Task VIII

TRAUBE'S RULE

I. Aim of the experiment

The purpose of this task is to verify the Traube's rule for a homologous series of capillary active substance solutions (i.e. alcohols or carboxylic acids) on the basis of measured surface tension results as a function of the concentration.

II. Introduction

1. Definition of the surface tension
2. The surface tension of solutions:
   a) Capillary active substances (surfactants)
   b) Szyszkowski's equation
   c) Traube's rule
3. Measurement of surface tension
   a) Capillary rise method
   b) Drop volume method (stalagmometric method)
   c) Ring method (tensiometric method)
   d) Maximum bubble pressure method (Rebinder method)
4. Variation of surface tension with temperature
5. Adsorption on the surface of solution
   a) The Gibbs adsorption equation
   b) The Gibbs adsorption isotherm equation
6. The structure of the adsorption surface layer
7. Effect of temperature on the surface tension of solutions

Bibliography:

1. J. Ościk, *Adsorption*, PWN Polish Scientific Publishers Warszawa, 1982, pp. 4–25
2. A.W. Adamson, *Physical Chemistry of Surfaces,* Interscience Publishers, Ltd., London 1960, pp. 13–40
3. D. J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworth Co. Publishers, Ltd, London 1970, pp.55-71
4. *http://en.wikipedia.org/wiki/Surface_tension#Methods_of_measurement*
5. *http://www.kruss.de/en/theory/measurements/surface-tension/ring-method.html*

III. Theory

III. 1. Surface tension

Cohesive forces (van der Waals) between molecules are unbalanced at the interface. For example, in the case of a liquid/gas interface the resultant force acting on the surface molecules from the liquid side exceeds that from the gas side (Fig.1). Surface molecules of the liquid are therefore drawn into the liquid phase, whose surface tends to reduce. Due to interactions among liquid molecules, the force directed normal to the surface into the liquid is accompanied by another force directed tangentially to the surface to prevent its area from increasing. This tangential force per unit length is a measure of **surface tension** (denoted by γ or σ).

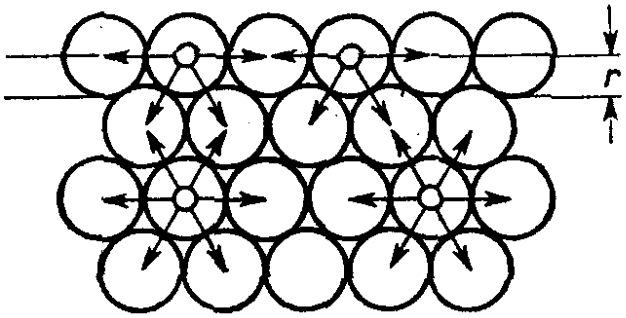

Fig. 1. Surface layer at the liquid/gas interface (*r* is the radius of intermolecular interaction).

Figure 2 shows a scheme of surface formation. Since the liquid tends to diminish its surface area, increase of that area requires work against the surface tension. We shift the lid to uncover a part of the liquid surface of the length equal to *dx*.

In general:

$$W = \gamma \, l \, dx \qquad (1a)$$

or

$$W = \gamma \, dA \qquad (1b)$$

where $dA = l\,dx$ is the change of surface area .

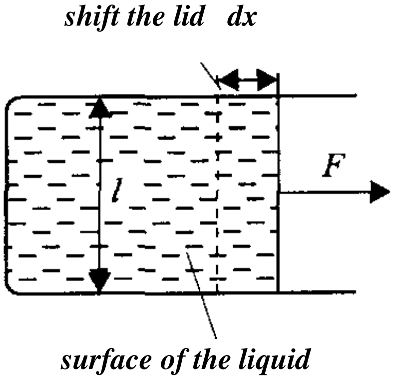

Fig. 2. Formation of a new surface of the liquid.

For the quasi-static process at a constant temperature and pressure, the work will be equal to the increase of Gibbs free energy of formation of the new area of surface ($G = f\,(T, p)$):

$$dG^s = \gamma dA \qquad (2)$$

or

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,p,n} \qquad (3)$$

It follows that the unit of surface tension is **N/m** (defined as a force) or it is surface free energy **J/m^2** (defined as work). Surface free energy represents the work necessary to form unit area of new surface or, equivalently, the increase of Gibbs free energy corresponding to the formation of unit area of the surface.

