Structure of adhesive emulsions

J. Bibette, T. G. Mason, Hu Gang, D. A. Weitz, and P. Poulin

More About This Article

The permalink http://dx.doi.org/10.1021/la00036a006 provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

Structure of Adhesive Emulsions

J. Bibette,[†,‡] T. G. Mason,[‡] Hu Gang,[‡] D. A. Weitz,[*,‡] and P. Poulin[†]

Centre de Recherche Paul Pascal, Ave A. Schweitzer, F-33600 Pessac, France, and Exxon Research and Engineering Co., Rt. 22E, Annandale, New Jersey 08801

We study oil in water emulsions when the interaction between the droplets becomes strongly adhesive, causing them to stick together. However, the droplets still retain their integrity and do not coalesce. By using emulsions with droplets that are monodisperse in size, we are able to clearly observe their structure when the emulsions become adhesive. We show that the structure of strongly adhesive emulsions reflects a complex interplay among the strength of the adhesion, the droplet volume fraction, ϕ, and the time evolution of the adhesion. Initially, strong adhesion of the droplets leads to the formation of an emulsion gel. Moreover, the gel possesses a well-defined characteristic length scale, d_c, as evidenced by an intense ring of small angle light scattering. The characteristic length scale decreases as the droplet volume fraction increases. At low ϕ, the structure of the emulsion gel is fractal on length scales shorter than d_c, and the measured fractal dimension suggests that the gelation mechanism is controlled by diffusion-limited cluster aggregation. However, at higher ϕ, the short range structure is more compact, rather than fractal, and a different mechanism must be responsible for the gelation. If the strength of the adhesion is increased still further, the droplets become more deformed, resulting in massive restructuring of the emulsion gel. The structure fractures into independent, more compact flocs, eliminating the overall rigidity of the emulsion gel. These results help rationalize some of the diverse structures that are observed upon flocculation of the more usually studied polydisperse emulsions.

Emulsions are inherently unstable dispersions of one, normally immiscible, fluid in a second.[1] Nevertheless, with appropriate surfactant molecules, or other surface active species, emulsions can be made to be stable nearly indefinitely.[2] Moreover, unlike the case of microemulsions, the solubilization of one fluid in a second is not limited by equilibrium thermodynamics. Under favorable conditions emulsification offers the opportunity to incorporate almost any ratio of one fluid in another. This leads to a wide range of important technological applications, ranging from cosmetics to coatings and from foods to medicines.[3] Emulsions are also fascinating dispersions of deformable spheres, which exhibit novel colloidal properties. For example, the interaction between droplets can be made strongly adhesive, ultimately leading to a nonzero contact angle between droplets.[4,5] If the droplets retain their integrity, this adhesion causes flocculation of the emulsion droplets. Emulsion flocculation, or creaming, is a commonly encountered phenomenon, which results in a wide variety of poorly understood morphologies.

A major limitation in elaborating a clear description of emulsion flocs is the polydispersity in the droplet sizes that is inherent in any emulsification process currently used. This polydispersity greatly complicates any interpretation of the origin of the structures formed because the strength of the adhesion, the nature of the local interactions, and the consequences of ancillary effects such as gravity may all be strongly dependent on the size of the droplets. In this paper, we overcome this limitation by using emulsions that are purified to have droplets whose

size is monodisperse.[6] This enables us to clearly elucidate the structure of these emulsions when they become strongly adhesive. Furthermore, the droplets are sufficiently small that the effect of gravity on the resultant structure is negligible during the course of our experiments. This enables us to clearly delineate the effects of the strong adhesion on the morphology of the emulsion flocs.

