

Pickering Emulsions with Controllable Stability

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We prepare solid-stabilized emulsions using paramagnetic particles at an oil/water interface that can undergo macroscopic phase separation upon application of an external magnetic field. A critical field strength is found for which emulsion droplets begin to translate into the continuous-phase fluid. At higher fields, the emulsions destabilize, leading to a fully phase-separated system. This effect is reversible, and long-term stability can be recovered by remixing the components with mechanical agitation.

Introduction

Emulsions are a common form of material and are encountered in products including foods, cosmetics, and pharmaceuticals. A proper formulation of an emulsion will ensure its stability against droplet coalescence and macroscopic phase separation. This is normally accomplished with the addition of amphiphilic molecules, such as surfactants that lower the interfacial tension of the liquid/liquid interface.¹ In 1907, Pickering observed that colloidal particles situated at the oil–water interface can also stabilize emulsions of oil and water.² These are referred to as either Pickering emulsions or solid-stabilized emulsions.³ Stabilization is achieved when nanometer to micrometer-sized particles diffuse to the interfacial region and remain there in a stable mechanical equilibrium. Thus, particles residing at the interface between the dispersed and continuous phases usually form rigid structures stabilizing the thin films that occur when droplets approach one another, by arresting rupture, and minimizing coalescence.^{4,5} A critical parameter in the design of a Pickering emulsion is the three-phase contact angle, θ , that establishes the position of the particles relative to the oil–water interface. This angle is pictured in Figure 1a for an ideal, spherical particle of radius a astride an oil–water interface with surface tension γ . In order for a particle at the interface to stabilize the emulsion properly, it must have a contact angle in the vicinity of 90° .⁶ Furthermore, the type of emulsion, water-in-oil (w/o) or oil-in-water (o/w), depends on the particle wettability.⁷ By analogy to surfactant molecules, the particle monolayers will curve such that the larger area of the particle surface remains on the external side. Thus, hydrophobic particles will form a contact angle higher than 90° , such that a larger fraction of the particle surface will reside in

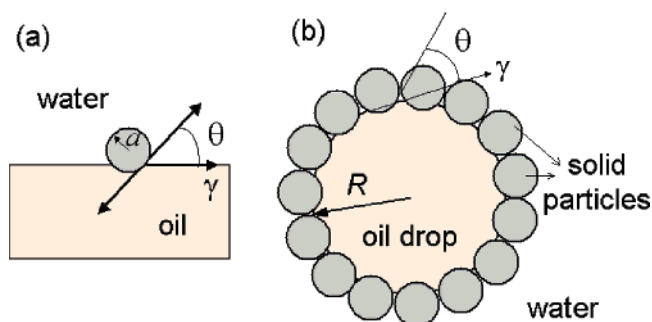


Figure 1. (a) Position of a spherical particle at a planar oil–water interface for a contact angle (measured through the aqueous phase) less than 90° . (b) Corresponding positioning of those particles at a droplet interface giving a solid-stabilized oil-in-water emulsion.

oil than in water so they will normally stabilize w/o emulsions; for hydrophilic particles, with a contact angle less than 90° , o/w emulsions will be more probable (this particular case is represented in Figure 1b). This fact has been experimentally corroborated for emulsions with oil and water volume fractions of approximately 0.5 (see for example Table 1 in ref 3). While a number of additional factors govern the character of the emulsions ultimately attained,^{4,7,8–10} this statement about the type of Pickering emulsions is probably the most general that can be made.

Such a particle is held at the interface by an energy⁹

$$E_\gamma = \pi a^2 \gamma (1 \pm \cos \theta)^2 \quad (1)$$

where the sign in the bracket is positive for removal into oil and negative for removal into water. A rough estimation of the interfacial energy can be done for a micrometer-sized particle with a contact angle close to 90° at an oil–water interface characterized by an interfacial tension around 50 mN/m. In this particular case the interfacial energy is calculated to be approximately $10^7 k_B T$, which means particles in this size range are essentially irreversible adsorbed at the interface.³ Here, k_B is Boltzmann's constant, and T is the room temperature.

