Homework Week 10:
Exercises: 22-23

Material to study for next week:
Lecture notes

List of constants:

The dielectric permittivity of free space: $\varepsilon_0 = 8.85 \times 10^{-12}\ C^2\ J^{-1}\ m^{-1}$
Avogadro constant: $N_A = 6.022 \times 10^{23}\ mol^{-1}$
Gas constant: $R = 8.314\ J\ K^{-1}\ mol^{-1}$

Interfaces

We have seen in the lecture that the change in interfacial tension is given by the Gibbs adsorption equation (under constant pressure and volume, P, V):

$$d\gamma = -\frac{S_\sigma^{(1)}}{\sigma} dT - \sum_{i=2}^{b} \Gamma_i^{(1)} d\mu_i \qquad (1)$$

Here, S is the entropy. Eq. (1) indicates that the surface excess is defined with respect to a vanishing surface excess of component 1 (usually the main phase), σ is the surface area. When σ is used as a subscript it indicates that we are dealing with a surface property. Γ is the surface excess of component *i*, *b* is the number of components in the system and $d\mu_i$ is the change in chemical potential of component i. In the following exercises we are going to examine the use of this equation.

22.
Suppose we have a single component system that consists of a rubber band. Rubber is a polymer that can exist in a variety of coiled or stretched structures. The chemical unit is as follows:

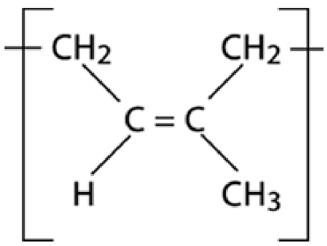

Figure 1: The chemical structure of a rubber monomer.There are >10000 monomers in a single polymer strand.

a. Assuming that our rubber band is infinitely thin, show with the aid of Eq. 1 that when we stretch it the temperature of the rubber increases. Consider what happens to the polymer molecules when we stretch it, and to each of the components in the Gibbs adsorption equation. You need to make an assumption here.

Now let us consider a 2-component system, for example an aqueous solution under constant temperature.

b. Using the definition of the chemical potential (per mole), show that Γ_2 obeys the expression:

$$\Gamma_2^{(1)} = -\frac{c_2}{RT}\left(\frac{d\gamma}{dc_2}\right)_T \qquad (2)$$

c. If a substance (for example dodecanol, $C_{12}H_{25}OH$) lowers γ, what happens to the surface excess if we add it to a bulk liquid (that is in equilibrium with its vapor)? Use the answer of b to clarify your answer.
d. If a substance (for example $MgSO_4$) increases γ, what happens to the surface excess if we add it to a bulk liquid (that is in equilibrium with its vapor)? Use the answer of b to clarify your answer.
e. SDS is an ionic surfactant with the following structure:

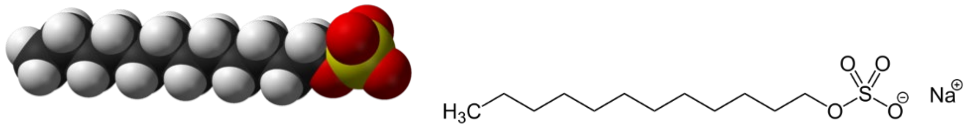

Figure 2: The chemical formula of SDS, with space filling and drawn structures.

By adding SDS to water, we create a three-component system. Do again the derivation of 33c but now use the condition of electric neutrality to show that for this case:

$$\Gamma_{DS-}^{(1)} = -\frac{c_2}{2RT}\left(\frac{d\gamma}{dc_{DS-}}\right)_T \qquad (3)$$

f. Show that the unit of Γ is mol/m^2. How is this possible considering that the interfacial volume should be finite?

23.
The interfacial energy or tension of the water-decane interface was measured at 20 °C for different concentrations of sodium dodecyl sulfate in 2 different aqueous solutions: one with 100 mM NaCl and a second one without NaCl. The data is shown below in Figure 3. The concentration where the surface tension has reached its lowest value is called the critical micelle concentration (cmc) and is assumed to correspond to the point at which the surface is fully covered. For these cases the cmc is 1.4 mM and 8 mM respectively.

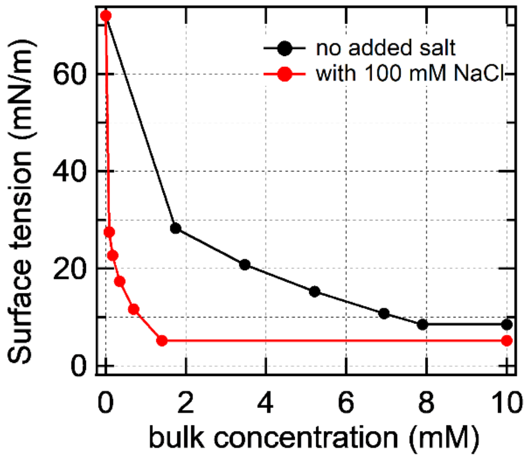

Figure 3: *Surface tension vs bulk concentration of added SDS for the decane-water system.*

a. Determine the surface density and projected molecular area of DS^- at the cmc, with and without 100 mM NaCl. Note that areas obtained in this way constituted the first experimental estimation of molecular size in the early 1900's.
b. The interfacial tension of the pure decane / water interface is 48.2 mN/m. Which interactions between SDS and water/oil can contribute to the lowering of the surface tension? If there is more than one relevant interaction, list them in order of importance and state what influence it could have on the structure. How will the SDS be situated on the interface?
c. Compare the values of γ at ~1-2 mM of added SDS. Explain why the value of γ is different.