III. SURFACE PROPERTIES

III.A. SURFACE TENSION

GOAL: _To investigate the influence of the solution concentration and/or the kind of the solute on the surface tension_

INTRODUCTION

Liquids tend to adopt shapes that minimize their surface area, for then the maximum numbers of molecules are in the bulk and hence surrounded by and interacting with neighbors. Droplets of liquids therefore tend to be spherical, because a sphere is the shape with the smallest surface-to-volume ratio.

However, there may be other forces present that compete against the tendency to form this ideal shape, and in particular gravity may flatten spheres into puddles or oceans. Surface effects may be expressed in the language of Helmholtz and Gibbs energies.

The link between these quantities and the surface area is the work needed to change the area by a given amount, and the fact that the dA and dG are equal (under different conditions) to the work done in changing the energy of the system. The work needed to change the surface area, σ of a sample by an infinitesimal amount $d\sigma$ is proportional to $d\sigma$ and we write:

$$dw = \gamma \cdot d\sigma$$

γ is called **_the surface tension_**; its dimensions are [energy/area] and its units are typically joules per meter squares [J/m^2]. However, values of γ are usually reported in newtons per meter [N/m]. The work of surface formation at constant volume and temperature can be identified with the change in the Helmholtz energy, and we can write:

$$dA = \gamma \cdot d\sigma$$

Because the Helmholtz energy decreases if the surface area decreases surfaces have a natural tendency to contract. This is more formal way of expressing what was already described.

The minimization of the surface area of the liquid may results in the formation of a curved surface, as in the bubble. Generally there are two consequences of curvature, and hence of the surface tension, that are relevant to the properties of the liquids. One is that the vapour pressure of a liquid depends on the curvature of its surface. The other is the capillary rise (or fall) of liquids in narrow tubes.

The surface tension can be measured quantitatively by various methods, we can measure the height to which the liquid rises in a capillary tube, we can pulling a wire ring from the surface of a liquid, we can weigh drops which fall from a special glass tip ect.

The contact angle

In many cases there is a nonzero angle θ_c between the edge of the meniscus and the wall. The origin of the contact angle can be traced to the balance of forces at the line of contact between the liquid and the solid. If the solid-gas or the solid-liquid, liquid-gas surface tensions are denoted γ_{sg}, γ_{sl}, γ_{lg} respectively the horizontal forces are in balance if:

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} + \theta_c$$
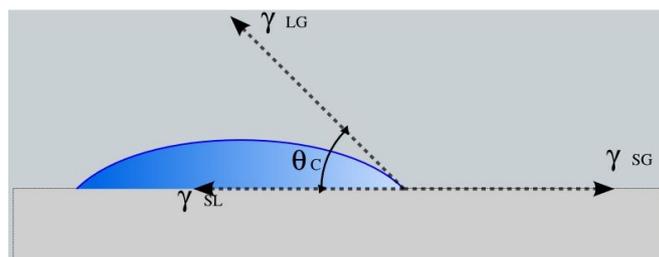
This expression solves to:

$$\cos\theta_c = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}$$

if we note that the work of adhesion of the liquid to the solid (per unit area of contact) is

$$w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}$$

Finally we can consider that:

$$\cos\theta_c = \frac{w_{ad}}{\gamma_{lg}} - 1$$

now one can see that the liquid completely 'wets' the surface fully, corresponding to $\theta_c > 0$, when $w_{ad} > 2\gamma_{lg}$. The liquid does not wet the surface ($\theta_c > 90^o$) when $w_{ad} < \gamma_{lg}$. For mercury in contact with glass $\theta_c = 140^o$ which corresponds to $w_{ad}/\gamma_{lg} = 0.23$, indicating a relatively low work of adhesion of the mercury bto glass on account of the strong cohesive forces within mercury.

Influence of temperature on surface tension

Surface tension depends on temperature; for that reason, when a value is given for the surface tension of an interface, temperature must be explicitly stated. The general trend is that surface tension decreases with the increase of temperature, reaching a value of 0 at the critical temperature. The correlation between the temperature and the force tension is described by Eötvös rule. There are only empirical equations to relate surface tension and temperature:

$$\gamma V^{2/3} = k(T_C - T)$$

V is the molar volume of that substance

T_C is the critical temperature

k is a constant for each substance.