The adhesive interaction in these emulsions is controlled by both temperature and the concentration of added salt. The detailed nature of the attractive interaction is not well understood. Nevertheless, several different regimes of behavior can be distinguished. If only a small amount of salt is added, the emulsion can undergo an equilibrium liquid–solid phase transition.[7] By contrast, if considerably more salt is added the droplets can become strongly adhesive and flocculate; yet they still retain their integrity and do not coalesce. Temperature also plays an important role; the strength of the adhesion increases as the temperature is decreased. Here we focus on the case of a very strong attractive interaction between the emulsion droplets. This is induced by increasing the salt concentration in the continuous phase, and then by lowering the temperature several degrees below the onset of the attractive interaction; this causes the droplets to become adhesive and flocculate. We show that strong adhesion initially leads to a gelation transition, which results in a rigid, but stable, gel network of droplets.[8] This gel has an unusual structure that possesses a well-defined, characteristic length scale which depends on the initial droplet volume fraction, ϕ. In the limit of low droplet volume fraction, this gelation transition can be described as a diffusion-limited cluster aggregation process.[9,10] However, at higher volume fractions, a different mechanism must be used to describe the gelation. Further increase of the adhesion causes contraction of the network because of the

(1) Becher, P. *Emulsions; Theory and Practice;* Reinhold: New York, 1965.

(2) Bibette, J.; Morse, D.; Witten, T. A.; Weitz, D. A. *Phys. Rev. Lett.* 1992, *69*, 2439.

(3) Lissant, K. J. *Emulsions and Emulsion Technology;* M. Decker: New York, 1974; Vol. 6.

(4) Aronson, M.; Princen, H. M. *Nature* 1980, *286*, 370.

(5) Aronson, M. P.; Princen, H. M. *Colloids Surf.* 1982, *4*, 173.

(6) Bibette, J. *J. Colloid Interface Sci.* 1991, *147*, 474.

(7) Bibette, J.; Roux, D.; Pouligny, B. *J. Phys. II* 1992, *2*, 401.

(8) Bibette, J.; Mason, T. G.; Gang, H.; Weitz, D. A. *Phys. Rev. Lett.* 1992, *69*, 981.

(9) Lin, M. Y.; Lindsay, H. M.; Weitz, D. A.; Ball, R. C.; Klein, R.; Meakin, P. *Nature* 1989, *339*, 360.