III. 2. Surface tension of solutions

In the case of two liquids solutions having similar surface tensions almost linear variation of the surface tension with the concentration is observed. In regular solution the surface tension is given by the Prigogine and Defay's relation:

$$\gamma = \gamma_1 x_1 + \gamma_2 x_2 - \beta_p x_1 x_2 \tag{4}$$

where: γ_1 and γ_2 are the surface tension of the pure liquids, x_1 and x_2 are their mole fractions and β_p is a semi-empirical constant.

If the surface tension of both liquids differ significantly, the addition of a small amount of liquid of lower surface tension usually diminishes the surface tension of the solution as compared to that of the solvent (Fig.3).

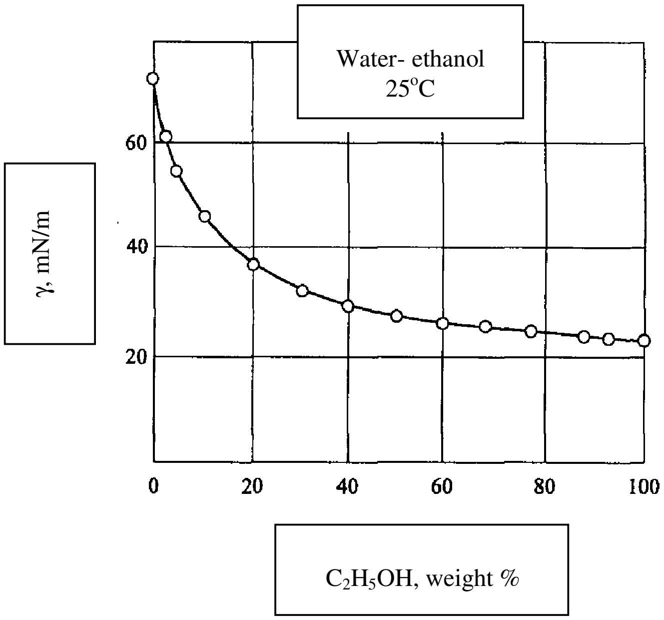

Fig. 3. Surface tension of aqueous solutions of ethanol at 25°C.

Substances which, in small concentrations, cause decrease in the surface tension of a solution are referred to as **capillary** or **surface active substances**. These include such organic compounds as alcohols, fatty acids, esters, ethers, etc.

In the case of dilute aqueous solution of organic substances, the **Szyszkowski's equation** describes the relation between the surface tension γ_o of the solvent , the surface tension γ of the solution, and its concentration *c*:

$$\frac{\gamma_o - \gamma}{\gamma_o} = B \ln\left(1 + \frac{c}{A}\right) \tag{5a}$$

or

$$\gamma_o - \gamma = b \ln(1 + a\,c) \tag{5b}$$

where: *B* and *b* are constant specific for a given homologous series and $a = 1/A$ is **the specific capillary activity** characteristic of a given compound.

The Traube's rule (1884) states that for a homologous series of various surface active substances, the concentration in the dilute aqueous solution at which a given lowering of surface tension is observed decreases 3.2 times for each additional methyl group in the series. *For equal lowering of the surface tension in a homologous series, e.g. by* $\Delta\gamma$*, it is sufficient to use a successive member of the series with a concentration 3.2 times lower.*

In the case of equal $\Delta\gamma$, for two members of a homologous series, we can write in accordance with the Szyszkowski's equation that:

$$b_n \ln\left(1 + \frac{c_n}{A_n}\right) = b_{n+1} \ln\left(1 + \frac{c_{n+1}}{A_{n+1}}\right) \tag{6}$$

where: *n* is the number of the homologue in the series.

Since $b_n = b_{n+1}$, the Traube's rule gives:

$$\frac{A_n}{A_{n+1}} = \frac{a_{n+1}}{a_n} = \frac{c_n}{c_{n+1}} = 3{,}2 \tag{7}$$

III. 3. Methods of measuring surface tension

The most frequently applied methods of measuring surface tension are:

- capillary rise method

The end of a capillary is immersed into the solution. The height at which the solution reaches inside the capillary is related to the surface tension by below equation [4]:

$$h = \frac{2\gamma_l \cos\theta}{\rho g r} \tag{8}$$

where

- h is the height of liquid inside the capillary,
- γ_l is the liquid surface tension,
- ρ is the density of the liquid,
- r is the radius of the capillary,
- g is the acceleration due to gravity,
- θ is the angle of contact liquid with the capillary wall.

