**Solutions to Soft Matter exercise, Chapter 11: Emulsions**

## 1. Fabrication of emulsions

a. To do the calculations we approximate the average velocity of the liquid to be determined by the peak-to-peak displacement, *l*, divided by the cycle time, $t_c$. $v = \frac{l}{t_c} = \frac{2\times 0.2m}{\frac{s}{10}} = 4\frac{m}{s}$

The shear rate is defined as $\dot{\gamma} = \frac{8v}{d}$ such that we find $\dot{\gamma} = \frac{8\times 4\frac{m}{s}}{0.01m} = 3200\frac{1}{s}$

b. Using Newton's law, we find $\tau = \eta\dot{\gamma} = 0.01Pas \times 3200\frac{1}{s} = 32\ Pa$.

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. Hence, we can equate the viscous stress with the Laplace pressure of the forming drops and we find $\tau = \eta\dot{\gamma} = \frac{\gamma}{r}$. Thus $r = \frac{\gamma}{\tau} = \frac{0.073N\times m^2}{m\times 32N} = 2.3mm$

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

d. In this case, we have $\eta = 0.001Pas$ such that $= \eta\dot{\gamma} = 0.01Pas \times 3200\frac{1}{s} = 3.2Pa$ and $r = \frac{\gamma}{\tau} = \frac{0.073N\times m^2}{m\times 3.2N} = 2.3cm$

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 into 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, one finds

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

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.

$$r = \sqrt{-\frac{k_B T}{4\pi\gamma}\left[ln\phi_b + \frac{1-\phi_b}{\phi_b}ln(1-\phi_b)\right]}$$

$$= \sqrt{-\frac{1.38\times 10^{-23}\frac{J}{K}293K}{4\times\pi\times 0.05\frac{N}{m}}\left[ln0.5 + \frac{1-0.5}{0.5}\ln(1-0.5)\right]}$$

$$= 9.44\times 10^{-11}m$$

This is of order of a size of an atom and much smaller than even very small drops can be. Thus, this emulsion would never be stable.

b. To calculate the critical interfacial tension, we use

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

$$\gamma_{ab,crit} = -\frac{1.38 \times 10^{-23}\frac{J}{K} 293K}{4\pi \times 10^2 \times (10^{-9})^2 m^2}\left[ln0.5 + \frac{1-0.5}{0.5} ln(1-0.5)\right]$$

$$= 4.5 \times 10^{-6}\frac{N}{m}$$

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

c. Using the same equation, we obtain

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

$$\gamma_{ab,crit} = -\frac{1.38 \times 10^{-23}\frac{J}{K} 293K}{4\pi \times 10^2 \times (10^{-9})^2 m^2}\left[ln0.1 + \frac{1-0.1}{0.1} ln(1-0.1)\right]$$

$$= 1 \times 10^{-5}\frac{N}{m}$$

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 of order 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. Hence, they are preferred in processes where emulsion drops can come in contact with each other shortly after they have been formed. However, they adsorb reversibly which can compromise the long-term stability of the emulsions.

Nanoparticles are larger than surfactants such that they diffuse slower and hence, it takes longer for them to go to the interface. Moreover, they only go to the interface if their surface chemistry is designed to have some affinity to both phases. However, if this is the case and once the particles are adsorbed, the energy required to remove them is very high. Hence, only very few nanoparticles will leave the interface. This makes nanoparticle stabilized emulsions, so-called Pickering emulsions, very stable even if stored for prolonged times at elevated temperatures and increased ionic strength.

## 4. Surfactants

Surfactants are molecules that lower the surface or interfacial tension. They are usually amphiphilic, meaning they contain both hydrophobic and hydrophilic parts. They are for example used in emulsions to prevent coalescence of drops. They are also used to lower the interfacial tension of fluids for example, to change their flow properties in channels.

## 5. Adsorption of surfactants

The adsorption kinetics of surfactants at the drop surface can be measured using the pendant drop method. This method analyzes the shape of the drop. The equilibrium shape is determined by the balance of the gravitational force that pulls the drop down and the surface tension force that pulls the drop towards the needle. By analyzing the shape of the drop and knowing its volume and density and thus its weight, the surface tension can be deduced. In general, the lower the surface tension, the more deformed the drop is. To measure the adsorption kinetics of surfactants, the drop shape is measured as a function of time. Hence, by acquiring time-lapse images of the pendant drop, the evolution of the interfacial tension with time can be extracted.

## 6. Stabilization of vinaigrette

Vinaigrette is an oil-in-water emulsion. The surfactant should be soluble in the continuous phase, which in this case is water. Therefore, the HLB value should be above 10. Food grade surfactants are typically nonionic. Hence, the surfactant should be a food grade, nonionic surfactant, such as a Pluronics or Span, with a HLB value above 10.

## 7. Emulsions in our daily life

See slides

## 8. Pickering emulsions

a. The energy required to remove particles from the liquid-liquid interface is essentially the energy required to create additional liquid-liquid interface that has previously been occupied by the adsorbed particle. This energy penalty 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

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

Hence, we obtain

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

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

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

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

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

## 9. 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 air bubbles will coarsen and disappear at the same rate: The Laplace pressure inside the small bubbles is much higher than the Laplace pressure inside the larger bubbles. Hence the smallest air bubbles will disappear first, as they are energetically most expensive. The lower the interfacial tension is, the lower is the driving force to coarsen: the Laplace pressure scales with the interfacial tension and hence decreases with decreasing $\gamma$.

If the air-liquid interface is covered with nanoparticles that very strongly adhere, the coarsening is significantly slowed down because for coarsening to occur, nanoparticles must be displaced from the air liquid interface. This is energetically very expensive.