Effectiveness of solid particles in stabilizing emulsions depends on particle properties (size, shape and wetta-

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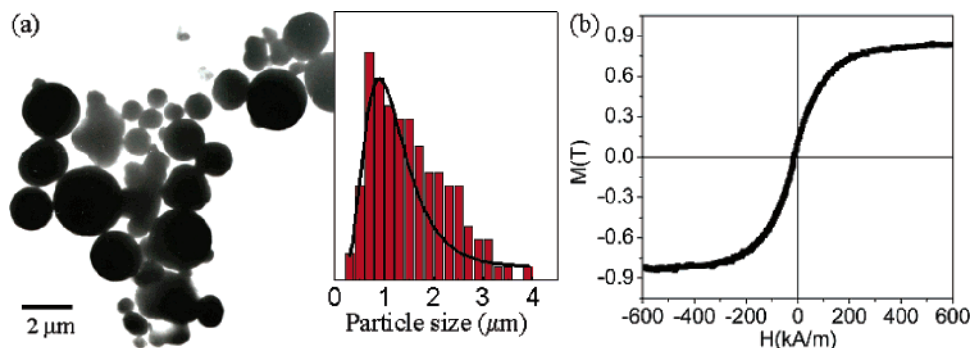


Figure 2. (a) Transmission electron micrograph for the carbonyl iron particles. Histogram of the particle size log-normal distribution revealed an average particle diameter of $2a = 1.11 \pm 0.07 \mu\text{m}$. (b) Magnetization curve measured for the carbonyl iron particles shows their superparamagnetic behavior (neither hysteresis nor magnetic remanence). The measured saturation magnetization is 211 emu/g.

bility), particle concentration and particle interactions.¹¹ The stability of Pickering emulsions has been studied extensively by Binks et al. in the case of silica particles,^{7,12} polystyrene latex particles,⁸ and disklike clay particles.¹³ Particulate stabilizers find use in pharmaceutical and personal-use products where the presence of surfactants can lead to side effects or unwelcome allergic reactions. Furthermore, the use of particles has other advantages, such as the robustness of the resulting emulsions, the ability to create emulsion droplets with narrow size distributions, and the possibility of inverting emulsions from o/w to w/o systems by changing the particulate material. However, until now, Pickering emulsions were believed to be unconditionally stable due to the large interfacial energy, E_{p} , that is required to move the particles away from the interface. In this paper we report the use of paramagnetic colloidal particles as emulsion stabilizers. It is demonstrated that such particles offer the possibility of precise external control of emulsion stability as well as offering the means of conveying an emulsion without the use of mechanical pumps and valves.

Experimental Section

The materials used in this work consist of Milli-Q water (specific resistance 18.2 MΩ·cm) and decane (purchased from Fisher at 99.9% purity), which is used as received. Spherical paramagnetic carbonyl iron particles were acquired from Lord Corporation. The size and shape of the iron particles were characterized by transmission electron microscopy (TEM) in a 200 kV JEOL-2000 FXII microscope. Figure 2a shows a TEM image of the carbonyl iron particles. Image analysis revealed that the particles are highly polydisperse in size (ranging from 0.2 to 4.0 μm), showing a log-normal distribution with an average diameter of $2a = 1.11 \pm 0.07 \mu\text{m}$. The magnetic properties of the iron powders have been measured using a vibrating sample magnetometer (from Oxford Instruments model MagLab-VSM9T). The magnetization curve shown in Figure 2b confirm their superparamagnetic character (neither hysteresis nor magnetic remanence is observed). The particles' response is linear for small fields, having a magnetic susceptibility value $\chi = 4.90 \pm 0.18$. For high fields, the magnetic moment induced in the particles is not directly proportional to the applied field due to saturation effects. The saturation magnetization has been measured to be 211 emu/g, smaller than that for pure bulk Fe (221.71 emu/g). Before preparing the emulsions, these particles have been previously cleaned several times to remove any possible surfactant or salt. Emulsions are formed by first dispersing a weighed amount of these particles in a known volume of water

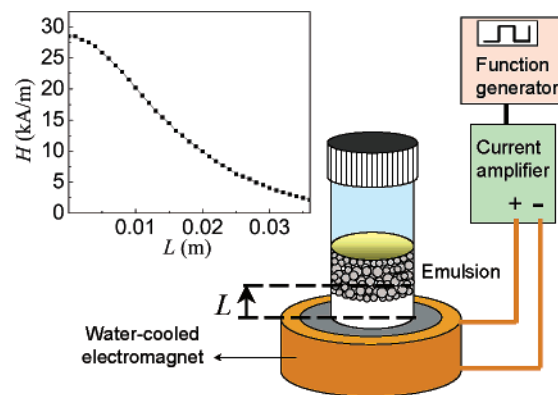


Figure 3. Experimental setup. Magnetic field generated by the electromagnet (when a current of 2 A is applied to the coil) as a function of the distance to the bottom of the vial.