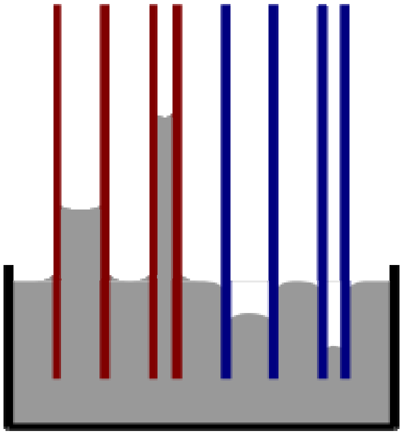

Fig.4 Scheme of capillary rise method. Contact angle less than 90° (red colour); contact angle greater than 90° (blue colour) [4].

If θ is greater than 90°, the liquid will be depressed rather than lifted.

- drop volume method

The drop volume (drop weight method) weights the mass of the liquid drop that falls off a dispense tip of known diameter when pumped very slowly. It is a very simple method but requires an empirical correction (fudge factor) for the wetted diameter of the dispense tip. Usually many drops (minimum three drops) are dispensed into a weighing boat and taken to a sensitive balance [5]. Knowing its density, the mass can be calculated.

The drop volume method is useful when it is difficult to form a pendant drop with sufficient stability. Because the pendant drop detachment process is irregular, it is best to average a number of measurements [5].

- ring (plate) method

It is known that the ring method was the first method to be developed. This is why many of the values for interfacial and surface tension given in the literature are the results of the ring method. In the ring method the liquid is raised until contact with the surface is registered.

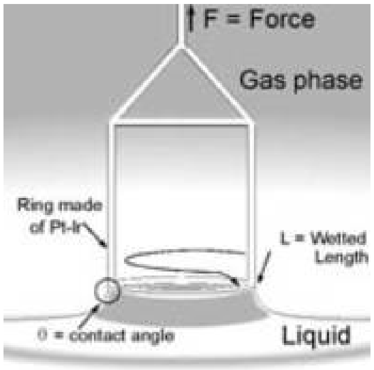

Fig.5. Scheme of ring method [5]

Similarly, in the plate method the liquid is raised until the contact between the surface (interface) and the plate is registered. The maximum tension acts on the balance at this moment.

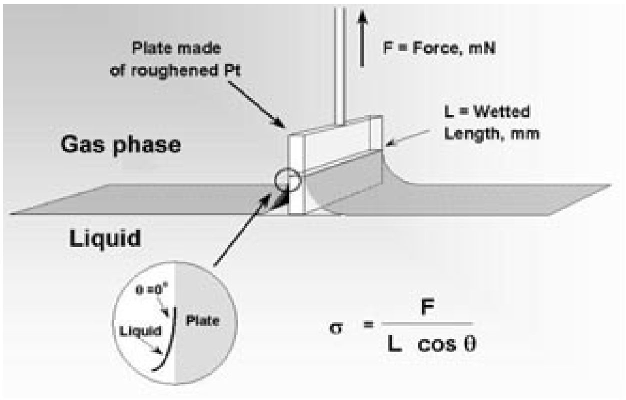

Fig.6. Scheme of plate method [5]

- maximum bubble pressure method

III. 4. Maximum bubble pressure method

One of the useful methods to determine the dynamic surface tension is measuring the maximum bubble pressure or simply **bubble pressure (Rebinder's method).**

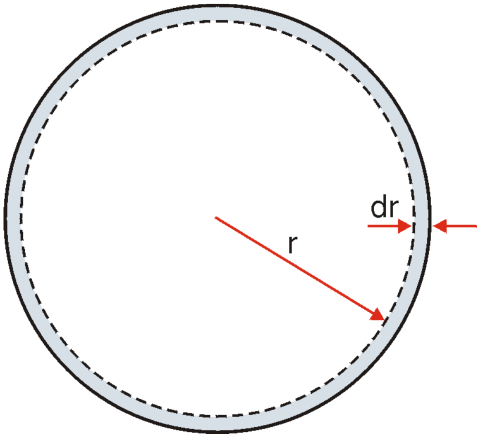

Fig. 7. The gas bubble (*dr* is decrease of radius)

