Exercise in physical chemistry: Surface tension and adsorption

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Overview

This exercise is designed to acquaint the students with the basic principles of surface chemistry. It is suitable for advanced undergraduate students.

Surface chemistry provides the key conceptual framework for both life- and nanoscience, where, following the decreased size of the systems under study, the properties are extensively determined by the interfacial chemistry of such systems. The rapid growth of these fields have created a demand for chemists with good knowledge of surface chemistry. Yet, surface chemistry is also one of the cornerstones in a wide variety of industries, ranging from pharmaceutical, cleaning and food industry to printing and paper industry.

The students measure the surface tension of various concentrations of aqueous SDS (Sodium Dodecyl Sulphate) and use this information to study adsorption phenomena. The exercise requires about 2 hours of laboratory time, and approximately 4-8 hours for the data-analysis and preparation of a laboratory report.

Theoretical background

The change in internal energy of a system can be written as (first law of thermodynamics)

$$dU = dq + dW, \tag{1}$$

where dq and dW are the energy transferred as heat to, and the work done on the system, respectively. If only work resulting in changes of volume is considered, equation 1 becomes

$$dU = TdS - pdV \tag{2}$$

where T is the temperature, dS is the change in entropy, p is the pressure and dV is the change in volume.

Consider a system of two phases with definite boundary, i.e. an interface, with area A. Obviously, the internal energy of such systems must also contain the energy pertaining to the interface. The work done to create new surface area of infitesimal size, dA, is given by

$$dW = \gamma dA \tag{3}$$

where dA is the change in area and the constant γ is the surface tension. The latter relates the area change to the change in free energy. When this term is taken
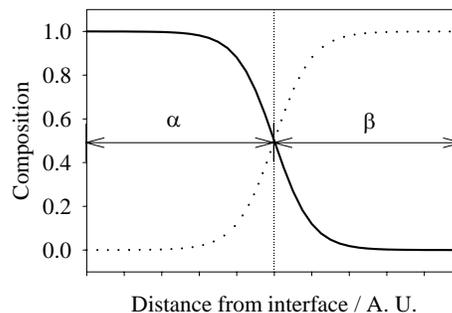

Figure 1: In the Gibbs dividing plane model the bulk properties of the two phases are extrapolated to the imaginary interfacial plane. The location of the dividing plane is chosen so that the excess of the solvent(s) is zero.

into account together with the chemical potential of the species in the interfacial region the change in the internal energy of the interface due to work on the system takes the following form (compare with equation 2)

$$dU^\sigma = TdS^\sigma - pdV^\sigma + \gamma dA + \sum_i \mu_i dn_i^\sigma \quad (4)$$

where i refers to all species in the interfacial region and σ denotes the interface. On the other hand, if we write the internal energy as

$$U = TS^\sigma + pV^\sigma + A\gamma + \sum n_i^\sigma \mu \quad (5)$$

the differential can be written as

$$dU^\sigma = TdS^\sigma + S^\sigma dT - pdV^\sigma - V^\sigma dp \quad (6)$$
$$+ \gamma dA + Ad\gamma + \Sigma\mu_i dn_i^\sigma + \Sigma n_i^\sigma d\mu_i$$

Subtracting equation 4 from 6 gives

$$S^\sigma dT + V^\sigma dp + Ad\gamma + \sum_i n_i^\sigma d\mu_i = 0 \quad (7)$$

This is the Gibbs-Duhem equation for the surface phase. At constant pressure and temperature this equation is further simplified to

$$Ad\gamma + \sum_i n_i^\sigma d\mu_i = 0 \quad (8)$$

The boundary between two adjacent bulk phases in equilibrium is often not sharp. That is, the local concentration of each component going from one phase to the other is not a step function but changes gradually. The interfacial region is that part of the system where the local concentrations deviate from either bulk concentrations. Equation 8 contains the amounts of all species, including the solvent, in the considered system. However, a unique definition of these is not possible since a clear boundary between the surface phase and the bulk phase cannot be defined.

A customary convention is to allocate an interface, the so-called dividing plane, at one arbitrary position. The two-phase system is thus split up in two bulk phases and an infinitesimal thin "membrane" separating both phases. The bulk values of quantities, e.g. the concentration, are extrapolated up to the dividing plane and all the deviations from the actual values, i.e. excess amounts, are assigned to the membrane. The excess amounts depend on the choice of the dividing plane.

In the Gibbs adsorption model, the position of the dividing plane is chosen so that the interfacial plane is located where the excess of solvent is zero, i.e.

$$\int_0^\infty (n_0(x) - n_0^v)dx + \int_{-\infty}^0 (n_0(x) - n_0^b)dx = 0 \quad (9)$$

where the subscript 0 refers to the solvent and b and v to the bulk and vapor phases, respectively. x is the distance from the interface.

The surface excess concentration Γ_i is defined as,

$$\Gamma_i = n_i^\sigma / A \quad (10)$$

Consider a a dilute solution of surfactant in water. Subscript 1 refers to the surfactant. Equation 8 can now be written on the following form, taking into account that the surface excess of solvent is zero,

$$\Gamma_1 = -\frac{d\gamma}{d\mu_1} \quad (11)$$
$$\approx -\frac{1}{RT}\frac{d\gamma}{d\ln c_1/c^*}$$

This equation relates the surface excess to the concentration and surface tension. Relationship for how the surface tension varies with the applied concentration can be derived by choosing an adsorption isotherm that relates the surface excess to the applied concentration, e.g. the Langmuir equation

$$\Gamma_1 = \frac{1}{A_m}\frac{K_1 c_1}{1 + K_1 c_1} \quad (12)$$

where A_m is the cross sectional area of the surfactant. The derivation is left as an exercise.