(10) Lin, M. Y.; Lindsay, H. M.; Weitz, D. A.; Klein, R.; Ball, R. C.; Meakin, P. *J. Phys.: Condens. Matter* 1990, *2*, 3093.
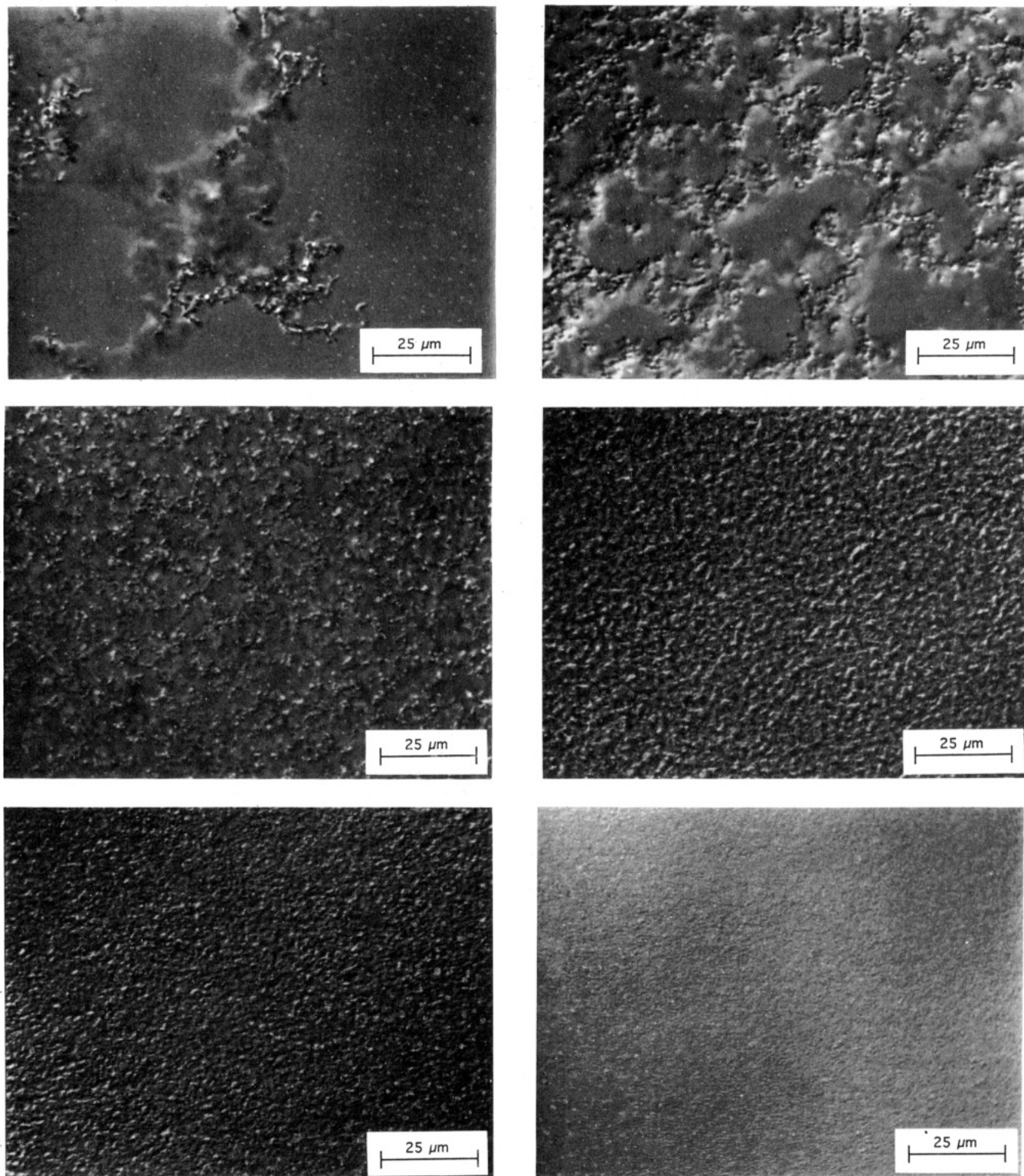
Figure 1. Photomicrographs of emulsion gels made with 0.5 M NaCl. The gelation temperature is $T_c \approx 25$ °C, and the photographs are taken at $T \approx 20$ °C. The initial volume fractions are (a, top left) 0.005, (b, top right) 0.01, (c, middle left) 0.05, (d, middle right) 0.3, and (e, bottom left) 0.4. The emulsion gels at the lower volume fractions exhibit a very tenuous structure at shorter length scales, while the gels at the two higher volume fractions exhibit only a characteristic length scale. For comparison, a liquid emulsion (f, bottom right) with $\phi = 0.4$ and $T > 25$ °C is also shown.

increased deformation of the droplets, due to the increased contact angle. This leads to marked fracture of the gel network.

The crude emulsion is formed from silicon oil droplets in water, stabilized by sodium dodecyl sulfate (SDS).[11] Highly monodisperse emulsion droplets, about 0.6 μm in diameter, are obtained by repeated crystallization fractionation.[6] This technique employs the depletion attrac-

tion induced by the addition of excess SDS micelles[7,12] to phase separate the emulsion droplets by their sizes, leading to fractionation by size and allowing us to produce monodisperse emulsions. The surfactant concentration in the continuous phase is adjusted to about 0.01 M, slightly

(11) M. Peignier of Rhone Poulenc St. Fons France very kindly provided the crude emulsion.