The pressure in the Rebinder's device produces air bubbles at constant rate and blows them through a capillary which is submerged in the sample liquid and its radius is already known. The surface free energy for bubble is equal to $4\pi r^2 \gamma$. The pressure inside the gas bubble continues to increase and the maximum value is obtained when the bubble has a completely hemispherical shape whose radius is corresponding to that of the capillary. A bubble appears on the end of the capillary. If the radius of a bubbles increases from r to $r+dr$, then the increase in surface free energy will be $8\pi r \gamma \, dr$. At the point of the maximum bubble pressure, the bubble has a complete hemispherical shape whose radius r is identical to that of the capillary denoted by R_{cap}. The surface tension can be determined using the Young and Laplace equation in the reduced form for the spherical bubble shape within the liquid:

$$\gamma = \frac{r \, \Delta P}{2} \tag{9}$$

where: r is the bubble radius identical to that of the capillary denoted by R_{cap}.

Bubble pressure in the capillary is measured by the Rebinder manometer filled with liquid (for example water, density d). Then:

$$\Delta P = \Delta h \cdot d \cdot g \tag{10}$$

where: Δh is the difference between height of liquid in the manometer arms

$$\gamma = \frac{\Delta h \, r \, g \, d}{2} \tag{11}$$

After achieving the maximum pressure, the pressure in the bubble decreases and the radius of the bubble increases until the bubble is detached from the end of the capillary and a new cycle begins. Usually relative measurements are used for standard (water, surface tension, γ_{w}) and tested liquids (surface tension, γ_{x}). Their surface tensions are given from the relation:

$$\frac{\gamma_x}{\gamma_w} = \frac{\Delta h_x}{\Delta h_w} \tag{12}$$

or

$$\gamma_x = \frac{\gamma_w \Delta h_x}{\Delta h_w} \tag{13}$$

where $\gamma_w / \Delta h_w$ is the constant and it can be substituted by symbol *k*. Then the surface tension of the tested liquid can be presented in the form:

$$\gamma_x = k\,\Delta h_x \tag{14}$$

The bubble pressure method is commonly used to measure the dynamic surface tension for the system containing surfactants or other impurities because it does not require contact angle measurement and has high accuracy even though the measurement is performed rapidly. Moreover this method is an appropriate technique to apply to biological fluids like serum because it does not require a large amount of liquid sample.

IV. Experimental

A. Apparatus and materials

1. Apparatus: Rebinder's device for measuring the surface tension by the maximum bubble pressure method.

2. Glass equipment:
   - calibrated flask (25 cm^3) – 4 p.,
   - plastic vessels (100 cm^3) – 21 p.,
   - calibrated pipettes (10 cm^3, 25 cm^3),
   - beaker (400 cm^3),
   - wash bottle,
   - thermometer,
   - absorbent paper.

3. Reagents: aqueous solutions :
   - alcohols: methyl, ethyl and propyl (concentrations 2.5; 1.0; 1.0 M),
   - acids: formic, acetic and propionic (concentrations 2.5; 1.0 ; 1.0 M),
   - NaCl or KCl (2.0 M).

B. Task scheme

1. Determination of surface tension values for the homologous series of alcohols or carboxylic acids aqueous solutions and inorganic electrolyte by the maximum bubble pressure method.

2. Verification of the Traube's rule.

C. Apparatus service

Before measurements check if water from **bottom vessel** [**6**] has overflown to the **upper vessel** and if a **cock** [**4**] is closed. Then the measuring vessel [**1**] (after precise cleaning) fill with water and set up capillary [**2**] (after precise cleaning and drying) to touch a liquid surface. Close the cock [**3**] and open the cock [**5**] in such a way that water drips very, very slowly to the vessel [**6**].

After determining the water flow from the upper to the bottom vessel during the whole measurement it must not be changed.

During measurements the pressure continues to increase to such a value thet bubbles appear on the end of the capillary and at this moment make a readout of the height of liquid in the Rebinder manometer.

