Temperature-induced Coalescence of Droplets Manipulated by Optical Trapping in an Oil-in-Water Emulsion

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Coalescence of oil droplets in an oil-in-water (O/W) emulsion was achieved with heating and optical trapping. Three types of O/W emulsions were prepared by adding a mixture of butanol and n-decane to an aqueous solution containing a cationic surfactant (cetyltrimethylammonium bromide, CTAB), an anionic surfactant (sodium dodecyl sulfate, SDS), or a neutral hydrophilic polymer (polyethylene glycol, PEG) as an emulsifier. Two oil droplets in the emulsions were randomly trapped in a square capillary tube by two laser beams in order to induce coalescence. Coalescence of the droplets could not be achieved at room temperature (25°C) regardless of the type of emulsifier. Conversely, the droplets prepared with PEG coalesced at a temperature higher than 30°C, although the droplets with ionic surfactants CTAB and SDS did not coalesce even at the elevated temperature due to their electrostatic repulsion. The size of the resultant coalesced droplet was consistent with that calculated from the size of the two droplets of oil, which indicated successful coalescence of the two droplets. We also found that the time required for the coalescence could be correlated with the temperature using an Arrhenius plot.

Keywords Optical trapping, laser, emulsion, coalescence, droplet

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Experimental setup

The experimental setup used in this study is shown in Fig. 1a. An inverted microscope, ECLIPSE TE2000-S (Nikon, Tokyo, Japan), was employed for manipulating and observing droplets being filled in a square capillary (fused silica, 77.6 × 73.8 μm i.d., 354.4 × 345.0 μm o.d., Polymicro Technologies Inc., AZ, USA). The beam of a Nd:YAG laser (532 nm, maximum power, 3 W, Beamtech Optronics, Beijing, China) was split in half via two beam splitters (50/50, Ø25.0 mm, #43-736, Edmund Optics, NJ, USA). The beams were introduced into a microscope objective (40×, NA = 0.6) by reflection with a dichroic mirror (Di02-R514-25 × 36, Semrock, NY, USA) mounted in the microscope. When the laser power was adjusted to 300 mW, the total power of the two beams was reduced to ~90 mW after passing through the microscope objective, because the power had been decreased to one-third of the original value. Images of the droplets were monitored using a CCD camera (WAT-221S, Watec, NY, USA) interfaced with a PC via a TV capture board (PCast, PC-MV5DX/U2, Buffalo, Aichi, Japan). A notch filter (Techspec® rugate notch filter, 532 nm, optical density >4, stock number #46-565, Edmund Optics, NJ, USA) was placed in front of the CCD camera to exclude scattered light from the laser beams. By tilting the mirrors (M1 and M2), each laser beam was adjusted so that it made contact with one of the trapped droplets.

The square capillary and the nichrome wires were held in an acrylic plate, as shown in Fig. 1b. The bottom of the acrylic plate was covered with a cover glass so that the hole could be filled with mineral oil. The top of the acrylic plate was also covered with a cover glass to prevent the forming of bubbles. The mineral oil was heated by connecting the nichrome wires to dry-cell batteries, and a thermometer monitored the temperature.

The square capillary and the other three ports were connected via a 4-way joint to fused silica capillaries (50 μm i.d. and 375 μm o.d., GL Sciences, Tokyo, Japan). An emulsion and water were introduced into the square capillary using three syringe pumps (MSPE-1, AS ONE, Osaka, Japan) connected to the fused silica capillaries. The square capillary was filled with an emulsion using syringe pump 2, and then two droplets were arbitrarily selected for trapping in the observed area. Excess droplets were flushed out by water using syringe pumps 1 and 3. After replacing the emulsion with water, the two droplets were merged.

Results and Discussion

The stability of oil droplets in water can generally be controlled using an emulsifier with amphiphilic properties. The emulsifier stabilizes the oil droplets and prevents spontaneous coalescence by covering the surface of the droplet while directing the hydrophilic heads toward an aqueous continuous phase. Conversely, it is necessary to destabilize the droplets in order to achieve coalescence when they are dispersed in an emulsion. Therefore, we initially explored the minimum concentrations of the emulsifiers that would be required to form emulsions.

The minimum concentration was determined by turbidity, which was judged by the naked eye. Krebs et al. reported that a concentration of more than 10–4 M was needed to avoid spontaneous coalescence in a microfluidic device, although the concentration depends on the preparation method. Under our experimental conditions, the minimum concentrations required to form stable droplets were determined to be 1 mM for SDS, 1 mM for CTAB, and 1% for PEG. These values were in relatively good agreement with the concentration at the stability threshold of emulsions prepared with silicon oil and SDS (2.7 mM), although we employed a mixture of 1-butanol and n-decane instead of silicon oil. At these concentrations, the emulsions were stable against coalescence for at least 1 day.