and then introducing the same volume of decane to the dispersion (volume fraction of water $\phi = 0.50$). We characterized the wetting behavior of these particles by spin-coating a thin film of these particles dissolved in toluene onto glass slides. Qualitative examination of decane droplets on these slides while immersed in water showed that the particles are composed of a material that is preferentially wet by the aqueous solution as compared to decane.¹⁴ The final emulsion, consisting of droplets of decane dispersed in an aqueous matrix and coated with paramagnetic particles (see Figure 1b), is created by either vigorous hand-shaking or by the use of a vortex mixer (a blender made by Fisher Scientific, Model 231).

In studies of the stability of these emulsions, magnetic fields are applied using a water-cooled electromagnet made from insulated copper wire (#20 AWG) that is turned 760 times around an iron core (Magnetic Sensor Systems, E-16-260-20; see Figure 3). This coil is powered using a current amplifier (Kepco, BOP20-10M) driven by a function generator (Hewlett-Packard 3325A). The coil is placed immediately underneath the vials containing the emulsions. The vial diameter of 2.5 cm is smaller than the iron core diameter of 3.6 cm so the applied magnetic field at each height within the vial remains uniform. In Figure 3 the magnetic field generated by the electromagnet is plotted as a function of the distance measure from the bottom of the vial, L , for an applied current of 2 A. In particular, at the distance where the interface of the fully phase-separated decane-water system is located ($L \sim 5 \text{ mm}$), the magnetic field has been measured to be $H = 26 \text{ kA/m}$, when a current of 2 A is supplied to the coil. Hereafter, the values of the magnetic fields will be referred to the ones measured at the bottom of the vial.

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(14) Determination of the contact angle from observations of individual particles at a decane-water interface has been attempted but giving a quantitative accurate value was found to be extremely difficult. To obtain a more accurate value of the contact angle, a more sophisticated method, such as the one reported by Paunov (Paunov, V. N. *Langmuir* **2003**, *19*, 7970), needs to be used.

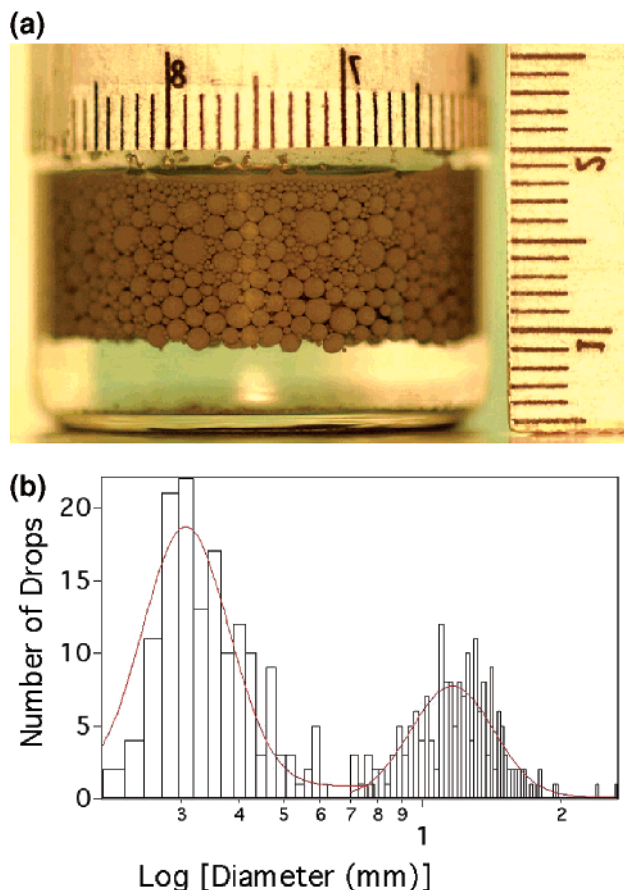


Figure 4. (a) Photograph of an oil-in-water emulsion stabilized with carbonyl iron paramagnetic particles at a concentration of 4 wt %. The emulsion consists of decane droplets with a bimodal size distribution. At the bottom of the vial we observe some extra water. (b) Histogram of the log-normal distribution of drops sizes corresponding to the emulsion presented in Figure 4a.

