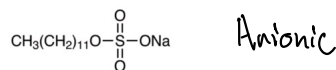


# Exercise 4

1

The following surfactants were dissolved in aqueous solutions:

Sodium dodecyl sulfate (SDS):



Polyoxyethylene (20) sorbitan monolaurate (Tween 20):



The dynamic (i.e. time dependent) interfacial tension between dodecane and aqueous solutions has been measured by the du Noüy ring method. The wetting diameter of the du Noüy ring is 18.7mm.

The measurements resulted in the following data sets:

Dynamic interfacial tensions:

Dodecane – pure water

Dodecane – 4 mM SDS in pure water

Dodecane – 4 mM SDS in 100mM NaCl

Dodecane – Tween20 in pure water

Dynamic force measurements:

Dodecane – Tween20 in 100mM NaCl

All the data were measured at 22°C

- a. Based on the chemical structure for Tween20 given above, what can you say about this compound?

It is a non-ionic surfactant with a relatively large head group. Its CIP is expected to be low due to the large head group taking up a lot of space.

- b. Convert the dynamic force measurements to dynamic interfacial tension. Assume that the du Noüy ring is completely wetted during the measurements.

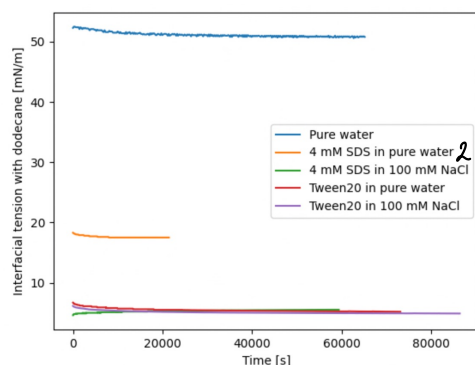
Plot the dynamic interfacial tensions of all five systems in the same figure.

List the main information you can get about the systems from the figure.

→ The data is corrected for this

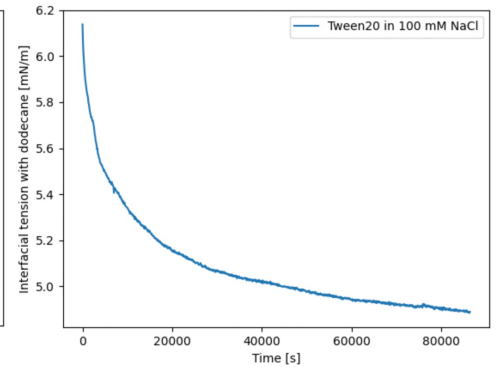
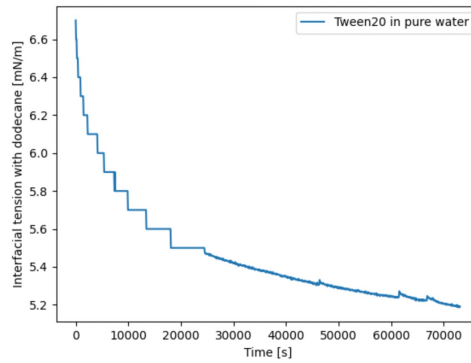
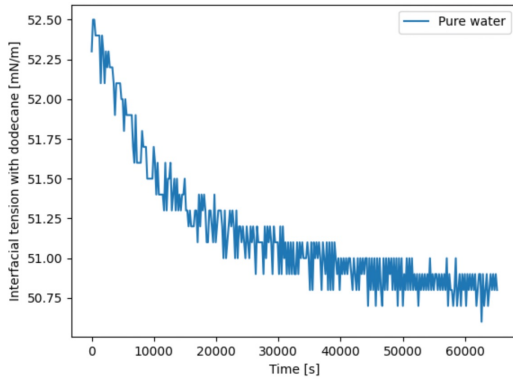
$$F = 2 \cdot 2\pi r \gamma$$

$$\Rightarrow \gamma = \frac{F}{2\pi r} = \frac{\mu\text{N}}{2\pi \frac{18.7}{2} \text{ mm}} = \frac{10^{-3} \text{ mN}}{2\pi \frac{18.7}{2} \cdot 10^{-3} \text{ m}} = \text{mN/m}$$



We can see that adding salt to the solutions decrease the interfacial tension. It decreases more for the anionic surfactant due to the salt ions being able to shield the head groups from the repulsive forces from other head groups. This makes it possible for more surfactants to be at the interface, which reduces the interfacial surface tension.

