Problem 31: Surfactant Micelles

Surfactants, amphiphilic molecules with a hydrophilic head group and a hydrophobic tail, have been used for washing since 2500 B.C. In aqueous solutions, they self-assemble, i.e. organize spontaneously into aggregated structures, so-called micelles. This concept of structuring is not only widely found in nature and in many every-day applications but it has recently become of interest for the controlled design of more complex structures in the nanometer size range as well.

Self-assembly takes place above a certain concentration, the so-called critical micelle concentration (cmc).

Micellar aggregates are separated from solutions of varying initial surfactant concentrations c_0, and the surfactant concentration in the remaining solution c_1 is determined.

$c_0 \cdot (gL^{-1})^{-1}$	0.5	0.75	1	1.5
$c_1 \cdot (gL^{-1})^{-1}$	0.5	0.75	0.75	0.75

31.1 What is the cmc of the surfactant?

31.2 Why do amphiphilic molecules aggregate in aqueous solution?

### 31.3 Sketch the osmotic pressure as a function of surfactant mass concentration and indicate the cmc.

There is the general aggregation equilibrium of N molecules of A in an aggregate B with the equilibrium constant K. c(A) and c(B) are the molar concentrations of monomers and aggregates, and c_0 the total concentration of monomers in the solution.

31.4 a) Determine a relationship between K, c_0, N and c(A).

N = 50 and K = 10^{90} $L^{49}mol^{-49}$ are values of self-assembly of a typical surfactant.

b) Calculate c_0, c(A) and c(B) if the fractions f = c(A)/c_0 of surfactant molecules present as monomers are 0.9999, 0.5, 0.01, 10^{-3} and 10^{-4} respectively.

Depending on the surfactant architecture, micelles can have different shapes. In this context, surfactant molecules are characterized by the area a of their head group, the length l of the molecule and the volume v of the molecule, being combined in the so-called packing parameter $v \cdot (a \cdot l)^{-1}$.
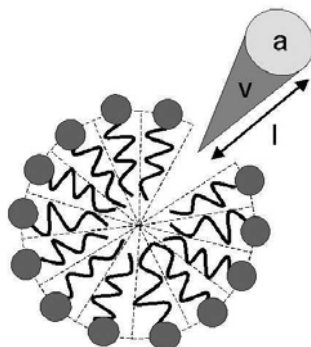
31.5 Based on geometrical considerations, determine conditions for the packing parameter so that the amphiphile can form:

      a) **spherical aggregates**

      b) **cylindrical aggregates (disregard end caps)**

      c) **flat aggregates (bilayers)**

for sodium dodecyl sulfate (SDS):
$v = 0.35$ nm^3, $a = 0.57$ nm^2 and the (maximum "liquid") length $l = 1.67$ nm

**31.6 a) Which shape do SDS micelles in aqueous solution have? Calculate.**
(Hint: Are the ideal values calculated in 31.5 lower or upper values?)

b) What do you think will form after the addition of base?

Problem 32: Self-assembly of Amphiphilic Block Copolymers

Block copolymers are polymers consisting of two chemically different polymeric blocks that are covalently attached one to the other. Amphiphilic block copolymers consist of a hydrophilic and a hydrophobic block. Such molecules behave in analogy to low-molecular mass surfactants, but they can form larger aggregates in a size range from 5 nm to several µm, so that they allow further applications.

Block copolymers can vary in the relative lengths of their blocks. In the illustration below, the hydrophobic parts are black and the hydrophilic parts are grey. Note that the polymers are flexible chains.

            I   II
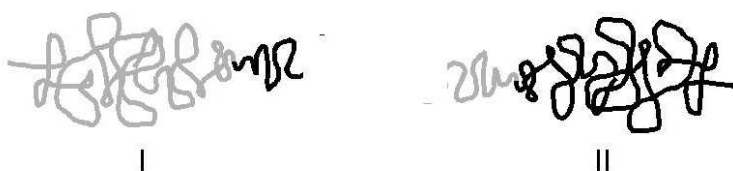
32.1 Which of these block copolymers do you expect to form spherical micelles, vesicles (bilayers), or which of them will show phase separations when given into a) water and b) toluene?

Two block copolymers consisting of poly(vinylpyridine) (PVP) and polystyrene (PS), PVP$_{23}$-b-PS$_{122}$ (**A**) and PVP$_{45}$-b-PS$_{122}$ (**B**), form "inverse" spherical micelles in toluene (PVP inside, PS outside). Aggregation numbers are determined via membrane osmometry. The solutions contain only micelles while monomers have been removed (which is possible for block copolymers). Here, we regard the solutions as ideal so that the van´t Hoff equation is valid:

$$\Pi V = nRT.$$

Π is the osmotic pressure.