Results and Discussion

Figure 4a is a photograph of a typical emulsion formed using the procedure described above. This particular system corresponds to an emulsion with particle concentration $c = 4$ wt % and, as can be observed, consists of decane droplets of different sizes. We observe that iron particles adsorb onto the surface of the decane droplets to reduce the total surface energy; the oil–water surface energy is substantially larger than the difference in the particle–oil and the particle–water surface energies. These emulsions are very stable over time and maintain their appearance for over 5 months. The obtained emulsion volume has around 10 mm height for all particle concentrations. An extra-water volume remains underneath the emulsion.

When the two separated phases are mixed with mechanical agitation, drops of different sizes form; the surfaces of some of the droplets are not completely covered by the paramagnetic particles. When the suspension is allowed to rest, the droplets coalesce, until there are enough particles to cover the entire surface of the remaining droplets. Also, as the droplets are coalescing, there are small drops that do not coalesce and, instead, remain within the interstitial regions between the larger droplets, protecting them from further coalescence (see Figure 4a). This leads to a bimodal droplet size distribution as can be observed in the histogram presented in Figure

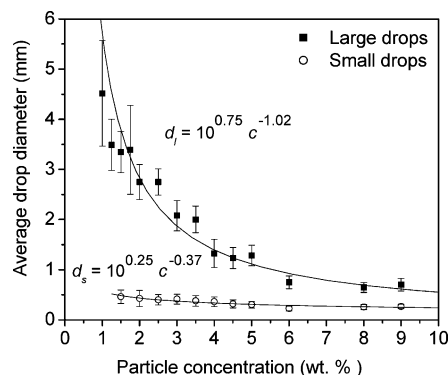


Figure 5. Change in the average drop size for large (squares) and small (circles) drops with varying paramagnetic particle concentration.

4b where the average drop diameter for the small drops is $d_s = 0.4 \pm 0.1$ mm and for the large drops is $d_l = 1.3 \pm 0.3$ mm.

The drop-size distribution in Pickering emulsions can be effectively varied by adjusting the concentration of the particles while keeping the relative proportion of oil and water constant.³ Figure 5 presents the average droplet diameter for large and small drops obtained for a sequence of emulsions formed from systematically increasing the particle concentration. In general, the average droplet diameter decreases with the particle concentration. However, a different behavior is found for both sizes of droplets in the bimodal distribution. Large droplets decrease in size with a power law, $d_l \sim c^{-1}$, as expected, since the total number of particles in the emulsion is inversely proportional to the droplet diameter. However the size of the small droplets decreases much more slowly at all concentrations range because they are initially covered with enough particles to make them stable. It is expected that the large droplets will decrease in size until they reach the size of the small ones.

The property that makes these *Pickering magnetic emulsions* unique is their ability to undergo phase separation upon application of external magnetic fields. Furthermore, decane drops in these peculiar emulsions show the ability to travel through the continuous phase with the help of magnetic field gradients. Application of magnetic fields of moderate strength from the coil below the emulsion induces transport of the decane drops from their initial position toward the bottom of the container, without affecting the emulsion stability. This transport can be observed in detail in Figure 6 for an emulsion of 3.5 wt % particle concentration when a magnetic field of 29.6 kA/m is applied. The drop movement can be externally controlled by the electromagnet (controlling both, the magnetic field strength and the field gradient). When the applied magnetic field is not strong enough to induce drop transport, a slight elongation along the field direction of those drops placed on the layer closer to the electromagnet can be observed. This elongation is more apparent for bigger drops, i.e., for emulsions with less particle concentration. As an example in Figure 7b we present the huge deformation produced on a drop of a 1 wt % particle concentration emulsion when a magnetic field of 50.3 kA/m is applied.

