sugar would be expected to decrease as the viscosity increases. Although the decrease in rate is qualitatively similar, the measured kinetics appear to decrease to a lesser extent than predicted by the collision frequency relation. It is possible that the difference is due to limitations in the Smoluchowski theory, such as multiparticle effects. Alternatively, the results in Figure 4 may be accounted for by the influence of viscosity on other kinetic processes occurring during crystallization, such as film thinning between flocculated droplets or motion of oil crystals at the droplet interface.

Effect of droplet size. The rate of induced crystallization at 8°C was measured for a series of 30 wt% *n*-hexadecane oil-in-water emulsions stabilized by Tween 20. Emulsions were prepared with mean droplet diameters ranging from 0.5 to 3.5 μm (Fig. 5). The droplet size distributions measured at the end of the experiment were the same (within experimental error) as those measured at the beginning. A higher temperature was used in these experiments because samples that contained completely liquid droplets with sizes greater than about 1 μm crystallized at 6°C. The NMR signal was independent of droplet diameter (within experimental error) for samples that contained either completely liquid or completely solid droplets.

The rate of interdroplet nucleation increased as the mean droplet size was reduced (Fig. 6). In comparing this result with Equation 5, we observe that the only predicted

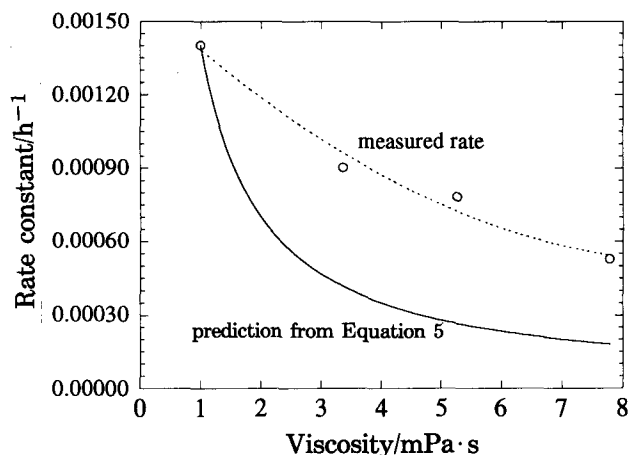


FIG. 4. Dependence of the rate of induced crystallization on the viscosity of the continuous phase for 30 wt% *n*-hexadecane oil-in-water emulsions stabilized by Triton X-100 at 6°C. The viscosity of the samples was varied by adding sucrose. The predicted rate constants were normalized to the value of an emulsion that contained no additional sucrose.

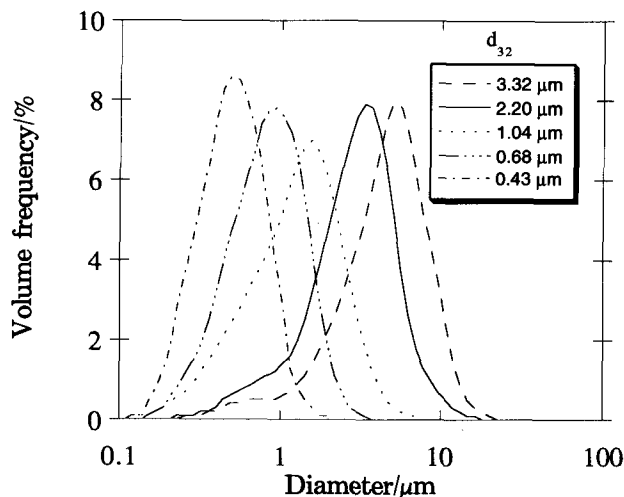


FIG. 5. Measured droplet size distribution of five 30 wt% *n*-hexadecane oil-in-water emulsions stabilized by Tween 20. No significant change in the measured droplet sizes occurred during the course of the experiment.

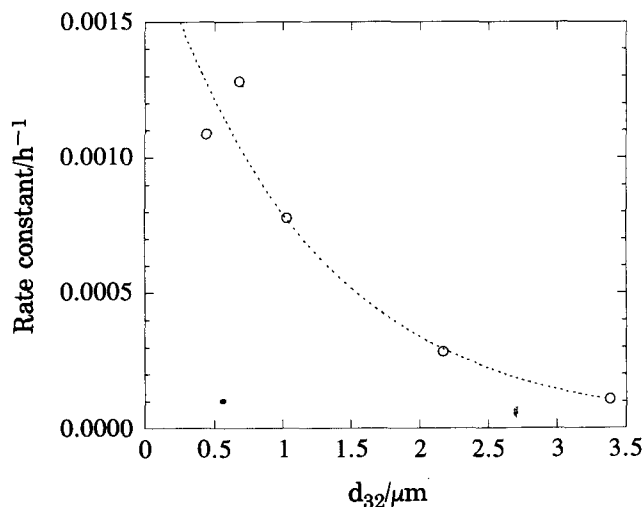


FIG. 6. Dependence of the rate of induced crystallization at 8°C on the mean droplet diameter of the emulsions shown in Figure 5.

dependence of N on the droplet diameter d is through its effect on the number density of particles n_0 . For a constant mass fraction of oil, the number density decreases with droplet size according to the relation $n_0 \propto d^{-3}$. Hence, the collision frequency should decrease as $N \propto d^{-6}$. Figure 6 demonstrates a much less dramatic decrease in overall crystallization kinetics. Again, this could be because of limitations of Equation 4, or because the rate of flocculation is not the limiting step in the nucleation process. Note that hindered diffusion effects, which were invoked in our discussion of droplet concentration effects, should not play a role in the results of Figure 6. The ratio of the diffusion coefficient D in a concentrated system to the Stokes-Einstein (infinitely dilute) result is dependent only on volume fraction, not on the size or number density of droplets (14).

