Exercise 6

Exercise 1:
Milk contains colloidal particles (micelles) consisting of casein. Two different sizes of these particles can be isolated by centrifugation under different conditions. The diffusion and sedimentation coefficients for the different conditions are given in the table below:

Centrifugation conditions	D $\times 10^8$ (cm^2/s)	s $\times 10^{13}$ (s)
5 minutes, 5000 rpm	0.97	2200
40 minutes, 20 000 rpm	2.82	800

The temperature was $25°C$
The continuous phase has the density ρ_1=1,0 g/cm^3
The dispersed phase has the (average) density ρ_2=1,43 g/cm^3.

Calculate the mass per particle and the molecular mass for the two micelle fractions.

5000 rpm

Einsteins diffusion law

$$D = \frac{k_B \cdot T}{f} \Rightarrow f = \frac{k_B \cdot T}{D} = \frac{1{,}38 \cdot 10^{-23}\ J/K \cdot (25+273)K}{\frac{0{,}97}{10^8}\ cm^2/s}$$

$$f = 4{,}24 \cdot 10^{-13}\ \frac{kg \cdot m^2/s}{cm^2}$$

$$\boxed{1\ m^2 = 10^4\ cm^2 \Rightarrow \frac{m^2}{cm^2} = 10^4}$$

$$\underline{f = 4{,}24 \cdot 10^{-9}\ kg/s}$$

Sedimentation coefficient

$$s = \frac{m}{f}\left(1 - \frac{\rho_1}{\rho_2}\right) \Rightarrow m = \frac{s \cdot f}{1 - \frac{\rho_1}{\rho_2}} = \frac{\frac{2200}{10^{13}}\ s \cdot 4{,}24 \cdot 10^{-9}\ kg/s}{1 - \frac{1}{1{,}43}} = 3{,}10 \cdot 10^{-18}\ kg = 3{,}10 \cdot 10^{-15}\ g$$

$$\underline{\underline{m = 3{,}10 \cdot 10^{-15}\ g}}$$

$$M_m = m \cdot N_A = 3{,}10 \cdot 10^{-15}\ g \cdot 6{,}022 \cdot 10^{23}\ mol^{-1}$$

$$\underline{\underline{M_m = 1{,}87 \cdot 10^{9}\ g/mol}}$$

20 000 rpm

$$D = \frac{k_B \cdot T}{f} \Rightarrow f = \frac{k_B \cdot T}{D} = \frac{1{,}38 \cdot 10^{-23}\ J/K \cdot (25+273)K}{\frac{2{,}82}{10^8}\ cm^2/s}$$

$$f = 1{,}46 \cdot 10^{-13}\ \frac{kg\ m^2/s}{cm^2}$$

$$f = 1{,}46 \cdot 10^{-9}\ kg/s$$

$$m = \frac{s \cdot f}{1 - \frac{\rho_1}{\rho_2}} = \frac{\frac{800}{10^{13}}\ s \cdot 1{,}46 \cdot 10^{-9}\ kg/s}{1 - \frac{1}{1{,}43}} = 3{,}88 \cdot 10^{-19}\ kg = 3{,}88 \cdot 10^{-16} g$$

$$m = 3{,}88 \cdot 10^{-16} g$$

$$M_m = m \cdot N_A$$

$$M_m = 2{,}34 \cdot 10^8\ g/mol$$

Exercise 2:
Phosphatidylcholine is a lipid that can be found in egg yolk. When phosphatidylcholine is mixed with water it will form micelles – *spherical "particles".*

Molecular mass (M_m) for the particles is 97 000 g/mole
Density (ρ_p) for the particles is 1.018 g/cm³
The temperature is $25°C$

a) What is the radius for the particles?

Assume that the particles are not hydrated.
The viscosity of water (η) at the given temperature is 0,9 mPa·s (milliPascal second)
Boltzmann constant: 1,38·10⁻²³ J/K
(Pa=kg/ms² and J=kgm²/s²)

b) Calculate the diffusion coefficient (D) for the particles in water

Under similar conditions, the diffusion coefficient has been determined experimentally to be 6.547·10⁻⁷ cm²/s.

c) Explain the reason for the difference between the calculated and experimental values.

d) Calculate $\frac{f}{f_0}$

The ratio between the friction factor of hydrated and non-hydrated particle can be expressed as follows:

$$\frac{f}{f_0} = \left[1 + \frac{m_{1,H}}{m_2}\left(\frac{\rho_p}{\rho_W}\right)\right]^{1/3}$$

where $m_{1,H}$ is the mass of hydrated water, m_2 is the mass of particles, and ρ_W is the density of water (1.0 g/cm³)

e) Calculate the degree of hydration for the lipid.