(12) Bibette, J.; Roux, D.; Nallet, F. *Phys. Rev. Lett.* **1990**, *65*, 2470.

above the critical micelle concentration, ensuring the stability of the emulsion.[2] To induce adhesion between the droplets, sodium chloride is added to the continuous phase. The strength of the adhesion is strongly temperature dependent: Above an onset temperature, T_c, the droplets remain repulsive, whereas adhesion is induced between the droplets when the temperature is reduced below T_c, and the strength of the adhesion increases as the temperature is further decreased. We believe that this may be associated with the formation of a nonzero contact angle between droplets, as has been observed for larger, polydisperse emulsion droplets.[5] The onset temperature depends sensitively on the concentration of sodium chloride, increasing with increasing NaCl concentration. For example, for a 0.5 M concentration of NaCl, $T_c \approx 25$ °C, while for a 1 M concentration $T_c \approx 50$ °C. All of our experiments are carried out by rapidly lowering the temperature several degrees below T_c to induce the attraction, ensuring strong adhesion between the droplets. We directly observe the structure of the flocculating emulsions using a phase contrast microscope with a variable temperature stage. In addition, we use small angle light scattering to probe the structure factor of the emulsion gels, which provides an ensemble-averaged measure of their structure.

While the temperature of the emulsion is maintained above T_c, the droplets undergo random Brownian motion, and there is a sufficiently large, short-range repulsive barrier between them to ensure stability against flocculation. When the temperature is lowered several degrees below T_c, a strong adhesion develops between the droplets. However, while the droplets adhere to one another, they retain their integrity and do not coalesce. Moreover, while the droplets deform somewhat, they do not form a compact floc, but instead they form a random network. At low volume fractions, the network is highly tenuous. This network ultimately spans the whole system, forming a gel. As viewed in the microscope, the network resists deformation, and the Brownian motion of the droplets is completely surpressed; the gel of the emulsion droplets appears to be a solid, despite the fact that it is comprised solely of liquid droplets. Thus the behavior of these adhesive emulsions is best described as a gelation transition of the droplets. However, this is a reversible gelation transition, as the adhesive interaction is eliminated and the droplets are redispersed if the temperature is raised above T_c.

This gelation transition implies that the adhesive energy between the droplets must be much greater than the thermal energy, $k_B T$, when the temperature is lowered below T_c. This large increase in adhesive energy with a small change in temperature is consistent with the observations reported by Aronson and Princen.[5] They show that the free energy of contact film increases by roughly $10^5 k_B T$ per μm^2 of surface for each degree C. Thus a change of only a fraction of a degree can result in a very large change in the adhesive energy. While the microscopic origin of this very large adhesion remains unclear, the behavior of the adhesive interfaces is somewhat analogous to Newton black films.[13]

The resultant structures of the emulsion gels are summarized in the series of photographs shown in Figure 1. The emulsion used for this series of pictures contains 0.5 M NaCl so that the onset temperature for gelation is $T_c \approx 25$ °C. All of the pictures in Figure 1 are obtained at a temperature of $T \approx 20$ °C. They show the effect on the structure of the gel as the initial volume fraction of
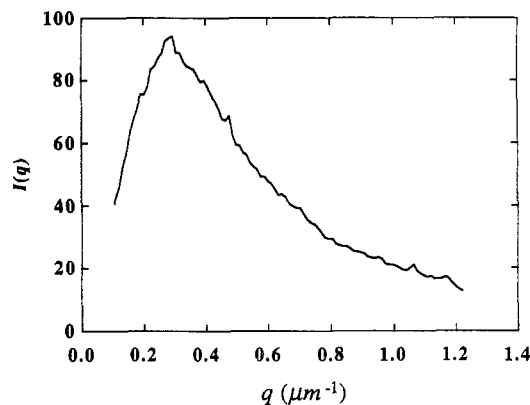

Figure 2. Scattered intensity as a function of scattering wave vector for an emulsion gel with $\phi = 0.005$, at $T = 20$ °C. The pronounced peak in the scattering intensity, reflecting the characteristic length scale of the gel, is apparent.

