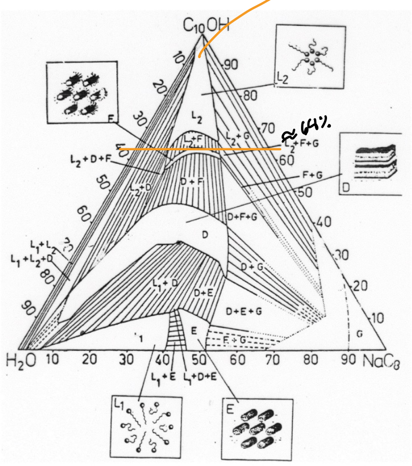
Exercise 5

Exercise 1:
The ternary phase diagram below shows the phase behaviour for the 3-component system of water, anionic surfactant NaC_8 and $C_{10}OH$ (co-surfactant).

a. What is the minimum amount of $C_{10}OH$ that is required to make a pure phase of inverted micelles in the 3-component system?
b. What is the composition of the 3-component system at the solubility limit for $C_{10}OH$ when the co-surfactant is added to a micellar solution with the binary composition of 30% NaC_8 and 70% water?
c. When the total composition of the system is 50% $C_{10}OH$, 24% water and 26% NaC_8 there is a phase separation into a lamellar phase and an inverted hexagonal phase. What is the composition of each of the two phases?

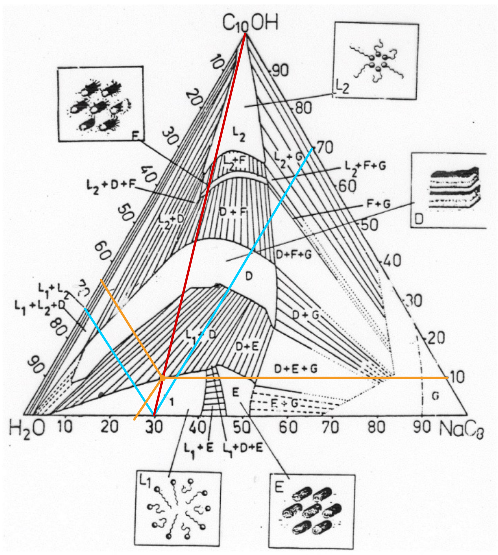
Inverted micelles

a)



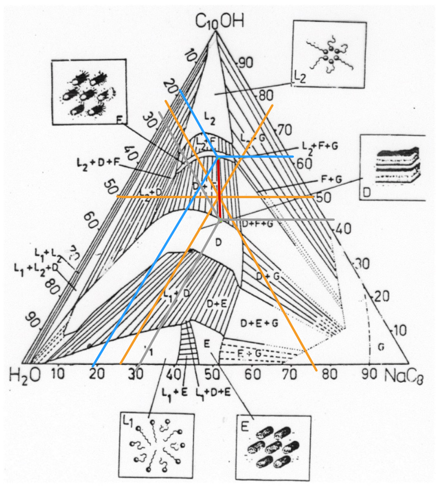
=> 64% $C_{10}OH$

b)



=> 10% $C_{10}OH$, 25% NaC_8, 65% H_2O

c)



- Inverted hexagonal phase: 62% $C_{10}OH$, 19% NaC_8, 19% H_2O
- Lamellar phase: 43% $C_{10}OH$, 30% NaC_8, 27% H_2O

Exercise 2:
The adsorption of four straight-chain fatty acids from n-heptane on Fe_2O_3 particles has been determined experimentally. The experimental adsorption isotherms are well described by the Langmuir isotherm, and the adsorbed amounts of fatty acid at saturation are given in the table below. n_2^s is the amount of fatty acid at saturation, while w is the weight of particles.

Fatty acid	$\left(\frac{n_2^s}{w}\right)_{sat}$ (mol/g)
Acetic acid	3.00×10^{-5}
Propionic acid	2.36×10^{-5}
Palmitic acid	0.91×10^{-5}
Stearic acid	0.81×10^{-5}

The specific surface area for the Fe_2O_3 particles is 3.45 m²/g.

a. Calculate the area per molecule at the saturated surface for each of the fatty acids.
b. Do the results indicate that the adsorbed molecules are in the same 2-dimensional state for all the acids?

a) Langmuir => Monolayer

$$A_{sp} = \frac{V_m N_A}{V_g} A_0 \Rightarrow A_0 = \frac{V_g \cdot A_{sp}}{V_m \cdot N_A} = \frac{1}{\left(\frac{n_2^s}{m_{tot}}\right)_{sat}} \cdot \frac{3,45\ m^2/g}{6,022\cdot 10^{23}\ mol^{-1}} \cdot 10^{20}\ \frac{Å^2}{m^2}$$

$$V_m = \left(\frac{n_2^s}{m_{tot}}\right)_{sat} \cdot 22,414\ L/mol \Rightarrow [V_m] = L/g$$

$$N_A = 6,022\cdot 10^{23}\ mol^{-1}$$

$$A_{sp} = 3,45\ m^2/g$$

$$V_g = 22,414\ L/mol$$

Using the formula above:

Acetic acid: $A_0 = 19.10\ Å^2$

Propionic acid: $A_0 = 24.28\ Å^2$

Palmitic acid: $A_0 = 62,96\ Å^2$

Stearic acid: $A_0 = 70,73\ Å^2$

b) The two last moleculecules have a much larger area per molecule than the first two. Looking at the molecules, the last two have a much longer tail group.

A long tail group have a large steric hindrance, which in turn makes it so that the molecule requires more area than a molecule with a smaller tail group.