a) $$m_{particle} = \frac{M_m}{N_A} = \frac{97000\ g/mol}{6{,}022 \cdot 10^{23}\ mol^{-1}} = 1{,}61 \cdot 10^{-19}\ g$$

$$m_{particle} = \rho \cdot V_{part} = \rho \cdot \frac{4\pi R^3}{3}$$

$$\Rightarrow R = \sqrt[3]{\frac{3m}{4\pi\rho}} = \sqrt[3]{\frac{3 \cdot 1{,}61 \cdot 10^{-19}}{4 \cdot \pi \cdot 1{,}018}} = 3{,}36 \cdot 10^{-7}\ cm$$

$$R = 3{,}36\ nm$$

b) Stokes relationship

$$f_0 = 6\pi\eta R$$
$$= 6\pi \cdot 0{,}9\ mPa \cdot s \cdot 3{,}36\ nm$$
$$= 6\pi \cdot 0{,}9 \cdot 10^{-3}\ kg/m\cancel{s^2} \cdot \cancel{s} \cdot 3{,}36 \cdot 10^{-9}\ \cancel{m}$$
$$= 5{,}7 \cdot 10^{-11}\ kg/s$$

Einstein's diffusion law

$$D = \frac{k_B \cdot T}{f} = \frac{1{,}38 \cdot 10^{-23}\ \cancel{kg}\ m^2/s^2 \cdot \cancel{K} \cdot 298\ \cancel{K}}{5{,}7 \cdot 10^{-11}\ \cancel{kg/s}} = 7{,}21 \cdot 10^{-11}\ m^2/s$$

$$D = 7{,}21 \cdot 10^{-7}\ cm^2/s$$

c) This is due to the particles being hydrated in the water. When using stokes law, we assume that the particles are non-hydrated, which is not the case. Therefore, we see a difference when comparing to experimental values.

d) As $D = \frac{k_B \cdot T}{f}$, then $\frac{f}{f_0} = \frac{D_0}{D} = \frac{7{,}21 \cdot 10^{-7} cm^2/s}{6{,}547 \cdot 10^{-7} cm/s} = 1{,}1$

e) $$\frac{f}{f_0} = \left[1 + \frac{m_{1,H}}{m_2}\left(\frac{\rho_P}{\rho_W}\right)\right]^{1/3}$$

$$\Rightarrow \frac{m_{1,H}}{m_2} = \frac{\rho_W}{\rho_P}\left[\left(\frac{f}{f_0}\right)^3 - 1\right] = \frac{1\, g/cm^3}{1{,}018\, g/cm^3}\left[1{,}1^3 - 1\right] = 0{,}33$$

$$\underline{\underline{\frac{m_{1,H}}{m_2} = 0{,}33}}$$

Exercise 3:

Calculate the diameter of a spherical particle (ρ = 4 g·cm^{-3}) for which the root mean square (rms) displacement due to diffusion is 1% of the distance of sedimentation during a 24-hr period. The temperature is $25°C$. The continuous phase has a density of 1 g·cm^{-3} and viscosity of 0,9 mPa·s.

For what diameter is the diffusion distance 1% and 10% of the settling distance respectively?

$$\bar{X} = \sqrt{2Dt}$$

Sedimentation distance: $u \cdot t$

$$\Rightarrow \bar{X} = 0{,}01 \cdot u \cdot t$$

$$\Rightarrow \sqrt{2Dt} = 0{,}01 \cdot u \cdot t$$

Stoke's-Einsteins eq:

$$R = \frac{k_B T}{6\pi\eta D} \Rightarrow D = \frac{k_B \cdot T}{6\pi\eta \cdot R}$$

Stoke's sedimentation eq:

$$u = \frac{2}{9}\frac{R^2(\rho_2 - \rho_1)g}{\eta}$$

$$\Rightarrow \left(\cancel{2}\frac{k_B \cdot T}{\cancel{6}3\pi\eta \cdot R} \cdot \cancel{t}\right)^{1/2} = 0{,}01 \cdot \frac{2}{9}\frac{R^{2,5}(\rho_2 - \rho_1)g}{\eta^{1/2}} \cdot t^{1/2}$$

$$R^{2,5} = \frac{9}{2 \cdot 0{,}01} \cdot \left(\frac{k_B \cdot T \cdot \eta}{3 \cdot \pi \cdot t}\right)^{1/2} \cdot \frac{1}{g(\rho_2 - \rho_1)}$$