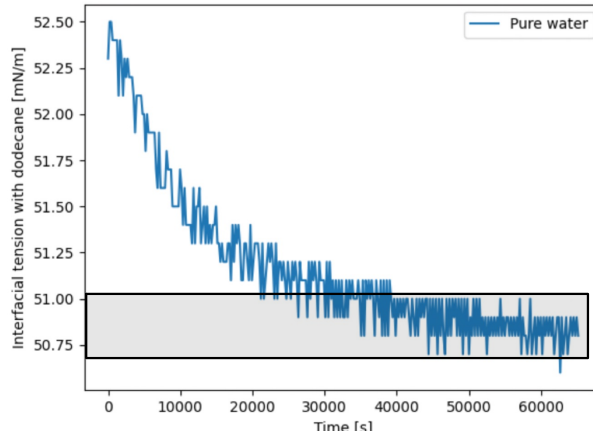
- c. Plot the dynamic interfacial tension of the dodecane-water in one figure.  
Plot the dynamic interfacial tension of the Tween20 system in pure water in another figure.  
Suggest why the interfacial tension decrease.



The interfacial tension decrease due to the system not being in equilibrium at the start of the measurements. The surfactants need time to move to the surface, which is what makes the interfacial tension decrease over time.

- d. Based on the data, estimate the equilibrium interfacial tension for the five systems.

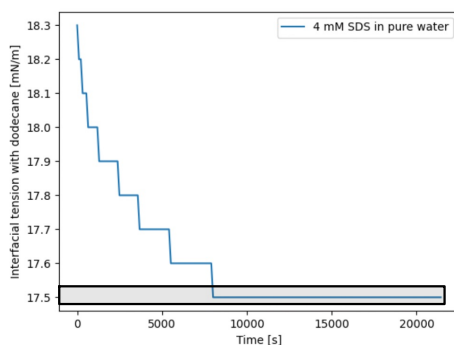
Pure water:



Looking at the final part (I was told to average the final 1/4 of the graph, and not just use the final value)

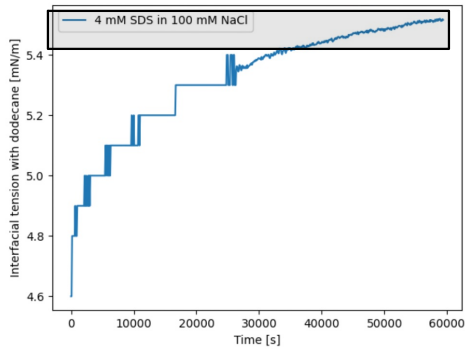
$$\gamma \approx 50.88 \text{ mN/m}$$

4mM SDS:



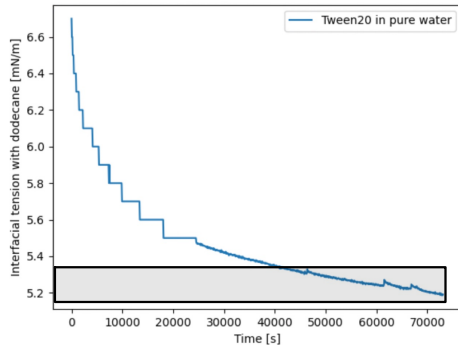
$$\gamma \approx 17.5 \text{ mN/m}$$

4 mM SDS + NaCl



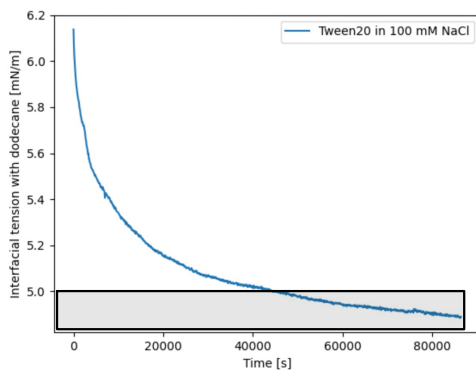
$$\underline{\underline{\gamma \approx 5,5 \text{ mN/m}}}$$

Tween20



$$\gamma \approx 5,23 \text{ mN/m}$$

Tween20 + NaCl



$$\underline{\underline{\gamma \approx 4,9 \text{ mN/m}}}$$

- e. Calculate the surface excess of surfactant for the four surfactant systems. Assume that the variation of interfacial tension with respect to concentration is linear.

Tween20 solutions

For dilute solutions

$$\Gamma_2 = -\frac{1}{RT} \left( \frac{d\gamma}{d \ln c} \right)_T$$

$$\frac{d \ln c}{dc} = \frac{1}{c} \Rightarrow \frac{1}{d \ln c} = \frac{c}{dc}$$

$$\Gamma_2 = -\frac{c}{RT} \left( \frac{d\gamma}{dc} \right)_T$$

Assuming linearity

$$\Gamma_2 = -\frac{c}{RT} \left( \frac{\gamma - \gamma_0}{c - c_0} \right)$$

SDS in water

For a strong electrolyte in a solution without other ions, it will dissociate

$$\Rightarrow \Gamma_2 = -\frac{1}{2RT} \left( \frac{d\gamma}{d \ln c} \right)_T \Rightarrow \Gamma_2 = -\frac{c}{2RT} \left( \frac{\gamma - \gamma_0}{c - c_0} \right)$$

### SDS in NaCl

According to the "P. Mark textbook", adding ions increase the surface excess

$$\Rightarrow \Gamma_2 = -\frac{1}{RT} \left( \frac{dx}{dx_{NaCl}} \right)_T \Rightarrow \Gamma_2 = -\frac{C}{RT} \left( \frac{Y-Y_0}{C-C_0} \right)$$

In the calculations, the pure water systems will be used as a reference.

### SDS in pure water

$$\Gamma_2 = -\frac{C}{2RT} \left( \frac{Y-Y_0}{C-C_0} \right) = -\frac{4 \text{ mM}}{2 \cdot 8,314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot (22+273,15) \text{ K}} \cdot \frac{(17,5 - 50,88) \text{ mN/m}}{(4-0) \text{ mM}} \cdot \frac{1}{\text{m}} = \underline{\underline{6,801 \cdot 10^{-6} \text{ mol/m}^2}}$$

### SDS in NaCl solution

$$\Gamma_2 = -\frac{C}{RT} \left( \frac{Y-Y_0}{C-C_0} \right) = -\frac{4 \text{ mM}}{8,314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot (22+273,15) \text{ K}} \cdot \frac{(5,5 - 50,88) \text{ mN/m}}{(4-0) \text{ mM}} \cdot \frac{1}{\text{m}} = \underline{\underline{1,849 \cdot 10^{-5} \text{ mol/m}^2}}$$

### Tween20 in pure water

$$\Gamma_2 = -\frac{C}{RT} \left( \frac{Y-Y_0}{C-C_0} \right) = -\frac{4 \text{ mM}}{8,314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot (22+273,15) \text{ K}} \cdot \frac{(5,23 - 50,88) \text{ mN/m}}{(4-0) \text{ mM}} \cdot \frac{1}{\text{m}} = \underline{\underline{1,860 \cdot 10^{-5} \text{ mol/m}^2}}$$