The transition of decane droplets in the presence of magnetic fields is presented in Figure 7a where the droplet displacement is plotted as a function of the magnetic field strength for different particle concentrations. Here, drop displacement has been calculated by measuring the translation of the center of mass of the drops placed on

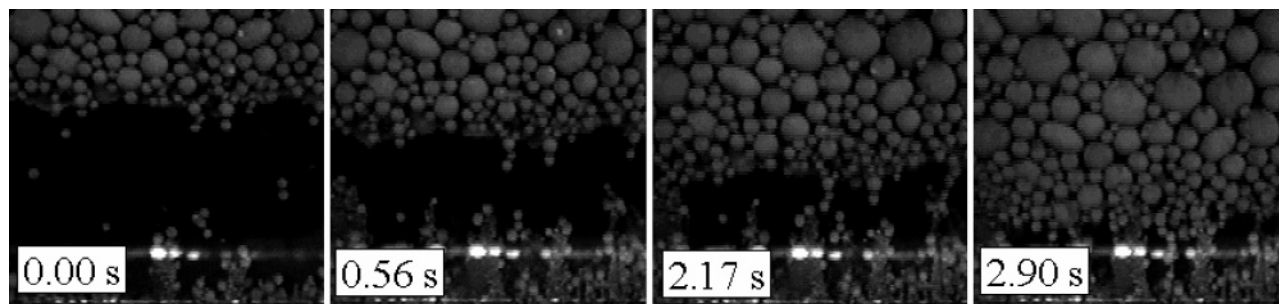


Figure 6. Time sequence to visualize transport of decane drops closest to the bottom of the vial. In this particular case, a magnetic field of 29.6 kA/m is applied on a magnetic Pickering emulsion with 3.5 wt % particle concentration. On the first photograph (left), emulsion drops are at rest, when no magnetic field is applied. Once we apply the magnetic field, the drops move through the continuous phase toward the bottom of the vial, without affecting the emulsion stability. Consecutive frames were recorded at 0.56, 2.17, and 2.90 s after turning ON the magnetic field. Frame size: 15 × 14 mm.

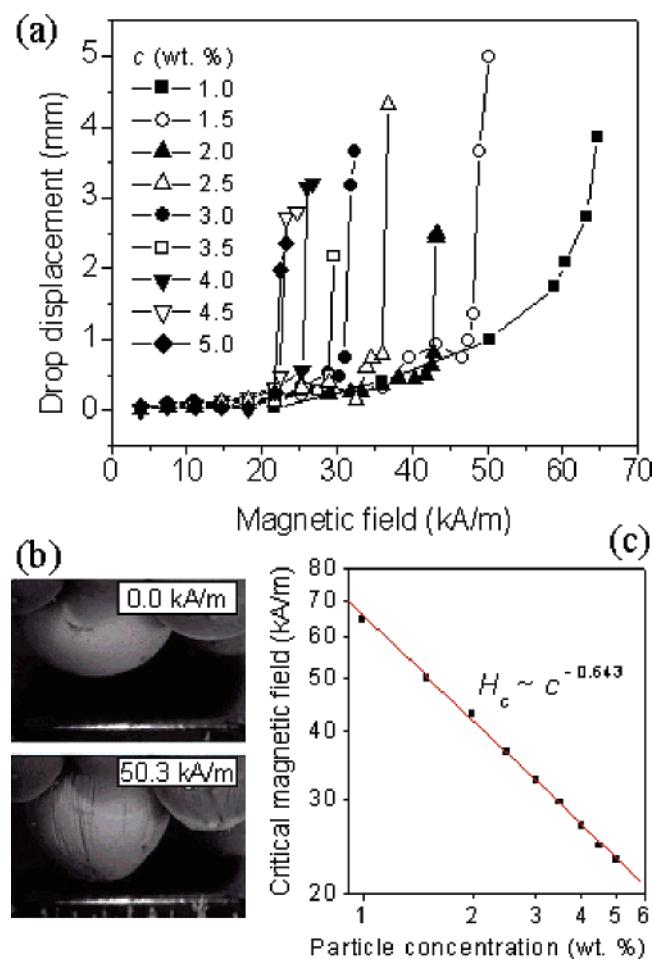


Figure 7. (a) Displacement of droplets with varying magnetic fields for different particle concentrations. (b) Detail of the shape deformation of decane drops on a 1 wt % particle concentration emulsion: on top, emulsion drop when no magnetic field is applied; on bottom, drop elongation in the direction of the field when applying a magnetic field of 50.3 kA/m. Frame size: 7.8 × 5.5 mm. (c) Critical field at which the decane drops move through the continuous phase for emulsions with different particle concentration.