Units

$$\left[\frac{k_B \cdot T \cdot \eta}{t}\right]^{1/2} = \left(\frac{J/\cancel{K} \cdot \cancel{K} \cdot mPa \cdot \cancel{s}}{\cancel{s}}\right)^{1/2} = \left(kg\, m^2/s^2 \cdot 10^{-3} \cdot kg/m \cdot s^2\right)^{1/2}$$

$$= \left(10^{-3} \cdot kg^2 m/s^2\right)^{1/2}$$

$$= 10^{-1,5}\, kg\, m^{1/2}/s$$

$$\frac{g}{cm^3} = \frac{10^{-3} kg}{10^{-6} m^3} = 10^3 \frac{kg}{m^3}$$

$$\left[\frac{1}{g(\rho_2 - \rho_1)}\right] = \left(m/s^2 \cdot g/cm^3\right)^{-1}$$

$$= \left(m/s \cdot 10^3\, kg/m^{3\,2}\right)^{-1}$$

$$= 10^{-3}\, m^2 \cdot s/kg$$

$$t = 24h = 24 \cdot 60^2 s = 86400\, s$$

1%

$$R^{2,5} = \frac{9}{2 \cdot 0{,}01} \cdot \left(\frac{k_B \cdot T \cdot \eta}{3 \cdot \pi \cdot t} \right)^{1/2} \cdot \frac{1}{g(\rho_2 - \rho_1)}$$

$$= \frac{9}{2 \cdot 0{,}01} \cdot \left(\frac{1{,}38 \cdot 10^{-23} \cdot 298 \cdot 0{,}9}{3\pi \cdot 86400} \right)^{1/2} \cdot 10^{-1{,}5} \cancel{kg}\ \cancel{m^{1/2}}/\cancel{s} \cdot \frac{1}{9{,}81\,(4-1)}\ 10^{-3}\, m^{2{,}5} \cdot \cancel{s}/\cancel{kg} = 3{,}26 \cdot 10^{-7}\, m^{2{,}5}$$

$$R = \left(3{,}26 \cdot 10^{-17}\, m^{2{,}5}\right)^{1/2{,}5}$$

$$\underline{R = 2{,}54 \cdot 10^{-7}\, m} \Rightarrow \underline{\underline{d = 0{,}508\ \mu m}}$$

10%

$$\left(\frac{R_{1\%}}{R_{10\%}} \right)^{2{,}5} = \frac{1/0{,}01}{1/0{,}1} = 10$$

$$\frac{R_{1\%}}{R_{10\%}} = 10^{1/2{,}5} \Rightarrow R_{10\%} = \frac{R_{1\%}}{10^{1/2{,}5}} \Rightarrow d_{10\%} = \frac{d_{1\%}}{10^{1/2{,}5}} = \frac{0{,}508\ \mu m}{10^{1/2{,}5}}$$

$$\underline{\underline{d_{10\%} = 0{,}202\ \mu m}}$$

Exercise 4:

a) What is the time a sucrose molecule in water needs to diffuse 1 mm and 1 cm, respectively, in a given direction? The diffusion coefficient for sucrose is: $D = 4{,}7 \cdot 10^{-6}\ cm^2/s$.

b) Compare the average diffusion velocities (x/t) in the two cases and explain why they are different.

c) What is the effective (hydrated) radius for the sucrose molecule at $25°C$? η (water) $= 8{,}9 \cdot 10^{-4}$ kg/m·s

a) $\bar{x} = \sqrt{2Dt}$

1mm

$$t = \frac{\bar{x}^2}{2D} = \frac{0{,}01\ cm^2}{2 \cdot 4{,}7 \cdot 10^{-6}\, cm^2/s} = 1064\ s = \underline{\underline{17{,}73\ min}}$$

1 cm

$$t = \frac{\bar{x}^2}{2D} = \frac{1\ cm^2}{2 \cdot 4{,}7 \cdot 10^{-6}\, cm^2/s} = 106383\ s = \underline{\underline{29{,}55\ h}}$$

b) 1 mm

$$\bar{V} = \frac{\bar{x}}{t} = \frac{0{,}1\ cm}{17{,}73\ min} = 5{,}64 \cdot 10^{-3}\ cm/min$$

1 cm

$$\bar{V} = \frac{\bar{x}}{t} = \frac{1\ cm}{29{,}55 \cdot 60} = 5{,}64 \cdot 10^{-4}\ cm/min$$