The soutions of **A** and **B**, both with concentrations of of c = 8.000 gL^{-1} are analyzed. The heights of the solvent columns above the solvent in osmotic equilibrium with the polymer-containing solutions are 11.02 mm for polymer **A** and 2.48 mm for polymer **B.**
(ρ(solvent) = 0.866 g·cm^{-3} and T = 298.15 K).

32.2 What are the aggregation numbers N of the two samples?

Colloidal metal particles are of high interest due to their special optical, electric and magnetic properties, applications as catalysts etc. Block copolymer micelles in organic solvent can be used as confined reaction compartments ("nanoreactors") for the preparation of such small metallic particles.

Two polymers **C** and **D** in toluene have the following properties
(R is the micelle radius and N is the aggregation number):

$$\textbf{C}: \quad PVP_{123}\text{-b-}PS_{118} \quad \text{with} \quad R = 25 \text{ nm, } N = 310$$

$$\textbf{D}: \quad PVP_{63}\text{-b-}PS_{122} \quad \text{with} \quad R = 21 \text{ nm, } N = 123$$

Tetrachlorogoldacid-tri-hydrate (HAuCl$_4$·3H$_2$O, "gold acid") is added to the polymer solution and the mixture is stirred for several hours. While the gold compound is normally insoluble in toluene, the yellow colour of the solution indicates that it has solubilized within the micelles.
Two experiments are made with each polymer: a) the addition of 0.01 g and b) the addition of 0.05 g of HAuCl$_4$·3H$_2$O to 10 mL of polymer solution (c(polymer) = 10 gL^{-1}). In all cases, the total amount of added HAuCl$_4$·3H$_2$O is solubilized.
In a second step, a reducing agent such as hydrazine or sodium borohydride (sodium boranate) is added. The solution turns red or blue indicating the formation of metallic gold nanoparticles.
The micelle size does not change after the solubilization of HAuCl$_4$·3H$_2$O and reduction.

32.3 Write down the reaction equations for the two reductions.

It is observed that one gold particle is formed in each micelle. Gold particles are spherical and show a narrow size distribution. There is no redistribution of gold during the process of particle formation, but HAuCl$_4$·3H$_2$O that has solubilized inside one micelle (by uniform distribution among the micelles) forms one particle.
ρ(Au) = 19.3 g cm^{-3}

32.4 Which gold particle diameters do you expect for the four experiments with the two polymers and the two given amounts of added gold acid ?

32.5 Why is one gold particle per micelle preferentially formed instead of multiple smaller particles inside one micelle ?

Problem 33: Microemulsions

Small polymer particles are of interest for many reasons, ranging from their use as coatings, effective support for catalysts due to their large surface area, to more "smart" applications such as biomedical carriers.

Well-defined spherical polymer particles within the size range from 10 nm to 200 nm can be synthesized by the method of microemulsion polymerization: a microemulsion consists of small oil droplets having surfactant layers on their surfaces and being dispersed in water. The system is in thermodynamic equilibrium. By using a monomer as an oil phase polymerization takes place resulting in small polymer particles in the volume of the initial oil droplet. The size of the droplets is controlled by the ratio of surfactant to oil.
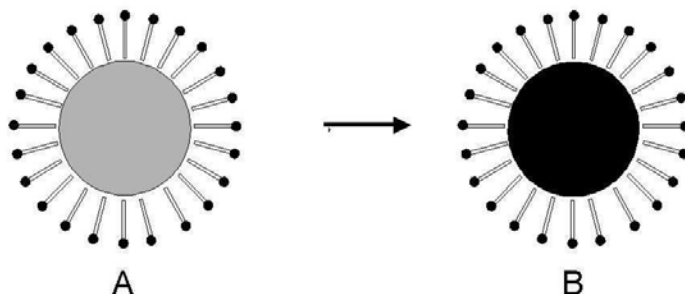
A: microemulsion droplet with liquid monomer inside
B: polymerized microemulsion: polymer particle covered with surfactant

You would like to synthesize small polystyrene spheres, using a mixture of styrene (vinylbenzene) and p-divinylbenzene (mass ratio 10:1) as a monomer and cetyltrimethylammoniumbromide as a surfactant. A hydrophobic starter is added so that a radical polymerization takes place within the droplets.

Density of monomer, polymer and surfactant: $1 g \cdot cm^{-3}$
Length of surfactant b = 2 nm.
The surfactant is assumed to be a dense layer on the oil surface where hydrocarbon tails do not penetrate the oil phase.

33.1 What is the function of p-divinylbenzene?

33.2 Calculate the mass ratio of surfactant to monomer you have to use in order to produce polymer particles with sizes of d = 20 nm, d = 40 nm and d = 120 nm (d = diameter of the particle without surfactant).