droplets, ϕ, is increased. At $\phi = 0.005$, the structure of the gel at short length scales consists of a highly random, tenuous network of droplets as shown in Figure 1a. The distinct branches of the network are roughly a single droplet in thickness. As ϕ is increased to 0.01 and then to 0.05, the average thickness of the branches increases slightly, but the structure still exhibits a random, tenuous network at short length scales, as shown in parts b and c of Figure 1. As ϕ is increased still further, the average thickness of the branches increases substantially and the tenuous network is no longer observed at short length scales. Instead, the gel has a dramatically different appearance, as shown for $\phi = 0.3$ and 0.4 in parts d and e of Figure 1. For comparison, we also show in Figure 1f an emulsion with $\phi = 0.4$, obtained at $T > 25$ °C, illustrating the very different structure of the random Brownian droplets, without any strong adhesion.

A surprising feature that distinguishes the emulsion gels for all volume fractions is a pronounced, characteristic length scale exhibited by their structures.[8] This is most clearly seen from small angle light scattering from the gels. To measure the small angle light scattering, the gel is formed in a 50 μm thick cell, sufficiently thin to eliminate any multiple scattering, yet thick enough to be much larger than any other length scale. A HeNe laser, with a wavelength of 632.8 nm, is directed through the sample, and the light scattered at angles from about 3° to 20° is observed on a screen. This scattering pattern is recorded with a camera, and the image is digitized for further analysis. An angular average of the data is performed to obtain the scattered intensity, $I(q)$, as a function of scattering wave vector, q. In Figure 2, we show the scattering intensity from the same emulsion gel shown in Figure 1a, which has an initial volume fraction of $\phi = 0.005$. There is a pronounced peak in the scattering intensity at $q_m \approx 0.27$ μm^{-1}, corresponding to a characteristic distance of $d_c = 2\pi/q_m$, or about 23 μm. The scattering from the gels at all volume fractions exhibits a similar peak, but the corresponding length scale decreases with increasing ϕ. This behavior is shown in Figure 3, where we plot d_c as a function of ϕ. The structure of these emulsion gels is quite different from that of most gels, which do not possess such a well-defined characteristic length scale.[14] The scattering from these other gels does not exhibit the pronounced peak that is observed here.

While the peak in the scattering intensity reflects the characteristic length scale in the gel, the structure at

---

(13) de Feijter, J. A.; Vrij, A. *J. Colloid Interface Sci.* **1978**, *64*.

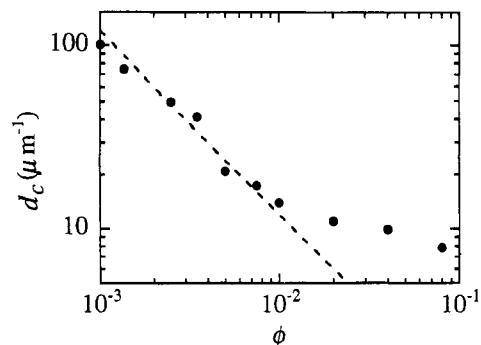(14) Dietler, G.; Aubert, C.; Cannell, D. S.; Wiltzius, P. *Phys. Rev. Lett.* **1986**, *57*, 3117.

Figure 3. Characteristic length scale, d_c, of the emulsion gel as a function of initial droplet volume fraction, ϕ. At low volume fractions, d_c decreases as ϕ^{-1} as shown by the dashed line.
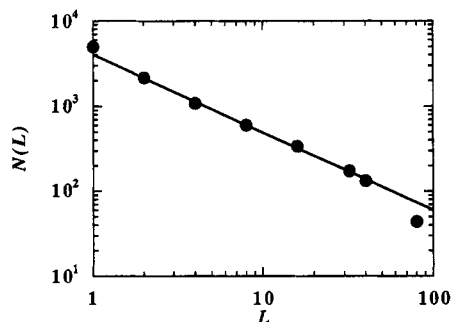