Using the experimental setup shown in Fig. 1, two droplets were successfully manipulated independently and were made to contact each other via the use of two independent laser beams. Manipulation of the two droplets prepared with SDS is shown in Fig. 2. When the two droplets contacted each other at room temperature (22 – 25°C), no coalescence was observed, although a change in the shape of the droplets is shown in Fig. 2c.

The same result was observed for the droplets prepared with CTAB. A possible reason for the unsuccessful coalescence of the droplets stabilized by SDS or CTAB is attributed to electrostatic repulsion, since these two had the same level of electric charge—a negative charge for SDS and a positive charge for CTAB. The stability of oil droplets in water is frequently explained using the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory in which electrostatic repulsion is larger than van der Waals attraction (hydrophobic interaction) under the conditions for maintaining stable droplets:}

\[
\Phi_{\text{net}} = \Phi_A + \Phi_R ,
\]

where \(\Phi_{\text{net}}\), \(\Phi_A\), and \(\Phi_R\) are the net interaction energy, van der Waals interaction energy, and electrostatic repulsion energy, respectively. Droplets formed with a charged surfactant, such as SDS or CTAB, would have an \(\Phi_R\) that would be larger than the absolute value of \(\Phi_A\), and this would result in an inability to merge the droplets.

Electrostatic repulsion energy would be reduced when using an uncharged emulsifier, as when PEG was employed as an emulsifier. In this case, the droplets were expected to have a
smaller level of $\Phi_R$ than the droplets covered with SDS or CTAB. The droplets prepared with PEG, however, also showed unsuccessful coalescence at room temperature, even though the surface charge of the droplets was expected to be electrically neutral. This result was attributed to an absolute value for the $\Phi_A$ that was smaller than the value for $\Phi_R$ following hydration of the hydrophilic moiety in PEG.

As expected, based on DLVO theory, coalescence will be easily achieved by removing the emulsifier from the surface of the oil droplets. However, no coalescence was observed even when the surrounding medium was replaced by water. This fact implies that the surfaces of the oil droplets were still covered with the emulsifier after replacing the surrounding medium with water, although there may have been some desorption of the emulsifiers from the surfaces of the droplets.

Shinoda and Saito have reported on the stability of O/W emulsions using a neutral surfactant, polyoxyethylene nonylphenylether, as an emulsifier. They demonstrated that the size of the emulsion droplets changes remarkably with temperature due to a strong interaction between the hydrophilic moiety of the surfactant and water at decreased temperature. This fact indicates that the level of the van der Waals interaction energy between the oil droplets was too small in the present study to allow for the two droplets to merge at room temperature, since the hydrophilic moiety of PEG was thoroughly hydrated with water molecules.

According to these results, temperature is obviously an important factor in inducing the coalescence of oil droplets. Some researchers have also induced the coalescence of oil droplets by elevating the temperature in microfluidic devices. Baroud et al. demonstrated the coalescence of oil droplets via local heating generated from a focused laser beam; Xu et al. also reported temperature-induced droplet coalescence in microchannels. Therefore, we decided to investigate the effect of temperature on the coalescence of oil droplets.

To induce the coalescence of the droplets manipulated by laser beams, we elevated the temperature using nichrome wires. The emulsion prepared with PEG was selected in this experiment because, in theory, the electrostatic repulsion energy of PEG should have been the smallest among the three emulsifiers. The manipulation of the two droplets prepared with PEG is shown in Fig. 3. Figures 3a and 3b show the two droplets trapped by two laser beams, then making contact with each other as the temperature was increased to 37°C. After 4 s, successful coalescence of the droplets was observed, as shown in Fig. 3c. In Fig. 3a, the sizes of the droplets were 4.8 and 2.8 μm in diameter (58 and 11 fL in volume), whereas the resultant droplet in Fig. 3c had a diameter of 5.2 μm (74 fL in volume). The volume of the droplet in Fig. 3c agreed well with the total volume of the two droplets before coalescence.

The results of Fig. 3 imply that coalescence will be induced above a threshold temperature. A system consisting of an aqueous poly(vinyl acetate) dispersion stabilized by poly(oxyethylene) is known to exhibit a threshold temperature, which is referred to as the critical flocculation temperature (CFT) at 291 K. Therefore, the oil (a mixture of 1-butanol and...
coalescence of th

due to poor precision in temperature control.

containing PEG with water in order to achieve successful

emulsifier in the surrounding medium stabilizes the droplets,

had a CFT of approximately 30

μ

m/pixcel.

As can be seen in Table 1, the time required for coalescence was decreased with increasing

temperature of the surrounding medium, indicating that the

droplets were destabilized by increasing temperature. Even in the temperature region of 30 to 37°C, however, the droplets prepared with SDS and CTAB could not be merged, which was attributed to strong repulsion by the charged emulsifiers.

We explained the temperature dependence of coalescence by modifying a model for the coalescence of two droplets in an emulsion.35 The coalescence of two droplets can be expressed as

\[ A(D_i) + A(D_j) \rightarrow A(D_k), \]

where \( A(D_i) \), \( A(D_j) \), and \( A(D_k) \) are droplets with different diameters of \( D_i \), \( D_j \), and \( D_k \). The coalescence rate of the two droplets is given by second-order kinetics, as follows:

\[ R(D_i, D_j) = k(D_i, D_j)C(D_i)C(D_j), \]

where \( R(D_i, D_j) \) is the coalescence rate, \( k(D_i, D_j) \) is the rate constant, and \( C(D_i) \) and \( C(D_j) \) are the density values of the oil droplets with diameters of \( D_i \) and \( D_j \). In our system, \( C(D_i) \) and \( C(D_j) \) can be considered to be 1, since only two droplets were selected to induce coalescence, i.e., \( R(D_i, D_j) = k(D_i, D_j) \). The rate constant, \( k(D_i, D_j) \), is evaluated by the activation energy for coalescence, \( E(D_i, D_j) \), as follows:

\[ k(D_i, D_j) = k_0 \exp(-E(D_i, D_j)/RT), \]

where \( k_0 \) is the frequency factor for coalescence. Since \( k(D_i, D_j) \) (= \( R(D_i, D_j) \)) is simply defined as the rate for forming a single droplet by merging two droplets, \( k(D_i, D_j) \) is expressed by the reciprocal of the time for coalescence. Equation (4) can thus be rewritten as

\[ -\ln(t) = \ln(k_0) - E(D_i, D_j)/RT, \]

where \( t \) is the time required for coalescence. Using Eq. (5), we constructed an Arrhenius plot between \( 1/T \) versus \(-\log(t)\),

as shown in Fig. 4. The proposed model reasonably explained the temperature-induced coalescence via good linearity, as shown in Fig. 4 (\( R^2 = 0.9814 \)). Differences in the diameters of the droplets and imprecise temperature control would cause slight deviations from linearity. Consequently, the energy of activation explains the temperature-induced coalescence.

The activation energy obtained from the slope in Fig. 4 was estimated to be 4 kJ mol⁻¹, whereas Miyagawa et al. reported that the activation energy for droplets smaller than 1 μm ranged from 10 to 10³ kJ mol⁻¹.35 The smaller level of activation energy in the present study can be attributed to the difference in the sizes of the droplets, since an emulsion with smaller oil droplets is more stable.35 The diameters of the droplets were larger than 1 μm in Fig. 4, so the activation energy was reasonable.

Table 1: Dependence of the time required for coalescence on temperature

| Temperature/°C | Time/s | \( D_i/\mu m \) | \( D_j/\mu m \) |
|----------------|--------|----------------|----------------|
| 30             | 57     | 4.0            | 3.2            |
| 31             | 29     | 8.4            | 7.2            |
| 34             | 9      | 2.8            | 2.8            |
| 37             | 4      | 4.8            | 2.8            |

\( D_i, D_j \): Diameters calculated using the images of the droplets. The resolution of the images, 0.4 μm/pixel.

Conclusions

We used optical trapping to demonstrate the successful manipulation and coalescence of two oil droplets stabilized by PEG in water. It was essential, however, to replace the solution containing PEG with water and to elevate the temperature of the surrounding medium. The charged droplets had electrostatic repulsion energy that exceeded that of van der Waals energy, so coalescence could not have been achieved even at a high temperature. The neutral hydrophilic nature of the PEG polymer made it a useful emulsifier. The coalescence phenomenon was reasonably explained by accounting for the CFT and the activation energy for coalescence. The temperature-induced coalescence of droplets would be useful for chemical analyses using oil droplets, water droplets, or biological cells when the chemical reaction between a sample droplet and a reagent droplet can be initiated by only increasing the temperature. Therefore, this technique shows promise for use in droplet-based analyses.

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