33.3 Calculate the total surface area of 1 g of polystyrene particles (after removal of the surfactant) for the three samples.

You would like to produce particles with an enzyme function by incorporating an enzyme into the polymer particle.

33.4 Which kind of enzyme would you choose for this purpose?

|	true	false
a) a hydrophilic enzyme	☐	☐
b) a hydrophobic enzyme	☐	☐
c) an amphiphilic enzyme with the active center in the hydrophilic part	☐	☐
d) an amphiphilic enzyme with the active center in the hydrophobic part	☐	☐

Problem 34: Silica Nanostructures

Porous silicates are important as ion exchangers, molecular sieves and catalysts in petrochemistry. Classic zeolites are silicates having defined channels with diameters of 0.4 nm to 1.5 nm. Materials with larger pore diameters are needed to accept larger molecules and make them react. Surfactants or block copolymers are used as "templates" for the production of amorphous silicates with pore sizes of 1.6 nm to 50 nm.
The production of SiO_2 is carried out according to the following equation:

$$A \xrightarrow[\text{(H}_2\text{O, pH}=2)]{-4\,CH_3OH} B \xrightarrow{-2\,H_2O} SiO_2$$
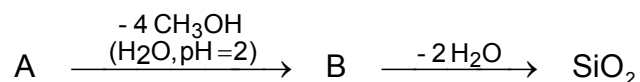
34.1 Write down the formulas of A and B.

When this reaction is carried out in the presence of surfactants, silica-organic hybrid materials form. The organic component can be removed by combustion or dissolution and pure minerals with pores can be obtained. In the following example, X-ray scattering detects hexagonal pore structures.
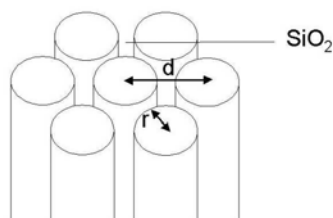
The table contains the scattering angles 2θ of the first diffraction peaks (wavelength $\lambda = 0.15$ nm) and the relative mass loss w after the removal of the surfactants.

surfactant	2θ	w
$C_{12}H_{25}N(CH_3)_3Cl$	2.262°	37.2 %
$C_{14}H_{29}N(CH_3)_3Cl$	2.046°	47.6 %
$C_{16}H_{33}N(CH_3)_3Cl$	1.829°	54.4 %
$C_{18}H_{37}N(CH_3)_3Cl$	1.719°	60.0 %

$\rho\,(SiO_2) = 2.2$ g·cm^{-3}, ρ(surfact.) = 1 g·cm^{-3}

34.2 a) Calculate the pore distance d using Bragg`s law for the diffraction peaks.
   b) What are the radii r of the pores? Calculate.
   (disregard possible end caps of cylindrical pores)

In another experiment, hexagonal pore structures form by using surfactants of different chain lengths but the same surfactant mass concentrations.

34.3 How do a) pore diameter and b) pore distance depend on the tail lengths of the surfactants? Answer qualitatively and explain.

The specific surface A_{sp} (surface area per mass) of porous materials can be determined by gas adsorption experiments.
The Langmuir adsorption isotherm can be derived from a kinetic consideration of adsorption and desorption in a monolayer.

34.4 a) Show that the relation between pressure p, volume of adsorbed gas V_{ads} and maximum adsorbable volume V* can be expressed as

$$\frac{p}{V_{ads}} = \frac{1}{KV*} + \frac{p}{V*} \qquad (K= constant)$$

Concerning the adsorption of N_2 to 1 g silica material at 77 K, the following volumes as functions of pressure are adsorbed. The volumes have been normalized to standard pressure. The area of one adsorbed N_2 molecule is $A(N_2) = 0.16$ nm^2.

p ⟍ surfactant	1.30 ·10⁵Pa	2.60 ·10⁵Pa	4.00 ·10⁵Pa	5.30 ·10⁵Pa	6.60 ·10⁵Pa	8.00 ·10⁵Pa
$C_{12}H_{25}N(CH_3)_3Cl$	4.6	8.2	11.9	14.5	16.7	19.0
$C_{14}H_{29}N(CH_3)_3Cl$	6.0	11.5	16.0	19.0	23.1	25.5
$C_{16}H_{33}N(CH_3)_3Cl$	7.8	14.0	19.0	24.0	28.0	31.3
$C_{18}H_{37}N(CH_3)_3Cl$	8.1	14.7	20.8	25.5	29.0	34.0

(volumes V_{ads} in cm^3)

34.4 b) Calculate the specific surfaces A_{sp} (m^{2}g^{-1}) of the materials.

Imagine you don't have an x-ray machine to measure the pore distances in 34.2.

34.4 c) Calculate the pore radii from mass loss (in 34.2) and the specific surfaces A_{sp} determined in b) _without_ using the pore distance d.