Surface tension in everyday life

Some examples of the effects of surface tension seen with ordinary water:

* **Beading** of rain water on the surface of a waxed automobile. Water adheres weakly to wax and strongly to itself, so water clusters in drops. Surface tension gives them their near-spherical shape, because a sphere has the smallest possible surface area to volume ratio

- **Formation of drops** occurs when a mass of liquid is stretched. Water adhering to the faucet gaining mass until it is stretched to a point where the surface tension can no longer bind it to the faucet. It then separates and surface tension forms the drop into a sphere. If a stream of water were running from the faucet, the stream would break up into drops during its fall. This is because of gravity stretching the stream, and surface tension then pinching it into spheres

Surface tension has a big influence on other common phenomena, especially when certain substances, surfactants, are used to decrease it:

Soap Bubbles have very large surface areas for very small masses. Bubbles cannot be formed from pure water because water has very high surface tension, but the use of surfactants can reduce the surface tension more than tenfold, making it very easy to increase its surface area.

Emulsions are a type of solution where surface tension is also very important. Oil will not spontaneously mix with water, but the presence of a surfactant provides a decrease in surface tension that allows the formation of small droplets of oil in the bulk of water (or vice versa).

GIBBS ISOTHERM

Starting from the consideration of thermodynamic equilibrium, Josiah Willard Gibbs proved that surface tension and concentration are linked through **surface concentration**, Γ, represents excess of solute per unit area of the surface over what would be present if the bulk concentration prevailed all the way to the surface, it can be positive, negative or zero. It has units of mol/m^2. In the derivation of the equation it is assumed that the solution is ideal, (so $\mu = \mu^o + RT\ln C$) and surface concentration of the solvent is zero, so it is only valid under these assumptions. It is also considered that the interface is bidimensional, which is not true, further models as Guggenheim's correct this flaw.

Gibbs isotherm is

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln c}\right)_{T,p}$$

c is the concentration of the substance in the bulk solution, R is the gas constant, T the temperature and γ is the surface tension of the solution.

Therefore inorganic salts have negative surface concentrations (which is logical, because they have strong attractions with the solvent) and surfactants have positive surface concentrations: they adsorb on the interface.

SURFACE TENSION MEASUREMENTS BY STALAGMOMETRIC METHOD

Introduction

Gravity force can be described using formula:

$$F_g = m \cdot g = \frac{V}{n} \cdot d \cdot g$$

where m is the mass of the drop, d is the density of the liquid, g is a earth acceleration. Because the surface tension force is equal:

$$F_\sigma = 2\pi r \sigma$$

the surface tension we can calculate using formula:

$$\sigma = \frac{V \cdot d \cdot g}{2\pi \cdot r \cdot n}$$

In the stalogmometric method to avoid the volume of the container and the radius of the capillary we use the model liquid with the well known surface tension-water

The surface tension of the examinated solution we calculate according to the formula:

$$\sigma = \sigma_m \cdot \frac{n_m}{n} \cdot \frac{d}{d_m} .$$

where: σ_m the surface tension of model liquid

n_m the number of drops flow out for the model liquid

n the number of drops flow out for the examinated liquid

d density of the examinated liquid

d_m density of the model liquid.

The surface tension of water at a given temperature can be calculated using formula:

$$\sigma_m = [72.9 - 0.155(t - 18)]x10^{-3}$$

PROCEDURE:

1. Prepare solutions of substances advisabled by the TA.

2. Flush the stalagmometer before each measurement using the liquid which will be examinated.

3. Count the drops flowing out of the stalagmometer (start your counting when the meniscus of the liquid achieves the upper contraction, stop your counting when the meniscus achieves the lower contraction).

4. Enclose your results in the table.

CALCULATIONS:

1. Calculate the surface tension for water and each solution.

2. Density of solutions read off form the plots performed using delivered tables of densities.

3. Plot σ=f(lnc) and using the slop calculate the Gibbs isotherm.

III.B. ADSORPTION

GOAL: *To investigate the influence of the solution concentration on the process of adsorption, to learn how to use the Freundlich isotherm*

INTRODUCTION

The attachment of particles to a surface is called **adsorption**. The substance that absorbs is the *adsorbate* and the underlying material is *adsorbent* or *substarte*. The reverse of adsorption is *desorption*.

Chemical reactions at solid surfaces may differ sharply from reactions in the bulk, for reaction pathway of much lower activation energy may be provided, and hence result in catalysis.