the layer closer to the electromagnet. Thus, as we move to lower particle concentrations, the gradually increases of drop displacement with the magnetic field strength becomes more appreciable due to the bigger deformation observed for bigger drops (see again Figure 7b). We see that the magnetic field needed to cause displacement of the droplets depends on the particle concentration and thereby on the drop size. In Figure 7c, we plot the critical magnetic field, H_c , at which the drops start moving as a

function of particle concentration, c , in a log–log plot. We find a power law behavior $H_c \sim c^{-0.643}$. This behavior can be predicted by taking into account that the drop displacement process begins when the magnetic force acting on the particles adsorbed on the drop surface, $F_{mag} = \mu_s V_p n \nabla[\chi(H)H^2]$, is greater than the buoyancy force acting on the drop, $F_{buoyancy} = (4/3)\pi R^3 \rho g$.¹⁵ Here $\chi(H)$ is the particle magnetic susceptibility; μ_s is the magnetic permeability of the solvent which can be considered equal to the magnetic permeability of a vacuum $\mu_0 = 1.256 \times 10^{-6}$ Tm/A; V_p is the particle volume; n is the number of particles per droplet and can be estimated as, $n = (2R/a)^2$, where $2R = d_l$ is the average droplet diameter; ∇H is the magnetic field gradient; g is the acceleration due to gravity, and $\rho = \rho_w - \rho_o$ is the difference in density of water and decane, $\rho_o = 0.7301$ g/cm³.¹⁶ In our experimental setup, the gradient of the magnetic field is linearly proportional to the magnetic field strength (as can be deduced from Figure 3) within the range of critical magnetic fields found in the experiments (20 kA/m to 65 kA/m). Furthermore, from the particle magnetization curve, we found that the particle magnetic susceptibility behaves as $\chi(H) \sim H^{-0.475}$ within the same range of magnetic fields. This simple model predicts that the critical field depends on particle concentration as $H_c \sim R^{0.656} \sim c^{-0.656}$, which is close to the power law found in the experiments.

Complete phase separation occurs in these peculiar emulsions when a strong magnetic field is applied. In this case, emulsions as a whole are compressed toward the bottom of the vessel due to the field gradient. Strong fields cause the particles stabilizing the drops to be stripped from the oil droplets and move toward the bottom of the vial. This releases the decane drops that move upward by buoyancy and coalesce with the bulk phase at the top of the vial. The magnitude of the field required for destabilization has been measured to be approximately $H_{dest} \sim 80$ kA/m for all particle concentrations. The destabilization process is rather complex. When a magnetic field of around 80 kA/m is applied, a clearing on the particle shell at the top of the drops is observed. This is followed by cracking the particle shell at the point furthest away from the horizontal equator of the oil droplets leading to a cylindrical shell with triangular endpoints around each

(15) We would like to point out that the contribution of the carbonyl iron particles located at the interface to the buoyancy force has been neglected. The correct expression would be $F_{buoyancy} = (4/3)\pi R^3 \rho g + \rho_{wp} V_p g n$. Here ρ_{wp} is the difference in density of water and particles. However, for the experimental values, the second term (due to the contribution of the particles) will be an order of magnitude smaller than the first one. The definition of the different parameters is given in the text.

(16) Note that on the estimation of the critical field dependence on the drop radius, $H_c \sim R^\alpha$, the particle contribution to the buoyancy force leads to a correction on the radius exponent, α , smaller than 3%.