Measurement principle

The surface tension measurement used in AquaPi is based on the Du Nouy / maximum pull force method, i.e. the maximum force exerted by the surface tension is recorded as the probe is withdrawn from the
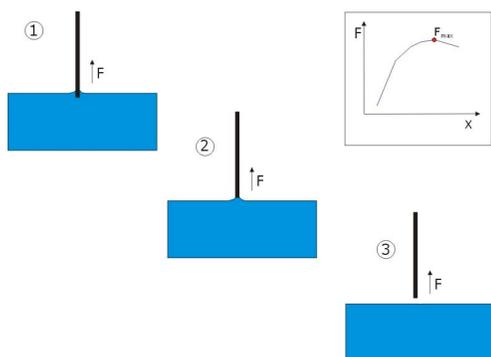
Figure 2: Phases of a measurement.

solution. Figure 2 shows the progression of the measurement.

The force acting on the probe can be divided into two components, buoyancy stemming from the volume displaced by the probe, and the mass of the meniscus of the liquid adhering to the probe. The latter is in equilibrium with the surface tension force, i.e.

$$2\pi r_\mathrm{p} \gamma \cos\theta = m_\mathrm{m} g \qquad (13)$$

where, r_p is the radius of the probe, γ is the surface tension and m_m the weight of the meniscus under the probe. In the situation considered here the volume displaced by the probe is included in the meniscus. θ is the contact angle between the probe and the solution that is measured, and is negligible for the majority of solutions with Kibron's probes. Thus, the force measured by the balance is given by

$$F_\mathrm{p} = m_\mathrm{m} g + F_\mathrm{buoyancy} = 2\pi r_\mathrm{p} \gamma + F_\mathrm{buoyancy} \qquad (14)$$

where, F_p is the force acting on the probe and F_buoyancy is the force due to buoyancy. At the point of detachment the volume of the probe immersed in the solution vanishes, and thus, also the buoyancy term. This is observed as a maximum in the force

curve, which relates to the surface tension through

$$\gamma = \frac{F_\mathrm{max}}{2\pi r_\mathrm{p}} \qquad (15)$$

The above derivation is only approximate.

Experimental

Clean the probe with a propane/butane torch. Calibrate the instrument by putting 3.0 ml of distilled water in a cuvette, and hold down `CAL` and press `MEAS`. The instrument will now show values between -38 and 38 for air and water respectively. The calibration takes 5-10 minutes and is ready when a value close to zero is shown.

10 ml of 50 mM SDS solution and 12 cuvettes are needed for the experiment. Please remember throughout the experiments that surface chemistry is very sensitive to surface active contaminants.

Prepare 12-concentrations of sodium dodecyl sulfate by the following procedure: Fill the cuvettes 12 and 11 with 3 ml of 50 mM SDS solution. Apply 1.5 ml of water to cuvettes 1-10. Transfer 1.5 ml from cuvette 11 to cuvette 10, and mix the contents by aspirating and dispensing. This "transfer and mix" procedure is repeated until cuvette 1 have been reached, halving the concentration in each step. 1.5 ml is disposed from cuvette 1 and 1.5 ml of water is added to cuvettes 1-11. Mix the contents of the cuvettes starting from cuvette 1 to avoid carry-over. Thus, a concentration series with $50 \times 2^{n-12}$ mM is obtained were n corresponds to the cuvette number, i.e n ranges from 1 to 12. The dilution series is then allowed to equilibrate for 10 minutes prior to the measurements. The measurements are carried out starting from cuvette 1 advancing to cuvette 12, i.e in order of increasing concentration, eliminating the need of cleaning the probe between the samples.

Data analysis and exercises

1. Plot the surface tension on a logarithmic concentration scale. Surface tension values measured versus log concentration should yield a plot similar to the plot shown in Figure 3.

2. Explain the concept of micelles and why the surface tension remains constant above the critical micelle concentration (CMC). Why is the transition sharp?

3. Derive the surface tension vs. concentration relationships for the Langmuir and Freundlich isotherms. Assume that the concentration of free surfactant is equal to the total surfactant concentration below CMC and constant above CMC. Fit your data.

4. Compare the cross-sectional area obtained from the Langmuir adsorption model with molecular size and structure.
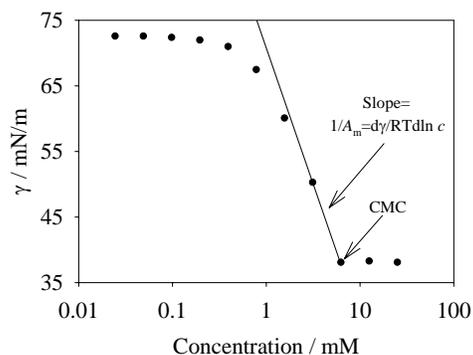

Figure 3: Surface tension of SDS in water as a function of concentration