Exercise 3:
The BET equation for the adsorption of nitrogen on silica at 77 K can be expressed by the following equation (fitted in the range of reduced pressures between 0.05 and 0.3):

$$\frac{P}{V(P_0 - P)} = 2.85 \times 10^{-4} + 0.0257\frac{P}{P_0}$$

where the units of the slope and of the intercept are g/cm³.

a. Estimate the volume for monolayer coverage V_m (in cm³/g) and the parameter C of the BET equation.
b. Estimate the specific surface area of solid silica (in m²/g) if the area occupied by one nitrogen molecule is $16.2 \times 10^{-20} m^2$.

a) Linearised BET equation - practical form

$$\frac{P}{V(P_0 - P)} = \frac{1}{C \cdot V_m} + \frac{C-1}{C \cdot V_m} \cdot \frac{P}{P_0}$$

Comparing the equations we get that

$$1: \quad \frac{1}{C \cdot V_m} = 2{,}85 \cdot 10^{-4} \ g/cm^3$$

$$2: \quad \frac{C-1}{C \cdot V_m} = 0{,}0257 \ g/cm^3$$

Combining:

$$(C-1) \cdot 2{,}85 \cdot 10^{-4} \ g/cm^3 = 0{,}0257 \ g/cm^3$$

$$C = \frac{0{,}0257 \ g/cm^3}{2{,}85 \cdot 10^{-4} \ g/cm^3} + 1$$

$$\underline{\underline{C = 91{,}18}}$$

Inserting into 1

$$V_m = \frac{1}{2{,}85 \cdot 10^{-4} \ g/cm^3 \cdot 91{,}2}$$

$$\underline{\underline{V_m = 38{,}48 \ cm^3/g}}$$

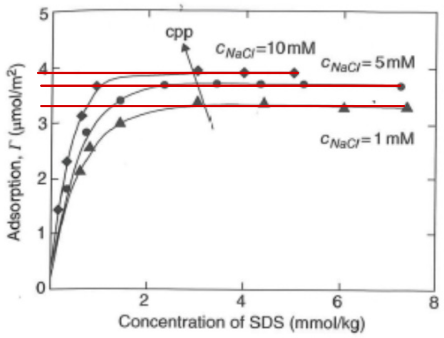
b)

$$A_{sp} = \frac{V_m N_A \cdot A_0}{22414 \ L/mol} = \frac{38{,}48 \ \cancel{cm^3}/g \cdot 6{,}022 \cdot 10^{23} \ \cancel{mol^{-1}} \cdot 16{,}2 \cdot 10^{-20} \ m^2}{22{,}414 \ \cancel{L}/\cancel{mol} \cdot 10^3 \frac{\cancel{cm^3}}{\cancel{L}}}$$

$$\underline{\underline{A_{sp} = 167{,}50 \ m^2/g}}$$

Exercise 4:

The plot below shows the adsorption of the anionic surfactant SDS (from aqueous solution) on a hydrophobic PS latex surface at three different salt concentrations.



a. Calculate in nm² the area occupied per surfactant molecule (at monolayer level).
b. How does CPP change with increasing salt concentration? Why?
c. Estimate the CPP values at the three salt concentrations. Do you expect differences in the micellar structure at the three concentrations? Make reasonable assumptions.
d. How would the adsorption of SDS on PS change with CPP and why?

$N_A = 6{,}022 \cdot 10^{23}\ mol^{-1}$

a) We can calculate this from: $A_0 = \frac{1}{\Gamma \cdot N_A}$

$[A_0] = \frac{1}{\cancel{\mu mol}/m^2 \cdot \cancel{mol^{-1}}} = 10^6 \cancel{m^2} \cdot \left(10^9 \frac{nm}{\cancel{m}}\right)^2 = 10^{24}\ nm^2$

$C_{NaCl} = 1\,mM$: $\Gamma \approx 3{,}3\ \mu mol/m^2$

$\underline{\underline{A_0 = 0{,}503\ nm^2}}$

$C_{NaCl} = 5\,mM$: $\Gamma \approx 3{,}7\ \mu mol/m^2$

$\underline{\underline{A_0 = 0{,}449\ nm^2}}$

$C_{NaCl} = 10\,mM$: $\Gamma \approx 3{,}9\ \mu mol/m^2$

$\underline{\underline{A_0 = 0{,}426\ nm^2}}$

b) The CPP increases with increasing salt concentration. This is because the extra salt ions blocks the repulsions between the head groups of the SDS, which allows the molecules to be packed more densely, this means that the area per molecule decreases, which in turn increases CPP.

c) Using the formula from the previous exercise:

$V_{surf} \approx (0{,}0274 + 0{,}0269 \cdot 12) \cdot 1 = 0{,}3502\ nm^3$

$l_c = (0{,}154 + 0{,}1265 \cdot 12) = 1{,}672\ nm$

$CPP = \frac{V_{surf}}{A_0 \cdot l_c}$

$\underline{\underline{C_{NaCl} = 1\,mM : \ CPP = 0{,}416}}$

$\underline{\underline{C_{NaCl} = 5\,mM : \ CPP = 0{,}466}}$

$\underline{\underline{C_{NaCl} = 10\,mM : \ CPP = 0{,}492}}$

At the lowest concentration, the CPP coincides with a spherical micelle. As the salt concentration increases, the CPP approaches 0.5 which coincides with cylindrical micelles. I expect the structure to become more oval, and become something closely related to a cylinder as the salt concentration increases.

d)

As the SDS molecules can be packed more densely, the adsorption will increase. This is because the molecules require less room between themselves, allowing more molecules per area. In addition, increasing the CPP, can make a micelle or bilayer structure across the surface, increasing the CPP also makes the surfactants to create more compact structures, which increases the amount of SDS adsorbed.