### Tween20 in NaCl solution

$$\Gamma_2 = -\frac{C}{RT} \left( \frac{Y-Y_0}{C-C_0} \right) = -\frac{4 \text{ mM}}{8,314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot (22+273,15) \text{ K}} \cdot \frac{(4,9 - 50,88) \text{ mN/m}}{(4-0) \text{ mM}} \cdot \frac{1}{\text{m}} = \underline{\underline{1,874 \cdot 10^{-5} \text{ mol/m}^2}}$$

- f. Calculate the molecular area for the four surfactant systems.
- What is your interpretation when comparing the molecular areas with and without salt for the anionic surfactant?
  - What is your interpretation when comparing the molecular areas with and without salt for the nonionic surfactant?
  - What is your interpretation when comparing the molecular areas for the anionic and nonionic surfactants in pure water?

The area per molecule in the interface can be calculated using  $A = \frac{1}{\Gamma \cdot N_A}$ ,  $N_A = 6,022 \cdot 10^{23} \text{ mol}^{-1}$

### SDS in water

$$A = \frac{1}{6,801 \cdot 10^{-6} \text{ mol/m}^2 \cdot 6,022 \cdot 10^{23} \text{ mol}^{-1}} = 2,44 \cdot 10^{-19} \text{ m}^2 = \underline{\underline{0,244 \text{ nm}^2}}$$

### SDS in NaCl

$$A = \frac{1}{1,849 \cdot 10^{-5} \text{ mol/m}^2 \cdot 6,022 \cdot 10^{23} \text{ mol}^{-1}} = 8,98 \cdot 10^{-20} \text{ m}^2 = \underline{\underline{0,0898 \text{ nm}^2}}$$

### Tween20 in water

$$A = \frac{1}{1,860 \cdot 10^{-5} \text{ mol/m}^2 \cdot 6,022 \cdot 10^{23} \text{ mol}^{-1}} = 8,93 \cdot 10^{-20} \text{ m}^2 = \underline{\underline{0,0893 \text{ nm}^2}}$$

## Tween 20 in NaCl

$$A = \frac{1}{1,874 \cdot 10^{-5} \frac{\text{mol}}{\text{m}^2} \cdot 6,022 \cdot 10^{23} \frac{1}{\text{mol}}} = 8,86 \cdot 10^{-20} \text{ m}^2 = \underline{\underline{0,0886 \text{ nm}^2}}$$

- Comparing SDS in pure water and in NaCl solution, we see that the molecular area is larger in pure water. This means that SDS has a low packing parameter in water solutions, but in salt solutions it can be packed more densely together (due to the extra ions blocking the repulsions between the headgroups)
- Comparing Tween20 with and without salt, there is a slight decrease in the molecular area after adding the salt. This means that the surfactants are packed more densely in the salt solution, but not much. This might be because the salt ions prefer to be in the water solution instead of the surface, which in turn means that there is less room in the bulk. This might cause a tiny increase in the amount of surfactants in the interface.
- The molecular area of SDS is larger than Tween20. This is due to repulsive forces between the head groups in SDS, Tween20 does not have similar repulsive forces. For this reason, Tween20 can be packed more densely than SDS in pure water solutions.

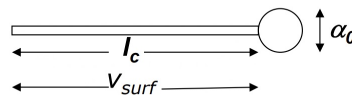
g. Estimate the CPP of the surfactant molecules. What is the possible shape of the surfactant molecules?

$$V_{\text{surf}} (\text{nm}^3) = (0.0274 + 0.0269n) m$$

$$l_c (\text{nm}) = (0.154 + 0.1265n)$$

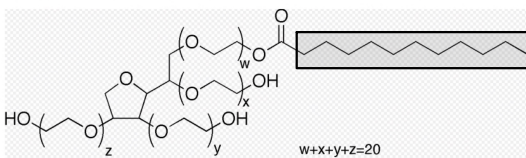
where  $n$  is number of carbon atoms in the hydrocarbon chain and  $m$  is the number of hydrocarbon chains.