Figure 4. Box size analysis of the short range structure of images of emulsion gels with $\phi = 0.005$. A logarithmic plot of the number of boxes required to cover the gel as a function of the box size shows a linear behavior, indicative of a fractal structure. Since the images are a two-dimensional cut of the three-dimensional structure, the fractal dimension is determined by adding 1 to the measured slope, giving $d_f \approx 1.8$, consistent with diffusion-limited cluster aggregation.

shorter length scales also provides important information about both the structure of the gel and the mechanisms which lead to its formation. At low volume fractions, the structure is very open and tenuous, as shown in parts a and b of Figure 1. To quantify this structure, the light scattering at high angles can be plotted logarithmically as a function of q. Clear power-law behavior is observed, suggesting that the structure can be described as a fractal.[8] To confirm this, we also analyze the real space images of the gel obtained with the microscope. The pictures are digitized and a threshold is set to distinguish the emulsion gel from the background. A box counting technique is then used to measure the scaling behavior of the structure.[15] The image was covered by a set of equally sized boxes, and the number, $N(L)$, required to cover the gel was determined as a function of the box dimension, L. In Figure 4, we show a logarithmic plot of $N(L)$ as function of L. These results are averaged over five images of different locations within the gel. Linear behavior is clearly observed in Figure 4, consistent with power-law scaling of $N(L)$ with L. This analysis is quite robust; the same behavior is obtained for a wide range of threshold settings. This box counting method was used previously[16] to analyze the fractal structure of images of colloidal aggregates obtained with a transmission electron microscope. In that case, the box counting method was shown to be in excellent agreement with several other techniques, including different image analysis methods as well as scattering measurements. This provides a high degree of confidence in the analysis method.

The fractal dimension of the gel network at short length scales can be obtained directly from the exponent of the data shown in Figure 4. Since the depth of field of the microscope is very short, roughly equal to the droplet diameter, the images represent a two-dimensional cut of the three-dimensional gels. Thus the fractal dimension of the gel can be determined[15] from the slopw of the data in Figure 4 by adding 1. We obtain $d_f \approx 1.8$ in this regime. The same fractal dimension is observed, both experimentally[10] and in computer simulations,[17,18] for diffusion-limited cluster aggregation (DLCA) of colloidal particles at low initial concentrations. This suggests that, at least at the early stages of the gelation, the dynamics are governed by diffusion-limited cluster aggregation.

The DLCA process is known to result in fractal clusters of very nearly monodisperse size. As an hypothesis, we assume that when the volume fraction of these fractal clusters is approximately unity, gelation occurs. We further assume that the clusters maintain their nearly monodisperse size distribution as they continue to grow and approach the gelation point. This hypothesis would then account for the origin of the characteristic length scale in the gel at low volume fractions.[8] Consistent with this hypothesis, at lower volume fractions, $\phi \leq 0.01$, we find that d_c decreases with ϕ as a power law, $d_c \sim \phi^{d_f - 3}$. This is shown in Figure 3; the dashed line represents a slope of -1.0 in accord with this prediction to within experimental uncertainty. Similar behavior is observed in other systems,[19] but a detailed theoretical understanding of its origin remains elusive. In particular, the peak in the scattered intensity is observed long before the gel point is reached; the cause for this has yet to be determined.

As the volume fraction of the droplets increases above $\phi \approx 0.01$, the characteristic length scale exhibited by the gel structure persists, but decreases with increasing ϕ. At these larger volume fractions, it is no longer possible to identify a fractal structure at short length scales that results from DLCA. Presumably, the early stages of the gelation are quite different from that of DLCA because the initial volume fraction of droplets is so large and may involve a contribution from the fluctuations in the particle concentration. Indeed, the patterns of the gels at larger ϕ bear a resemblance to those formed by spinodal decomposition. The gelation mechanism, and the origin of the length scale at large ϕ, may be significantly different than the behavior at low volume fractions and requires more theoretical work.