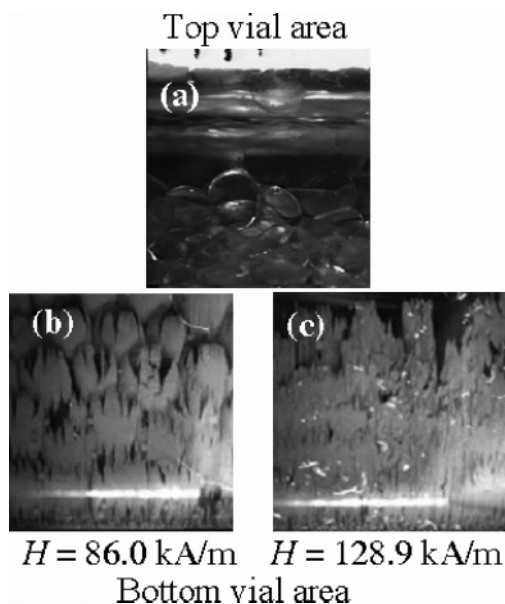


Figure 8. Destabilization of *magnetic Pickering emulsions* with 2 wt % particle concentration when applying magnetic fields of two different strengths. (a) Decane drops that have moved upward by buoyancy and are coalescing with the bulk phase at the top of the vial. (b, c) Detail of the decane drops closest to the bottom of the vial. (b) A magnetic field of 86.0 kA/m is sufficient to devoid of particles the drops at the two lower layers. Some of the drops at the upper layers still remain covered by a solid shell which presents some signs of destabilization. (c) A stronger magnetic field, 128.9 kA/m, destabilizes all the emulsion leading to a completely phase-separated system. Frame size: $12 \times 13 \text{ mm}$.

drop. The pressure exerted by the surrounding drops and by the particles moving downward often breaks this cylindrical structure. Furthermore, this additional pressure forces the films between droplets to thin and become unstable.^{4,17} The particles that are separated from the drop slowly fall toward the magnetic field. This process continues until the oil droplet is completely devoid of magnetic particles, at which point decane drop moves upward by buoyancy and coalesces with the bulk phase at the top of the vial. As an example, Figure 8 shows a magnetic Pickering emulsions with 2 wt % particle concentration which has been destabilized by applying magnetic fields of two different strengths. Figure 8a shows the view of the top area of the vial where decane drops are coalescing with the bulk phase. In Figure 8b, we show the bottom part of the vial when a magnetic field of 86.0 kA/m is applied. We observed that this field strength is sufficient to eliminate the particles from the drops at the two lower layers. However some of the drops at the upper layers still remain covered by a solid shell that presents some signs of destabilization. A stronger magnetic field, 128.9 kA/m, destabilizes the entire emulsion leading to a completely phase-separated system (see Figure 8c).

We tested the stability of the emulsions after several destabilization cycles. The protocol we follow consists of

(17) A rather similar situation appears when the emulsion is destabilized by means of centrifugation in Tcholakova, S.; Denkov, N. D.; Ivanov, I. B.; Campbell, B. *Langmuir* **2002**, *18*, 8960.

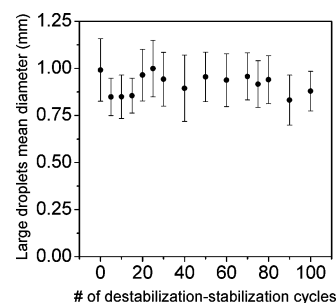


Figure 9. Variation of mean droplet diameter d_l (for the larger drops) on an emulsion with particle concentration 5.5 wt % after being subject to continuous de-stabilization and reformation processes. As can be seen, the reproducibility after a large number of destabilization–stabilization cycles is remarkable.

applying square-wave magnetic fields (ON–OFF) with strength 143 kA/m and frequency 0.5 Hz. A sufficient number of cycles are used to make the emulsion fully separate into two phases. Then, the destabilized emulsions are vigorously re-dispersed using a vortex mixer. This process was repeated a hundred times, recording an image every five cycles to measure the average mean diameter of the large droplets. As an example, we show these results for an emulsion of 5.5 wt % in Figure 9. We see that each time we re-disperse the components we produce stable emulsions with drop-size distributions equivalent to the original emulsions. This shows that, unlike most emulsion-destabilizing techniques, there are no long-lasting effects due to the destabilization.

Conclusions

In summary, solid-stabilized emulsions using paramagnetic particles at an oil/water interface are shown to offer the ability to induce reversible macroscopic phase separation upon application of external magnetic fields. A field, independent of droplet size, will be able to destabilize the emulsion, leading to a fully phase-separated system. Mechanically remixing the components restores emulsions with long-term stability. Furthermore, small-strength magnetic fields present the possibility of making the emulsion drops flow in the continuous phase. The magnetic field required to cause the decane droplets to move decreases with the particle concentration. The possibility of controlling the stability of emulsions in the food, cosmetic, and pharmaceutical industries can prove to be an important discovery for the development of novel materials and drug-delivery mechanisms.^{18,19}

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