Finding  $n$  and  $m$ :



- I'm not sure how to determine  $n$  and  $m$ , but as far as I can tell (from the picture above), we are only looking at the tail group

## Tween 20

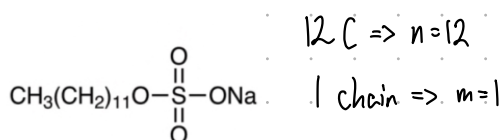


Tail: 11 C (not sure if the  $\text{C=O}$  - carbon should count)  $\Rightarrow n=11$   
Only one tail.  $\Rightarrow m=1$

$$\Rightarrow V_{\text{surf}} = (0.0274 + 0.0269 \cdot 11) \cdot 1 = 0.3233 \text{ nm}^3$$

$$l_c = (0.154 + 0.1265 \cdot 11) = 1,5455 \text{ nm}$$

## SDS



12 C  $\Rightarrow n=12$

1 chain  $\Rightarrow m=1$

$$\Rightarrow V_{\text{surf}} = (0.0274 + 0.0269 \cdot 12) \cdot 1 = 0.3502 \text{ nm}^3$$

$$l_c = (0.154 + 0.1265 \cdot 12) = 1,672 \text{ nm}$$

SDS in water

$$CPP = \frac{V_{surf}}{\alpha_o l_c} = \frac{0,3502 \text{ nm}^3}{0,244 \text{ nm}^2 \cdot 1,672 \text{ nm}} = \underline{\underline{0,858}}$$

SDS in NaCl

$$CPP = \frac{V_{surf}}{\alpha_o l_c} = \frac{0,3502 \text{ nm}^3}{0,0898 \text{ nm}^2 \cdot 1,672 \text{ nm}} = \underline{\underline{2,33}}$$

Tween20 in water

$$CPP = \frac{V_{surf}}{\alpha_o l_c} = \frac{0,3233 \text{ nm}^3}{0,0893 \text{ nm}^2 \cdot 1,5455 \text{ nm}} = \underline{\underline{2,34}}$$

Tween20 in NaCl

$$CPP = \frac{V_{surf}}{\alpha_o l_c} = \frac{0,3233 \text{ nm}^3}{0,0886 \text{ nm}^2 \cdot 1,5455 \text{ nm}} = \underline{\underline{2,36}}$$

Match the 4 systems to the corresponding CPP values

- ☐ A. CPP of 4mM SDS
- ☐ B. CPP of 4 mM SDS with NaCl
- ☐ C. 4mM Polysorbate 20
- ☐ D. 4mM Polysorbate 20 with NaCl

- A. 0.85
- B. 2.33
- C. 2.34
- D. 2.36

$\Rightarrow$

SDS in water, has CPP between 0.5 and 1, this indicates a truncated cone shape of the surfactant molecules. (Flexible bilayers)

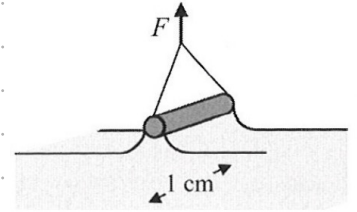
The rest of the molecules has CPP above 1, this indicates that the surfactant molecules has an inverted truncated cone (wedge) shape. (Inverted micelles)

- h. Based on the plots from question b, which system(s) do you think would give the most stable emulsion upon emulsification? Why?

Tween20 in 100 mM NaCl will most likely give the most stable emulsion as it has the lowest interfacial tension with dodecane, meaning that there are less forces that will try to separate the phases.

2

To measure the surface tension of a liquid, a thin cylindrical wire of  $r = 1 \text{ mm}$  radius and  $l = 1 \text{ cm}$  length is dipped horizontally into the liquid (see figure). The force required to pull the wire out of the completely wetting liquid is measured to be  $0,49 \text{ mN}$ . What is the surface tension of the liquid?