As was the case with viscosity effects, changes in droplet size can affect other colloidal processes besides flocculation kinetics. Film thinning rates should decrease as the droplet radius increases. In addition, the size of flocs formed (as opposed to the rate at which they are formed) may also have a droplet size or droplet concentration dependence, and the size and/or reversibility of these flocs may influence the interdroplet nucleation process (see next section). Indeed, any interfacial process should decrease as the specific surface area A (m^2 per m^3 oil droplets) decreases, and an increase in droplet size will decrease that area:

$$A = \frac{6}{d_{32}} \quad [6]$$

Such a dependence on droplet size is more consistent with the observations shown in Figure 6 than are the predictions of Equation 5.

Role of flocculation in interdroplet mechanism. The fact that solid droplets must be present for crystallization to occur in supercooled liquid droplets indicates that the crystallization mechanism involves interactions between the two types of droplets, most likely occurring over a short distance. Earlier work has shown that the fraction of contacts between droplets that leads to interdroplet nucleation is small ($\approx 10^{-7}$), which suggests that flocculation kinetics do not dominate the overall rate of crystallization (10). In other words, the rate at which interdroplet nucleation occurs between two droplets is slow relative to the rate at which two droplets come together. As a result, these measurements indicate that the system may reach steady state, in terms of the number of temporary flocs formed, on a much shorter time scale than is required for the overall nucleation process. However, time-independent attributes of the flocs may still play an important role in the rate of interdroplet nucleation. For example, the size distribution of flocs formed, the separation between droplets within a floc and the reversibility of the floc formation may all be important factors. The latter factor is of particular interest because the floc reversibility (which is related to the ratio of the rate constants for floc formation/breakup) will determine the lifetime of the floc and, in turn, whether that lifetime is long enough to allow the nucleation event to take place.

Comparison with ultrasound results. The results obtained from the pulsed NMR technique are in good agreement with those determined earlier by ultrasonic velocity measurements (7,8). Both techniques are capable of fully

automated, nondestructive and nonintrusive measurements of the fraction of crystalline droplets. The ultrasonic technique is more suitable for studying crystallization kinetics in emulsions containing low concentrations of oil droplets and in which measurement times are shorter (\approx ms). However, ultrasonic measurements are dependent on the emulsion droplet size (15) and can be difficult to interpret in systems that undergo rapid crystallization because of adsorption of ultrasound associated with solid-liquid phase transitions (16).

Qualitatively, our results support the hypothesis that induced crystallization is initiated by colloidal interactions between droplets. However, Smoluchowski's theory for calculating the frequency of collisions between particles in dilute emulsions was not suitable for describing the interactions between droplets in the concentrated emulsions used in this work. Our results suggest that the flocculation kinetics are not rate-limiting in the overall process of crystallization induced by interdroplet heterogeneous nucleation.

The study of colloidal interactions in concentrated systems is often limited by the lack of suitable techniques available for investigating this phenomena. Monitoring of induced crystallization may provide a useful method for probing colloidal interactions in these systems. Nevertheless, more research is needed to establish the mechanism of interdroplet nucleation and the various factors that affect it, e.g., crystal morphology, droplet-droplet interactions, characteristics of the flocs formed and, perhaps most intriguingly, the nature of the surfactant interface surrounding the droplets.

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REFERENCES

1. Everett, D.H., *Basic Principles of Colloid Science*, Royal Society of Chemistry, London, 1989.
2. Van Boekel, M.A.J.S., and P. Walstra, *Colloids Surfaces* 3:109 (1981).
3. Dickinson, E., and G. Stainsby, *Colloids in Food*, Elsevier Applied Sciences, London, 1982.
4. Boode, K., C. Bisperink and P. Walstra, *Colloids Surfaces* 61:55 (1991).
5. Turnbull, D., and R.L. Cormia, *J. Chem. Phys.* 34:820 (1961).
6. Dickinson, E., D.J. McClements and M.J.W. Povey, *J. Colloid Interface Sci.* 142:103 (1991).
7. McClements, D.J., E. Dickinson and M.J.W. Povey, *Chem. Phys. Lett.* 172:449 (1990).
8. McClements, D.J., E. Dickinson, S.R. Dungan, J.E. Kinsella, J.G. Ma and M.J.W. Povey, *J. Colloid Interface Sci.* 160:293 (1993).
9. McClements, D.J., and S.R. Dungan, *J. Phys. Chem.* 97:7304 (1993).
10. van Putte, K., and J. Van den Enden, *J. Am. Oil Chem. Soc.* 51:316 (1974).
11. Simoneau, C., M.J. McCarthy, R.J. Kauten and J.B. German, *Ibid.* 68:481 (1991).
12. Ozilgen, S., J.B. German, C. Simoneau, M.J. McCarthy and D.S. Reid, *J. Sci. Food Agriculture* 61:101 (1993).
13. Simoneau, C., M.J. McCarthy, D.S. Reid and J.B. German, *J. Food Eng.* 19:365 (1993).
14. Ottewill, R.H., and N.S.J. Williams, *Nature* 325:232 (1987).
15. McClements, D.J., *Adv. Colloids Interface Sci.* 37:33 (1991).
16. McClements, D.J., M.J.W. Povey and E. Dickinson, *Ultrasonics International 91 Conference Proceedings*, Butterworth-Heinemann, Oxford, 1989.

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