For the 1 mm diffusion, the average speed is 10 times the average speed of the 1 cm diffusion. As the movement happens due to random collisions, the particles do not travel in a straight line. Although the molecules have the same relative speed, when it comes to the average speed in a given direction, the particle with the shortest travel distance will be the quickest due to it having less collisions with other particles, leading to less directional changes, which again means that it travels more efficiently, and therefore it will have the largest average diffusion velocity.

c) Spherical particle: $f = 6\pi\eta R$

$$D = \frac{k_B \cdot T}{f}$$

$$\Rightarrow R = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot D} = \frac{1{,}38 \cdot 10^{-23}\ \mathrm{kg \cdot m^2/s^2 \cdot K} \cdot 298\ \mathrm{K}}{6\pi \cdot 8{,}9 \cdot 10^{-4}\ \mathrm{kg/m \cdot s} \cdot 4{,}7 \cdot 10^{-6} \cdot 10^{-4}\ \mathrm{m^2/s}} = 5{,}22 \cdot 10^{-10} = \underline{\underline{5{,}22\ \text{Å}}}$$

$$\boxed{1\ m^2 = 10^4\ cm^2 \Rightarrow cm^2 = 10^{-4}\ m^2}$$

Exercise 5:

(Video1)

Two vials filled with dodecane and (dyed) water are mixed with the same force over the same amount of time.

a) Which of the two vials contains a surfactant dissolved in one of the phases? Mention at least two effects the addition of surfactant has. Give one example where emulsion stability is desirable and one where it is not desirable (process, product, etc.)

(Video 2)

A stirrer was used to mix equal volumes of dodecane (750 kg/m^3) and water (1000 kg/m^3, 1 mPa*s). The total height of the mixture is 8 mm.

b) It took 8 and 60 seconds for the phases to separate completely after low- and high-speed mixing, respectively. Estimate the average drop size in the two emulsions. Assume that the emulsion is water continuous.

c) Will the Stokes equation provide reliable values of drop sizes for these systems? Justify your answer.

a) The system on the right (system 2) contains surfactant, as it makes the two components more soluable in each other. Which is why it doesnt separate in the filmed timeframe.

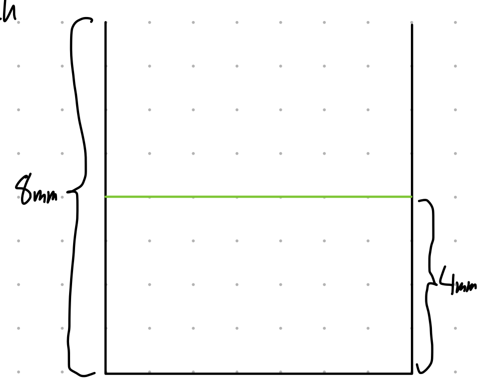
Two effects: Reduces the interfacial tension, prevents coalescense (repulsion between the surfactants embedded in the droplets)

Positive: Conserving products: paint, milk...

Negative: Separation processes: Separating oil and gas.

b) Stokes:

Sketch



$$u = \frac{d_s^2 (\rho_2 - \rho_1) g}{18\eta}$$

The drops only travel to the interface

$$\Rightarrow u = \frac{4\ mm}{t} = \frac{d_s^2 (\rho_2 - \rho_1) g}{18\eta}$$

$$\Rightarrow d_s = \sqrt{\frac{4\ mm \cdot 18\eta}{t \cdot (\rho_2 - \rho_1) g}}$$

Low speed

$$d_s = \sqrt{\frac{4\cdot10^{-3}\cancel{m}\cdot 18\cdot 1\cdot 10^{-3}\cdot \cancel{kg}/\cancel{m\cdot s}}{8\cancel{s}(1000-750)\cancel{kg}/\cancel{m^3}{}^{2}\cdot 9{,}81\cancel{m}/\cancel{s^2}}} = 6{,}058\cdot10^{-5}\ m = \underline{\underline{60{,}58\ \mu m}}$$

High speed

$$d_s = \sqrt{\frac{4\cdot10^{-3}\cancel{m}\cdot 18\cdot 1\cdot 10^{-3}\cdot \cancel{kg}/\cancel{m\cdot s}}{60\cancel{s}(1000-750)\cancel{kg}/\cancel{m^3}{}^{2}\cdot 9{,}81\cancel{m}/\cancel{s^2}}} = 2{,}212\cdot10^{-5}\ m = \underline{\underline{22{,}12\ \mu m}}$$

c) Probably not. Stokes equation does not take into consideration that there are more droplets going in different directions, slowing down the separation. It is valid for single droplets moving at a constant pace. (It does not take diffusion into account either.)