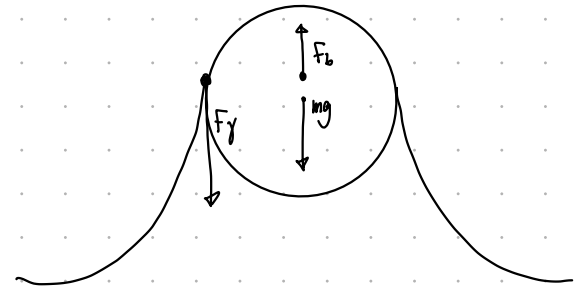


$$F_y + F_b + mg = F_{\text{measured}}$$

Assuming that the measurement corrects for buoyancy and the weight of the wire

$$F_y = 2(l + 2r) \cdot \gamma \cos \theta = 2(l + 2r)$$

$$\gamma = \frac{0,49 \text{ mN}}{2(l + 2r)} = \frac{0,49 \text{ mN}}{2(0,01 \text{ m} + 2 \cdot 10^{-3} \text{ m})} = \underline{\underline{20,42 \text{ mN/m}}}$$



3

A 3M aqueous NaCl solution has the surface excess  $\Gamma_2^1 = -3 \cdot 10^{-11} \text{ mol/cm}^2$ .

Assume that the surface tension of the solution varies linearly with the salt concentration.

$\gamma(\text{water}) = 72,8 \text{ mN/m}$ .

- Calculate the surface tension of the solution.
- Explain why the surface excess is negative

$$\begin{aligned} \text{a)} \quad \Gamma_2 &= -\frac{1}{2RT} \left( \frac{d\gamma}{d \ln c} \right)_T \\ &= -\frac{c}{2RT} \left( \frac{d\gamma}{dc} \right)_T \end{aligned}$$

$$\frac{d \ln c}{dc} = \frac{1}{c} \Rightarrow \frac{1}{d \ln c} = \frac{c}{dc}$$

$$\Gamma_2 = -\frac{c}{2RT} \frac{\gamma - \gamma_0}{c - c_0}$$

Assume  $25^\circ\text{C} = 298 \text{ K}$

$$\Rightarrow \gamma = \gamma_0 - \frac{\Gamma_2(c - c_0)}{c} \cdot 2RT$$

$$\gamma = 72,8 \text{ mN/m} + \frac{3 \cdot 10^{-11} \text{ mol/cm}^2 \cdot (3 - 0) \text{ mol/L}}{3 \text{ mol/L}} \cdot 2 \cdot 8,314 \text{ N/m}^2\text{K} \cdot 293 \text{ K} \cdot (10^2)^2 \frac{\text{cm}^2}{\text{m}^2} \cdot 10^3$$

↑  
convert to milli

$$\underline{\underline{\gamma = 74,29 \text{ mN/m}}}$$

b)

The salt ions are hydrophilic, and in a water solution, they will prefer to be in the bulk phase rather than the surface of the liquid.

This means that the concentration of salt ions at the surface is less than the concentration in the bulk. If the concentration of salt ions at the surface is more than or equal to the concentration in the bulk, the ions will migrate to the bulk.

This is the reason why the surface excess is negative.



4

The table shows CMC and Krafft temperatures for four sulfate esters.

Surfactant	CMC (ppm)	Krafft temperature (°C)
C12	2300	10
C14	700	28
C16	190	44
C18	50	62

Which sulfate ester will you choose if you are interested in cleaning with the minimum amount of surfactant? Why?

We want to choose a sulfate ester with the lowest possible CMC. Which one we can choose depends on the temperature of the water we clean with.

C12 is one of the worst choices in almost all cases, as it is beaten by C14 for most normal temperatures.

For cleaning by hand, C14 might be the best choice, as it has a krafft temperature of 28 degrees, which is not very warm water, and the CMC is lower than for C12.

For a washing machine on the high temperature programs, C18 is the best choice, as for high temperatures, it is able to form micelles, and its CMC is the lowest.