A remarkable feature of these emulsion gels is the fact that they form a tenuous network, which must maintain some inherent rigidity, despite the fact that it is composed entirely of liquid droplets. This rigidity has a profound implication about the nature of the adhesion: It suggests that there must be no slip between two adjacent droplets. If slip could occur, the droplets would be able to rotate about their bonds, and the resultant rearrangement would lead to a significantly less tenuous structure. This suggests that a rigid film is formed by the adhesion between neighboring droplets. However, this is not sufficient to preclude any slip; in addition, the remaining surfactant molecules, away from the adhesive region, must also resist flow and, hence, resist rearrangement. The origin of this resistance to slip is not clear. One possibility is that the surfactant forms a solid layer at the interface. Another possibility is that packing constraints of the gel preclude rearrangement, even though the surfactant layer at the

(15) Feder, J. *Fractals*; Plenum, New York, 1990.
(16) Weitz, D. A.; Oliveria, M. *Phys. Rev. Lett.* **1984**, *52*, 1432.

(17) Meakin, P. *Phys. Rev. Lett.* **1983**, *51*, 1119.
(18) Kolb, M.; Botet, R.; Jullien, R. *Phys. Rev. Lett.* **1983**, *51*, 1123.
(19) Carpineti, M.; Giglio, M. *Phys. Rev. Lett.* **1992**, *68*, 3327.

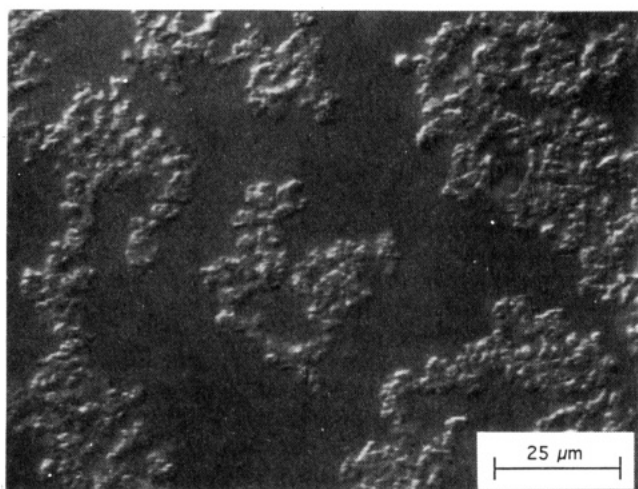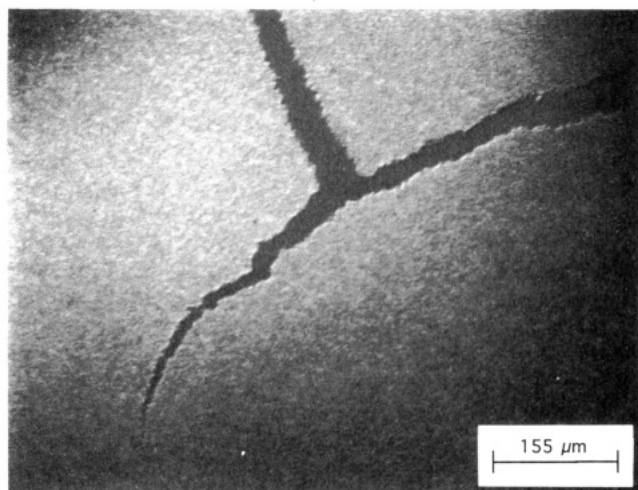**Figure 5.** Photomicrographs of flocculated emulsions made with 1 M NaCl. The gelation temperature is $T_c \approx 50$ °C, and the photograph are taken after the emulsion is cooled rapidly below T_c and then more slowly to $T \approx 15$ °C, so that the adhesion is significantly increased. The initial volume fractions are (a, top) 0.4 and (b, bottom) 0.05. The contraction of the gel structure, caused by the increased adhesion, leads to large scale fractures at higher ϕ, and to well separated, compacted flocs at lower ϕ.