The basic theory of adsorption of gases on solids is due to Langmuir, who considered the surface of a solid to be made up of elementary spaces each of which could adsorb one gas molecule. Furthermore, it was assumed that all the elementary spaces were identical in their affinity for a gas molecule and that the presence of a gas molecule on one space did not affect the properties of neighboring spaces. At adsorption equilibrium the rate of evaporation of the adsorbed gas is equal to the rate of condensation.

PHYSISORPTION AND CHEMISORPTION

Molecules and atoms can attach to surfaces in two ways.

In physisorption (an abbreviation of 'physical adsorption'), there is a van der Waals interaction (for example, a dispersion or a dipolar interaction) between the adsorbate and the substrate. Van der Waals interactions have a long range but are weak, and the energy released when a particle is physisorbed is of the same order of magnitude as the enthalpy of condensation. Such small energies can be adsorbed as vibrations of the lattice and dissipated as thermal motion, and, a molecule bouncing across the surface will gradually lose its energy and finally adsorb to it in the monitoring the rise in temperature of a sample of known heat capacity, and typical values are in the region of 20 kJ/mol. This small enthalpy change is insufficient to lead to band breaking, so a physiosorbed molecule retains its identity, although it might be distorted by the presence of the surface.

__In chemisorption__ (an abbreviation of 'chemical adsorption'), the molecules (or atoms) stick to the surface by forming a chemical (usually covalent) bond, and tend to find sites that maximize their coordination number with the substrate. The enthalpy of chemisorption is very much greater that that for physisorption, and typical values are in the region of 200 kJ/mol.
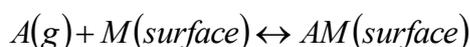
ADSORPTION ISOTHERMS

a) _The Langmuir isotherm_

The simplest physically plausible isotherm is based on three assumptions:

1. Adsorption cannot proceed beyond monolayer coverage.
2. All sites are equivalent and the surface is uniform
3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

The dynamic equilibrium is:

$$A(g) + M(surface) \leftrightarrow AM(surface)$$

with rate constants k_a for adsorption and k_d for desorption. The rate of change of surface coverage due to adsorption is proportional to the partial pressure p of A and the number of vacant sites $N(1-\theta)$, where N is the total number of sites, and θ is the fractional coverage.

The rate of change of θ due to desorption is proportional to the number of adsorbed species, $N\theta$:

$$\frac{d\theta}{dt} = -k_d N\theta$$

At equilibrium there is no net change, and solving for θ gives the *__Langmuir isotherm__*:

$$\theta = \frac{Kp}{1+Kp} \quad K = \frac{k_a}{k_d}$$

b) <u>*the BET isotherm*</u>

If the initial adsorbed layer can act as a substarte for further (for example, physical) adsorption then, instead of the isotherm leveling off to some saturated value at high pressures, it can be expected to rise indefinitely. The most widely used isotherm dealing with multilayer adsorption was derived by Stephen Brunauer, Paul Emmett, and Edward teller, and is called *the BET isotherm*:

$$\frac{V}{V_{mon}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \quad z = \frac{p}{p^*}$$

in this expression, p^* is the vapour partial pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid, V_{mon} is the volume corresponding to monolayer coverage, and c is a constant which is large when the enthalpy of desorption from a monolayer is large compared with the enthalpy of vaporization of the liquid adsorbate.

c) <u>*the Freundlich isotherm*</u>

When the temperature is constant the amount a [mol] of the substrate adsorbed by the mass unit of the adsorbate is proportional to the concentration c of the substrate in the solution. The Freundlich isotherm is given by the equation:

$$a = K \cdot c^n$$

the constants K and n that characterize the substrate-adsorbate system can be named experimentally according to the formula:

$$\log a = \log K + n \log c$$

PROCEDURE:

1 Prepare solutions of acetic or oxalic acid

2 Weigh a sample of active carbon and add this sample to the flask

3 To the flask containing active carbon add 50ml of prepared acid's solution, mix each sample10 minutes, after this time filtrate the sample

4 Determine the concentration of NaOH solution using HCl solution

5 Using NaOH denote the concentration of initial acid solutions c_1

6 Using NaOH denote the concentration of strained acid solutions c_2

7 Enclose your results in the table

CALCULATIONS:

1 Calculate a

$$a = \frac{(c_1 - c_2) \cdot V}{m_c}$$

where: m_c -mass of the active carbon [kg]

V - volume of solution used for the adsorption [dm^3]

c_1 and c_2 concentrations of the solutions before and after adsorption respectively [mol/dm^3].

2 Plot $\log a = f(\log c_2)$, the slope is equal n, intercept is equal $\log K$