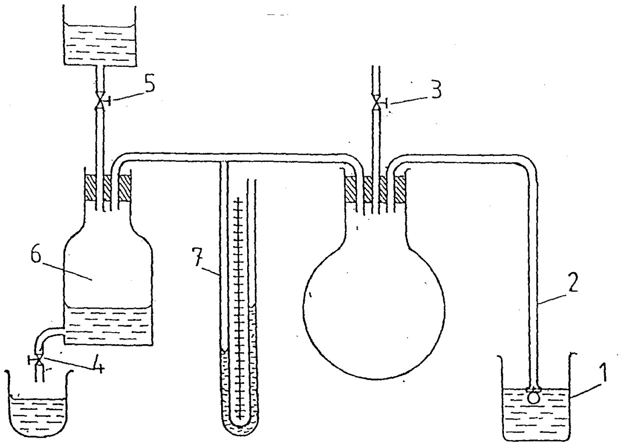

Fig. 7. Scheme of the Rebinder's device to measure the surface tension by the maximum bubble pressure method

In the next measurement open a cock [**3**], to balance a pressure in the apparatus with the external pressure (same height of liquid in the manometer arms). Close the cock again [**3**], and increase pressure to the value that a bubbles will appear on the end of the capillary. Read the differences in the liquid levels in the manometer for the maximal deflection. Δh_w and Δh_x (for water and investigated solutions) are sum of liquid heights in the left and right arms of manometer (starting from zero level).

D. Program of activity

1. Prepare 25 cm^3 aqueous solution of alcohols or acids (according to the demonstrator's instructions). To accomplish this, **2.5 cm^3** of initial solution concentration:

   - 2.5 M CH_3OH (or $HCOOH$),
   - 1.0 M C_2H_5OH (or CH_3COOH),
   - 1.0 M C_3H_7OH (or C_2H_5COOH),
   - 2.0 M NaCl (or KCl).

   drop to the calibrated flask (capacity 25 cm^3), then filled with distilled water to the scale mark. Transfer a prepared solution to a plastic vessel with number 1. For the residual solutions there are the same readings but: **5, 10, 17.5 or 25 cm^3** of stock solution. Calculate a final concentration of thus prepared solutions

2. Measure temperature of distilled water used to prepare the solutions.

3. Measure a surface tension of distilled water and all prepared solutions in the Rebinder's device conforming the instructions of the apparatus. After measurements the distilled water must be flown from the bottom to the upper vessels.

E. Results and discussion

1. Read a surface tension of distilled water, γ_w from Table I at the measurement temperature.

Table I.

T [^oC]	γ_w [mN/m]	T [^oC]	γ_w [mN/m]
11	74.07	21	72.59
12	73.93	22	72.44
13	73.78	23	72.28
14	73.64	24	72.13
15	73.49	25	71.97
16	73.34	26	71.82
17	73.19	27	71.66
18	73.05	28	71.50
19	72.90	29	71.35
20	72.75	30	71.18

2. Calculate a constant k for capillary in accordance with:

$$k = \frac{\gamma_w}{\Delta h_w} \tag{15}$$

3. Calculate the surface tension of the solutions according to equation:

$$\gamma_x = k\,\Delta h_x \tag{16}$$

4. Plot the relation of the surface tension of the investigated homologous solutions as a function of their concentration, $\gamma = f\,(c)$ **(all curves start from the surface tension of distilled water, for the concentration c = 0).**
On the same plot illustrate the relation, $\gamma = f\,(c)$ for NaCl (or KCl).

5. Based on the obtained plot verify the Traube's rule. For the same value of surface tension, calculate the ratio of concentrations for two members of a homologous series:

$$\frac{c_{CH_3OH}}{c_{C_2H_5OH}} \text{ and } \frac{c_{C_2H_5OH}}{c_{C_3H_7OH}} \tag{17}$$

6. Put the obtained results in Table II.

Table II.

Substance	Concentration [mol/dm^3]	Δh_x [cm]	γ_x [mN/m]
CH_3OH			
C_2H_5OH			
C_3H_7OH			
NaCl			

or

Substance	Concentration [mol/dm^3]	Δh_x [cm]	γ_x [mN/m]
HCOOH			
CH_3COOH			
C_2H_5COOH			
NaCl			

6. Verify the Traube's rule on the common graph $\gamma = f\,(c)$.

For example: