Solutions to Soft Matter Exercise - Chapter 10: Emulsions

1. Fabrication of Emulsions

a. To do the calculation, we approximate the average velocity of the liquid, as determined by the peak-to-peak displacement, l, divided by the cycle time, t_c:

$$v = \frac{l}{t_c} = \frac{2\times 0.2\ \text{m}}{0.1\ \text{s}} = 4\ \text{m/s}$$

The shear rate is defined as $\dot{\gamma} = 8v/d$ such that we find:

$$\dot{\gamma} = \frac{8\times 4\ \text{m/s}}{0.01\ \text{m}} = 3200\ \text{s}^{-1}$$

b. Using Newton's law, we find:

$$\tau = \eta \times \dot{\gamma} = 0.01\ \text{Pa.s} \times 3200\ \text{s}^{-1} = 32\ \text{Pa}$$

c. To estimate the average drop size, we assume that all the energy caused by the viscous stress is used to generate liquid-air surfaces. Therefore, we can equate the viscous stress with the Laplace pressure of the forming drops and we find:

$$\tau = \eta \times \dot{\gamma} = \frac{\gamma}{r} \rightarrow\ r = \frac{\gamma}{\tau} = \frac{0.73\ \text{N/m}}{32\ \text{Pa}} = 2.3\ \text{mm}$$

Attention! γ is the surface tension (in N/m), $\dot{\gamma}$ is the shear rate (in s^{-1}).

d. In this case, we have $\eta = 0.001$ Pa.s, such that:

$$\tau = \eta \times \dot{\gamma} = 0.001\ \text{Pa.s} \times 3200\ \text{s}^{-1} = 3.2\ \text{Pa}$$

$$r = \frac{\gamma}{\tau} = \frac{0.73\ \text{N/m}}{3.2\ \text{Pa}} = 2.3\ \text{cm}$$

These drops are very large and emulsion drops with these diameters are usually not stable. In addition, such large drops rapidly sediment if the density of the drop is higher than that of the surrounding liquid (or cream if the density of drops is below that of the surrounding liquid) such that they are typically difficult to work with (unless they are quickly converted to stable capsules).

2. Stability of Emulsions

a. It is possible to form a thermodynamically stable emulsion if the increase in entropy, caused by the formation of drops, overcompensates the energy that must be paid to form new interfaces. By equating the entropy gain with the energy penalty associated with the formation of new interfaces, we find:

$$\gamma_{ab,\ \text{crit}} = -\frac{k_B T}{4\pi r^2}[\ln \phi_b + \frac{1-\phi_b}{\phi_b}\ln(1-\phi_b)]$$

From the text, we know $\phi_b = 0.5$. Using $\gamma = 0.05\ \frac{N}{m}$, we calculate the maximum drop radius, r, where the emulsion is thermodynamically stable.

$$r = (-\frac{k_B T}{4\pi\gamma}[\ln\phi_b + \frac{1-\phi_b}{\phi_b}\ln(1-\phi_b)])^{1/2} =$$
$$(-\frac{1.38\times10^{-23}\ \frac{\mathrm{J}}{\mathrm{K}}\times293\ \mathrm{K}}{4\times\pi\times0.05\ \frac{\mathrm{N}}{\mathrm{m}}}[\ln 0.5 + \frac{1-0.5}{0.5}\ln(1-0.5)])^{1/2} = 9.44\times10^{-11}\ \mathrm{m}$$

This is on the order of the size of an atom, which is much smaller than even the smallest drops could be. Therefore, this emulsion would never be stable.

b. To calculate the critical interfacial tension, we use:

$$\gamma_{ab,\ \mathrm{crit}} = -\frac{k_B T}{4\pi r^2}[\ln\phi_b + \frac{1-\phi_b}{\phi_b}\ln(1-\phi_b)] =$$
$$-\frac{1.38\times10^{-23}\ \frac{\mathrm{J}}{\mathrm{K}}\times293\ \mathrm{K}}{4\times\pi\times(10\times10^{-9}\ \mathrm{m})^2}[\ln 0.5 + \frac{1-0.5}{0.5}\ln(1-0.5)] = 4.5\times10^{-6}\ \mathrm{N/m}$$

Immiscible fluids have a much higher interfacial tension than the critical interfacial tension for this system. Therefore, in this system, drops would not spontaneously form.

c. Using the same equation, we obtain:

$$\gamma_{ab,\ \mathrm{crit}} = -\frac{1.38\times10^{-23}\ \frac{\mathrm{J}}{\mathrm{K}}\times293\ \mathrm{K}}{4\times\pi\times(10\times10^{-9}\ \mathrm{m})^2}[\ln 0.1 + \frac{1-0.1}{0.1}\ln(1-0.1)]$$
$$= 1\times10^{-5}\ \mathrm{N/m}$$

This is still a very low surface tension that typically cannot be obtained if two fluids are immiscible. This is the reason why most emulsions are thermodynamically unstable.

d. Surfactants lower the interfacial tension. Interfaces coated with surfactants that lower the interfacial tension efficiently usually have tensions on the order of 5 mN/m. Lower interfacial tensions can be obtained if the two solvents have some solubility in each other (e.g. water/1-butanol).

3. Stabilization of Emulsions

Emulsions can be stabilized with *surfactants* or *nanoparticles.*

Surfactants are typically more mobile than nanoparticles and thus adsorb faster at the liquid-liquid interfaces. As such, they are preferred in processes where emulsion drops may come into contact with each other shortly after they have been formed. However, their adsorbtion is reversible, which can compromise the long-term stability of the emulsions.

Nanoparticles are larger than surfactants so they diffuse slower, taking longer to reach the interface. Moreover, they only move to the interface if their surface chemistry is designed to have some affinity to both phases. If this is the case, the energy required to remove them after they have been adsorbed is very high. As a result, very few nanoparticles will leave the interface. This makes nanoparticle-stabilized emulsions, Pickering emulsions, very stable even if stored for prolonged times at elevated temperatures and increased ionic strength.

4. Pickering Emulsions

The energy required to remove particles from the liquid-liquid interface is essentially the energy required to create additional liquid-liquid interface which was previously occupied by the adsorbed particle. This energy penatly must be corrected for the energy change associated with the particle that is surrounded by the different fluids. As derived in the course, this energy is equal to:

$$E = \pi r^2 \gamma_{ow}(1 - |\cos\theta|)^2$$

From this we can calculate:

a. $E = \pi(100 \times 10^{-9}\ \text{m})^2 \times 0.03\ \text{N/m} \times (1 - |\cos 90°|)^2$
$= 4.9 \times 10^{-16}\ \text{J} = 2.3 \times 10^{5}\ k_B T$

b. $E = \pi(100 \times 10^{-9}\ \text{m})^2 \times 0.03\ \text{N/m} \times (1 - |\cos 120°|)^2$
$= 2.4 \times 10^{-15}\ \text{J} = 5.7 \times 10^{4}\ k_B T$

c. $E = \pi(10 \times 10^{-9}\ \text{m})^2 \times 0.03\ \text{N/m} \times (1 - |\cos 90°|)^2$
$= 4.9 \times 10^{-18}\ \text{J} = 2.3 \times 10^{3}\ k_B T$

d. $E = \pi(10 \times 10^{-9}\ \text{m})^2 \times 0.03\ \text{N/m} \times (1 - |\cos 120°|)^2$
$= 2.4 \times 10^{-18}\ \text{J} = 573\ k_B T$

In all cases, the energy needed to remove particles from the interface is much higher than the thermal energy, so the probability that particles are removed is very low. However, we also see that the energy needed to remove particles from the interface decreases with particle radius.

5. Foams

The system tries to minimize its energy by minimizing the air-liquid interfacial area, resulting in a coarsening of the air bubbles. However, not all of the air bubbles will coarsen and disappear at the same rate as the Laplace pressure within the small bubbles is much higher than that within the larger bubbles. As a result, the smallest bubbles will disappear first, as they are energetically the most expensive.

The lower the interfacial tension is, the lower the driving force to coarsen will be; the Laplace pressure scales with the interfacial tension and decreases proportionally with decreasing γ. If the air-liquid interface is covered with strongly-adhered nanoparticles, the coarsening is slowed significantly because, for coarsening to occur, nanoparticles must be displaced from the air-liquid interface, which is energetically very expensive.