interface remains fluid. Alternatively, it is possible that the short range structure of the network is comprised not of chains of single droplets but of chains that are several droplets thick. This additional thickness would prevent rearrangement. This certainly occurs at higher volume fractions, where it is clear from the microscope images that the arms of the network become increasingly thick. However, at very low ϕ, the arms of the network are much thinner, although it is difficult to ascertain whether their thickness is restricted to a single droplet. Thus, the origin of the rigidity remains an important, but unresolved, puzzle. The rigidity of the emulsion gels persists during the course of our experimental observation. However, bulk samples of gels formed at lower volume fractions do exhibit slight creaming due to gravity over periods of several days.

Increasing the salt concentration to 1 M results in an increased onset temperature, $T_c \approx 50$ °C. This higher T_c allows us to conveniently form the gel, and then cool still further, thereby investigating the consequences of a further

increase in the strength of the adhesion. Thus the gel is initially formed slightly below T_c, where the structure is very similar to that shown in Figure 1. The gel is then cooled further, increasing the strength of the adhesion, whereupon a dramatic restructuring of the gel is observed. Now the adhesion between the droplets is sufficiently large to cause them to undergo massive deformation. Locally, the stronger adhesion results in a contraction of the gel, leading to massive fracturing of the structure, as shown in Figure 5a. This picture is obtained with a gel having an initial volume fraction of $\phi = 0.4$, which is first cooled rapidly to just below T_c, and then more slowly to 15 °C. Ultimately, the gel loses its rigidity due to the propagating fractures. Similar effects are observed for a gel formed at lower ϕ. However, the fracture is not as clearly defined, but instead, we observe well separated, and more compact, emulsion flocs, as illustrated in Figure 5b, for a gel with $\phi = 0.05$.

The picture that emerges from these observations is that the behavior of emulsion gelation induced by strong adhesion is, in many cases, similar to that of other colloidal suspensions. For example, colloidal silca particles suspended in organic solvents can also display flocculation and gelation as the temperature is varied.[20] The origin of the gelation is primarily determined by the interaction between the colloidal particles or the emulsion droplets. However, for these emulsions, this adhesive interaction has two key features: First, the strength of the attraction is governed by temperature which leads to experimental control of the droplet interaction, enabling us to study the previously inaccessible regime of very rapid gelation in highly concentrated dispersions. Secondly, for the emulsions, the strength of this attraction can also be increased substantially by further lowering the temperature. Consequently, the structure of the final flocs depends on the time evolution of the strength of the adhesion. Initially, the adhesion results in the formation of a random, solid gel network in the emulsion. Further increase of the adhesion causes massive fracturing of the gel, disrupting the rigidity of the structure and leading to well separated, and more compact, flocs. Finally, the behavior of the adhesive emulsion when the interaction is not as strongly attractive may also have analogs to colloidal suspensions. A weaker attractive interaction would lead to an equilibrium liquid–solid phase separation. Alternatively, a stronger attraction, but with a finite repulsive barrier would again lead to flocculation, but in this case it would be analogous to reaction-limited cluster aggregation.[9,21]

The polydisperse emulsions which are more extensively studied and more widely used can often be adhesive. Then, large irregular flocs are observed. The growth and structure of these flocs depend not only on the adhesion but also on the effects of gravity and polydispersity. Nevertheless, the results presented here suggest that the effects of both strong adhesion and the deformability of the droplets on the mechanism of the flocculation can be understood within a simple picture.

(20) Grant, M. C.; Russel, W. B. *Phys. Rev.* **1993**, *E47*, 2606.
(21) Lin, M. Y.; Lindsay, H. M.; Weitz, D. A.; Ball, R. C.; Klein, R.; Meakin, P. *Phys. Rev.* **1990**, *A41*, 2005.